# A Simple Homoleptic Gallium(I) Olefin Complex: Mimicking Transition-Metal Chemistry at a Main-Group Metal?

*Kim Glootz, Antoine Barthélemy, and Ingo Krossing\**
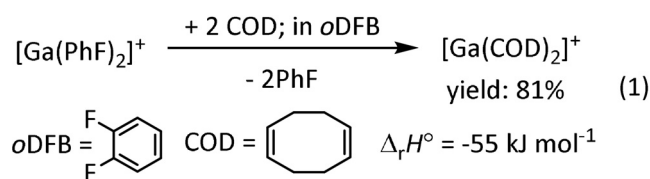
***Abstract:*** *The earth-metal olefin complex* $[Ga^I(COD)_2]^+[Al-(OR^F)_4]^-$ *(COD = 1,5-cyclooctadiene; $R^F = C(CF_3)_3$) constitutes the first homoleptic olefin complex of any main-group metal accessible as a bulk compound. It is straight forward to prepare in good yield and constitutes an olefin complex of a main-group metal that—similar to many transition-metals—may adopt the +1 and +3 oxidation states opening potential applications. Crystallographic-, vibrational- and computational investigations give an insight to the atypical bonding between an olefin and a main-group metal. They are compared to classical transition-metal relatives.*

**T**ransition metal olefin complexes are widely known and used as (pre-)catalysts in a variety of reactions. Since their first discovery in the 1820ies by Zeise,[1] they developed into a mature class of compounds with a manifold of applications. Especially the properties of chelating 1,5-cyclooctadiene (COD) to stabilize low valent transition-metal complexes like $[M(COD)_2]^{0,+}$ (M = Ni, Pd, Pt)[2,3] or $[ClM(COD)]_2/[M(COD)_2]^+$ (M = Rh, Ir)[4,5] sufficiently to be isolated, furnished a large interest into follow-up chemistry. Since the COD-ligands are easily displaced by other ligands such as phosphines, or alternatively may be hydrogenated in the course of the reaction and thus are removed from the metal atom leaving free and reactive coordination sites, they rapidly developed into very useful (pre-)catalysts for a variety of reactions.[6] For example, Crabtree's famous catalyst $[Ir(COD)(py)(PCy_3)]^+[PF_6]^{-}$ [4] or the Rhodium analogues[7] activate $H_2$ and hydrogenate, but also isomerize and hydroborate alkenes.

By contrast to transition-metal olefin complexes, *homoleptic* olefin complexes of a main-group metal remain unknown as isolable bulk compounds. Only a few examples are known under the special conditions of matrix isolation

[*] K. Glootz, A. Barthélemy, Prof. Dr. I. Krossing
Institut für Anorganische und Analytische Chemie and Freiburger Materialforschungszentrum (FMF), Universität Freiburg
Albertstr. 21, 79104 Freiburg (Germany)
E-mail: krossing@uni-freiburg.de

spectroscopy, that is, $Li(C_2H_4)_n$[8] or $M(C_2H_4)_n$ (M = Al,[9] Ga,[10,11] In;[12] n = 1–3) as well as inside a mass spectrometer, that is, $[M(C_2H_4)_n]^+$ (M = Na[13] or Al[14]). Turning to group 13, only a few bulk compounds are related; for example, the Al atom in $AlCp_3$, but not $GaCp_3$, is $\eta^2$-coordinated by at least one charged $[C_5H_5]^- = Cp^-$ ligand showing a related behaviour to olefins.[15] Somewhat related are the classical Ga-cyclophane and -arene complexes.[16] The first true group 13 olefin complex, the cyclohexene complex $[Al(C_6F_5)_3\cdot(C_6H_{10})]$, was published by Stephan et al.[16c] Very recently, Crimmin reported systems that could be described as $Al^I$ olefin complexes or $Al^{III}$ metallacyclopropanes,[17] Aldridge added versions, which include such situations as intermediates of $Al^I$ reactions with arenes[18] and Inoue reactions of a dialumene with olefins and acetylenes giving the respective dialumina-cyclobutanes.[19] Still, the simple access to an isolable bulk *homoleptic* olefin complex of any main-group metal—most favourably to an entry with switchable redox states that supports ligand substitution by steering ligands—is missing. The delineated profile suggests that possibly Ga or In, with their propensity to occur in the +I and +III oxidation states as well as their known capacity to bind phosphines,[20,21] appeared an interesting target for synthesis. In addition, the use of Ga and In in catalysis is increasing steadily.[22] Moreover, we showed that the polymerisation of isobutene (IB) induced by $[Ga^I(arene)_2]^+$ complexes most likely proceeds by formation of a $[Ga^I(IB)_x]^+$ complex (x = 3 or 4) that dismutates in the course of the reaction to a cyclo-galla(III) cation.[23] Thus, we were interested to prepare a prototype $Ga^+$-olefin complex. Starting point was our facile access to arene complexes of $Ga^+$ salts with the non-reactive weakly coordinating anion (WCA) $[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$) that led to interesting coordination chemistry with a variety of σ-donors including phosphines,[20,21] carbenes,[24] pyridines,[25] and also crown ethers.[26] And although $\eta^6$-arene-coordination of gallium(I) is known since 1957,[27] the classical $\eta^2$-olefin-coordination was hitherto only matrix isolated[10,11] and calculated[28] to occur, but never observed in an isolated compound. Here we report on the prototype complex salt $[Ga(COD)_2]^+[Al(OR^F)_4]^-$ that contains four $\eta^2$-bound double bonds in two COD ligands.

Thus, upon reacting a solution of $[Ga(PhF)_2]^+[Al(OR^F)_4]^-$ at room temperature in $1,2\text{-}F_2C_6H_4$ (= *o*DFB) with two



$$[Ga(PhF)_2]^+ \xrightarrow[\text{- 2PhF}]{\text{+ 2 COD; in }o\text{DFB}} [Ga(COD)_2]^+ \quad \text{yield: 81\%} \quad (1)$$

$$o\text{DFB} = \text{(difluorobenzene)} \quad COD = \text{(cyclooctadiene)} \quad \Delta_r H° = \text{-55 kJ mol}^{-1}$$

equivalents of COD as in Equation (1), the desired complex salt $[Ga(COD)_2]^+[Al(OR^F)_4]^-$ (**1**) formed in 81% yield.

The formation of **1** followed from NMR and vibrational spectra as well as a single crystal structure determination. Thus, upon coordination, the $^1H$-/$^{13}C$-NMR resonances of the double bond in COD shift by about $+0.2/+3$ ppm to lower field and the $^{71}Ga$-NMR of the arene-complex in $o$DFB at $\delta^{71}Ga = -746$ is replaced by a new signal at $-635$ ppm. In addition, Equation (1) was calculated to be exothermic (exergonic) by $-55$ ($-64$) kJ mol$^{-1}$ (@B3LYP/D3(BJ)/def2-TZVPP). This is nearly identical to the calculated enthalpy for exchange of 2 PhF with 2 1,4-Me$_2$C$_6$H$_4$ ($-52$ kJ mol$^{-1}$),[22b] placing the COD ligand at a similar ligand strength like xylene. Upon addition of three equivalents of triphenylphosphine PPh$_3$ to a solution of **1** in $o$DFB, the known [Ga-(PPh$_3$)$_3$]$^+$[Al(OR$^F$)$_4$]$^-$ salt[21] formed according to Equation (2) and the NMR investigations.

$$[Ga(COD)_2]^+ \xrightarrow[\text{- 2 COD}]{+ 3\ PPh_3;\ oDFB} [Ga(PPh_3)_3]^+$$

$$\delta^{71}Ga = -635 \qquad\qquad \delta^{71}Ga = \text{no signal} \qquad (2)$$

$$\Delta_r H^\circ = -237\ \text{kJ mol}^{-1} \qquad \delta^{31}P = +0.5$$
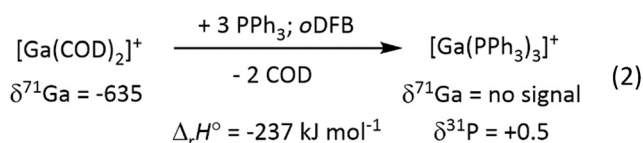
Formation of the complex [Ga(PPh$_3$)$_3$]$^+$ followed from the disappearance of the $^{71}Ga$-NMR signal of the COD complex and the appearance of the known $^{31}P$-NMR signal of the phosphine complex.[21] In addition, Equation (2) is in agreement with B3LYP/D3(BJ)/def2-TZVPP calculations[*] and exothermic (exergonic) by $-237$ ($-142$) kJ mol$^{-1}$.

**Molecular Structure of 1:** The complex salt shown in Figure 1 contains one Ga$^+$ ion coordinated distorted tetrahedrally by the four double bonds of two COD ligands and
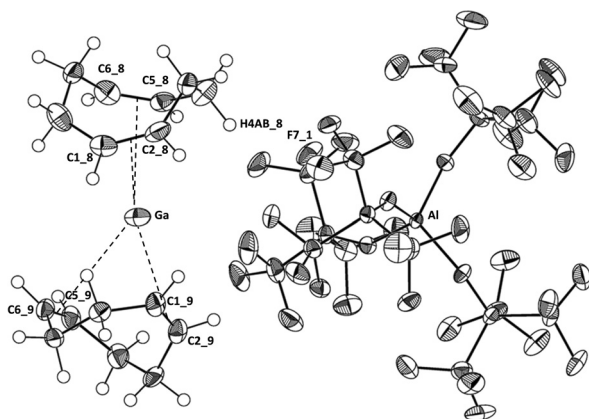


***Figure 1.*** Molecular structure of **1**. The carbon atoms of the double bonds (C1_9=C2_9; C5_9=C6_9) and the centroid metal distance are highlighted, as well as the shortest anion–cation contact ($d_{\text{H4AB 8–}}$ $_{F7\ 1}=265$ ppm). Thermal ellipsoids are set at 50% probability and hydrogen atoms are included as isotropic spheres of arbitrary radius. See Supporting Information for details and CCDC numbers.

[*] Contributions to entropy had to be calculated at the more economic BP86/D3(BJ)/def-TZVP level.

includes an almost non-interacting $[Al(OR^F)_4]^-$ anion. The shortest cation-anion H–F (Ga–F) contacts in **1** amount to 264.6 (306.5) pm. They are close to the sum of the van der Waals radii (H + F: 256 pm; Ga + F: 337 pm) and thus should influence the structure only little.[29] One COD ligand is bound **c**loser (COD$_c$) and one is **f**urther away (COD$_f$) to the Ga$^+$ attractor: $d_{Ga-C} = 285.1(6)$ to 321.3(6) pm in COD$_c$ vs. 297.4(5) to 323.2(5) pm in COD$_f$. All C$_2$Ga-triangles include by 9 to 26 pm asymmetric Ga-C distances. These $d_{Ga-C}$ values are in a similar range to the ones observed in several [Ga(arene)$_{2-3}$]$^+$ complexes with the like counterion [in pm]: 291–308 [Ga(PhF)$_3$]$^+$, 287–303 [Ga(PhF)$_2$]$^+$ or 286–302 [Ga(1,3,5-Me$_3$C$_6$H$_3$)$_2$]$^+$. Yet, they are much longer than the sum of the radii $r_{cov., C+Ga}$ of 203 pm.

In the tighter bound COD$_c$ ligand, $d_{C=C}$ are longer at 136.3(8) and 136.6(8) pm. The two double bonds in COD$_f$ are shorter at $d_{C=C} = 134.0(8)$ and 132.5(8) pm and resemble more closely to $d_{C=C} = 134$ pm found for free COD by gas phase electron diffraction.[30] The only structures that are reasonable to compare are "π-associated" dimers in [(CH$_3$)$_2$Ga-C≡C-Ph)]$_2$ with a very asymmetric coordination of the gallium(III) atom to one triple bond of a second molecule ($d_{Ga-C} = 224.0(6)$ and 279.0(6) pm)[31] or an intramolecular π-type coordination in [GaCl$_3${Me$_2$Si(C$_5$Me$_4$)(N-$t$-Bu)}GaCl$_2$]$^-$ with an average symmetric Ga-C distance to the Ga$^{III}$Cl$_2$-unit of 239.9-(4) pm,[32] respectively. Both of the structures contain gallium in the oxidation state $+3$ and are by far stronger bound, since their multiple bond has anionic character. Therefore, and due to the much larger ionic radius of Ga$^I$ vs. Ga$^{III}$, all Ga-C distances in **1**$^+$ are by 18 to 99 pm longer than the distances in the cited Ga$^{III}$ compounds.

But how does the structure compare to transition-metal relatives? A mixture of experimental and DFT-calculated data on [M(COD)$_2$]$^+$ with M = Ga, Ag, Ni, Rh as well as free COD are compared in Table 1.

Analysis of Table 1 shows that the closest structural relative of the collected entries in terms of impact on the C=C bond is the d$^{10}$ complex cation [Ag(COD)$_2$]$^+$, but all transition-metal complexes are much tighter bound with by on average 60 to 80 pm shorter M-C interactions. Interestingly, the torsion angle $\theta$ of the planes, which are defined by the C=C bond centroids of adjacent COD rings and the central metal atom M, amount to 51.3° for **1**, which is very close to the d$^9$ complex cation [Ni(COD)$_2$]$^+$ with 53.1° (cf. Ag$^+$: $\theta = 88.5°$; Rh$^+$ with a d$^8$ configuration: $\theta = 10.0°$; see Table 1).[3] Vibrational spectra show the expected redshift, despite the weak coordination of the COD ligands with on average $d_{db-Ga} = 299.9$ pm ($r_{vdW}(Ga + C) = 380$ ppm). Thus, the C=C stretching mode of the COD ligand in **1** at 1635 (IR)/1639 cm$^{-1}$ (Raman) shows a redshift by 21–22 cm$^{-1}$ compared to the free ligand ($\nu_{C=C} = 1656$ (IR)[34]/1661 cm$^{-1}$ (Raman)). Again, the Ag$^+$ complex is with a shift $\Delta\nu$ of 49 cm$^{-1}$ closer to the situation in **1**$^+$ (21 cm$^{-1}$), than the more strongly interacting Ni- and Rh-complex cations (86–165 cm$^{-1}$). This speaks for some σ-donation of the π-electron density of the double bond (see ESI S1,S2 for full spectra) and an almost free ligand in **1**$^+$ rather than a more covalent bonding as in the Ni- and Rh complexes. To evaluate the thermodynamic exchange of the COD ligands in the com-

**Table 1:** Important descriptors for the bonding in $[M(COD)_2]^+$ (M = Ag, Ni, Rh).[3] Enthalpies $\Delta H^0$ in kJ mol$^{-1}$.

| Parameter | Ga$^{+[a]}$ | Ag$^+$ | Ni$^+$ | Rh$^+$ | COD |
|---|---|---|---|---|---|
| $d_{(C=C)}$ [pm] | 132.5(8)–136.6(8) av. 134.7 | 134.2(4)–135.2(5) av. 134.5 | 135.0(4)–135.7(4) av. 135.3 | 136.1(4)–137.2(4) av. 136.8 | 134.0[d] |
| $d_{(M-C)}$ [pm] | 285.1(6)–323.3(6) av. 306.7 | 243.2(3)–255.6(3) av. 248.7 | 217.1(3)–228.5(3) av. 222.3 | 222.2(2)–227.3(2) av. 224.1 | – |
| $\theta$ [°] | 51.3 | 88.5 | 53.1 | 10 | – |
| $\nu_{(C=C)}$ [cm$^{-1}$][b] | 1635 (1636) | 1607 (1589) | 1570 (1548) | 1491 (1499) | 1656 (1669) |
| $\Delta\nu_{(C=C)}$ [cm$^{-1}$][b] | −21 (−35) | −49 (−80) | −86 (−121) | −165 (−179) | – |
| $^{13}$C-NMR [ppm][c] | 131.2, 27.4 | 126.0, 28.0 | paramagnetic[33] | 127.7, 29.6 | 128.2, 27.9 |
| $\Delta_r H^0$ [kJ mol$^{-1}$][e] | 0 | −193 | −419 | −571 | – |

[a] This work. [b] Experimental values; *italic* values in parentheses are calculated (BP86-D3(BJ)/def-TZVP), $\Delta\nu_{(C=C)}$ is the difference to the $\nu_{(C=C)}$ values of free COD. [c] sp$^2$-**C**H, sp$^3$-**C**H$_2$ in COD. [d] From Ref. [30]. [e] Isodesmic exchange enthalpies for Equation (3): $[Ga(COD)_2]^+ + M^+ \rightarrow [M(COD)_2]^+ + Ga^+$ calculated at BP86-D3(BJ)/def2-TZVP.

plexes $[M(COD)_2]^+$, the isodesmic reaction Equation (3) was calculated at BP86-D3(BJ)/def2-TZVP level.

$$[Ga(COD)_2]^+ + M^+ \rightarrow [M(COD)_2]^+ + Ga^+ \qquad (3)$$

With $\Delta_r H^0$ [Eq. (3)] = −193 to 571 kJ mol$^{-1}$, all transition-metal complexes are tighter bound than **1**$^+$. Solitary exchange with Na$^+$, yielding the clearly electrostatic $[Na(COD)_2]^+$ complex, is unfavorable, but only by $\Delta_r H^0$[Eq. (3)] =+ 75 kJ mol$^{-1}$. Apparently, the bonding energetics in **1**$^+$ is closer to $[Na(COD)_2]^+$ than even the least favorable else investigated silver complex $[Ag(COD)_2]^+$ ($\Delta_r H^0$[Eq. (3)] = −193 kJ mol$^{-1}$). Therefore, the bonding situation in **1**$^+$ and related $[M(COD)_2]^+$ complexes including M = Na was investigated by AIM analyses (Table 2).

Without π-back donation, the electron density at the bond critical points is rather T-shaped,[35] in contrast to metalla-cyclopropanes[36] with a more V-shaped electron density and more covalent bond character, for example, in the Rh complex in Table 2. A hypothetical $[Na(COD)_2]^+$ complex with clearly only electrostatic interaction to the ligands presents the other extreme. However, this compound shows the highest similarity in comparison to **1** with comparably low electron densities of $\rho$ = 0.08/0.14 e Å$^{-3}$ residing on the TCP$_{M-C}$ and therefore suggests more of an electrostatic bond between ligand and metal.[37] In addition, also the very long calculated Na-C distances in $[Na(COD)_2]^+$ (277 to 302 pm, av.: 288 pm) including their asymmetry (9–17 pm) are in a similar range to the Ga-C interactions. These findings are

very much supported by the $^{13}$C-NMR shifts of the sp$^2$-carbon atoms (see Table 1): Here the resonances of the transition-metal complexes shift to higher field, while the gallium complex shifts to lower field resonance. This observation indicates an inverse bonding situation in **1** with a very weak orbital-based ligand to metal bonding, but mainly electro-static bonding interaction. This is also in agreement with the donor and acceptor orbital energies (cf. ESI, Table S10) and the calculated exchange energy according to Equation (3), which is close for M = Na and Ga, but by far inferior than for Ag.

In conclusion, we presented with $[Ga(COD)_2]^+[Al-(OR^F)_4]^-$ the first representative of the novel class of *homoleptic* main-group metal-olefin complexes. The facile synthesis gives the title compound as a room temperature stable compound, IR and Raman spectroscopy find a slight redshift of the C=C vibration, which is much smaller than that of related transition-metal compounds. The AIM and frontier orbital energy analysis suggests similarity of **1** to the hypo-thetical $[Na(COD)_2]^+$ complex with no back-bonding to the ligands and would be in agreement with a predominantly electrostatic interaction between Ga$^+$ and COD. Upon addition of phosphine, **1** reacts to give $[Ga(PPh_3)_3][Al-(OR^F)_4]$[20] and demonstrates its synthetic use.

### Acknowledgement

### Conflict of interest

The authors declare no conflict of interest.

**Table 2:** Selected descriptors for the bonding in $[M(COD)_2]^+$ (M = Rh, Ag, Ga, Na) grouped according to decreasing interaction of M$^+$ and COD. Nature of the M-C critical point (XCP$_{M-C}$; X = B or T), electron densities $\rho$ [e Å$^{-3}$] residing on the CPs and average bond ellipticities $\varepsilon$ (dimensionless).

| Parameter | Rh(COD)$_2^{+[a]}$ | Ag(COD)$_2^{+[a]}$ | Ga(COD)$_2^{+[a]}$ | Na(COD)$_2^{+[a]}$ | Free COD[a] |
|---|---|---|---|---|---|
| CP$_{M-C}$ type | BCP | TCP | TCP | TCP | – |
| $\rho$ XCP, (M-db) | 0.51 | 0.27 | 0.14 | 0.08 | |
| $\varepsilon$ XCP, (M-db) | 1.60 | 1.27 | 0.47 | 0.31 | |
| $\rho$ BCP, (C=C) | 2.22 | 2.33 | 2.36 | 2.36 | 2.39 |
| $\varepsilon$ BCP, (C=C) | 0.26 | 0.30 | 0.32 | 0.34 | 0.36 |

[a] This work, Na$^+$ complex cation is hypothetical; optimized structures at B3LYP/D3(BJ)/def2-TZVPP.

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