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Insertion of Ga(DDP) into the Au–Cl Bond of (PPh$_3$)AuCl: A First Structurally Characterized Au–Ga Bond

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The reaction of (PPh$_3$)AuCl with the low valent gallium compound Ga(DDP) (DDP = 2-((2,6-diisopropylphenyl)amino-4-((2,6-diisopropylphenyl)imino)-2-pentene) yields the insertion products [{Ga(DDP)}Au{Ga(DDP)Cl}] (**1**) and [(PPh$_3$)Au{Ga(DDP)Cl}] (**2**), the first examples of molecular compounds with Au–Ga bonds.

The coordination of main group metals to transition metals has been in the focus of inorganic research during the past few decades. Apart from the well studied group 14 elements,[1] group 13 metals have attracted widespread attention in this respect.[2,3] Complexes and clusters involving late transition metal−group 13 metal bonds can be prepared employing many different routes and are known virtually for all metal−metal combinations. However, the group 11 metals Cu, Ag, and Au have so far remained an exception. Apart from borane clusters,[4−6] which generally exhibit strongly bridging hydrides, only a few compounds involving the Au−Tl pair[7] and two examples of Au−In clusters are known.[8,9] No molecular Au complexes of the lighter group 13 metals Al or Ga have been isolated and characterized so far. This can probably be attributed to the special character of Au, generally forming stronger bonds to heavier elements due to relativistic effects. Indeed, in the reaction of ECp* (E = Al, Ga, In) with (L)AuCl (L = PPh$_3$, CO) only unselective decomposition is observed, e.g., reduction and deposition of metallic gold. In contrast to this, these ligands generally insert readily into M−Cl bonds of late transition metals (e.g., Fe,[10] Ru,[11] Rh,[12,13] or Pd[14]). With the aim of stabilizing unsaturated metal centers by low valent group 13 compounds E^{I}R, we recently started to investigate the coordination chemistry of the sterically encumbered Ga(I) compound Ga(DDP).[15] Herein we wish to report on the reaction of Ga(DDP) with (PPh$_3$)AuCl, leading to molecular insertion products featuring Au−Ga bonds.

Treatment of (PPh$_3$)AuCl with an excess of Ga(DDP) in hexane at 70 °C and cooling the resulting yellow solution to −20 °C for 15 h yields pale yellow crystals of [{Ga(DDP)}-Au{Ga(DDP)Cl}] (**1**).[16] The ^{1}H NMR spectrum shows two typical sets of signals for the DDP ligand, one of the two sets showing C_{2v} symmetry (e.g. one CH signal for ^{i}Pr), the second set having a reduced (C_s) symmetry (e.g. two CH signals for ^{i}Pr), indicating a typical Ga−Cl bond rather than a contact ion pair in solution.

Compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$ (Figure 1).[17] The molecular structure consists of a central gold atom almost linearly coordinated by one Ga(DDP) and one [ClGa(DDP)] ligand (Ga1−Au−Ga2 =

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(16) [{Ga(DDP)}Au{Ga(DDP)Cl}] (**1**): yellow crystals. Yield: quantitative (NMR), 72% isolated yield. Anal. Calcd for $AuGa_2N_4C_{58}H_{82}Cl$: C, 57.32; H, 6.76; N, 4.37. Found: C, 57.72; H, 6.80; N, 4.64. ^{1}H NMR (C_6D_6, RT): δ 7.15 (arom, 12H); 4.97 (s, CH, 1H); 4.95 (s, CH, 1H); 4.13 (sept, MeC*H*Me, 2H); 3.39 (sept, MeC*H*Me, 2H); 2.65 (sept, MeC*H*Me, 4H); 1.67 (s, C*Me*, 6H); 1.49 (s, C*Me*, 6H); 1.46 (d, MeCH*Me*, 6H); 1.32 (d, MeCH*Me*, 6H); 1.13 (d, MeCH*Me*, 6H); 1.08 (d, MeCH*Me*, 12H + 6H); 1.04 (d, MeCH*Me*, 12H). ^{13}C NMR (C_6D_6, RT): δ 168.2 (CN); 166.5 (CN); 146.5 (Ar); 143.4 (Ar); 142.8 (Ar); 139.6 (Ar); 129.2 (Ar); 129.1 (Ar); 127.4 (Ar); 126.1 (Ar); 124.6 (Ar); 123.5 (Ar); 100.6 (γ-C); 97.2 (γ-C); 29.9 (C*Me*); 29.2 (C*Me* + CH-(CH_3)$_2$); 28.6 (*C*H(CH_3)$_2$); 28.1 (*C*H(CH_3)$_2$); 25.5 (CH(CH_3)$_2$); 25.4 (CH(CH_3)$_2$); 25.3 (CH(CH_3)$_2$); 24.5 (CH(CH_3)$_2$); 24.2 (CH(CH_3)$_2$).

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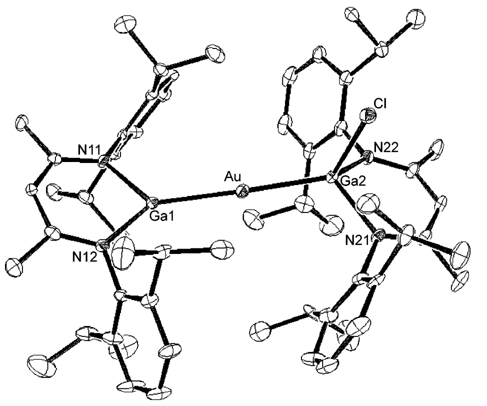


Figure 1. Molecular structure of **1**; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles [deg]: Au−Ga1 2.4125(7), Au−Ga2 2.4117(7), Ga1−N11 1.949(5), Ga1−N12 1.936(5), Ga2−N21 1.990(5), Ga2−N22 1.995(5), Ga2−Cl 2.2837(16); Ga1−Au−Ga2 177.88(2), N12−Ga1−N11 94.53(19), N22−Ga2−N21 94.11(19), N21−Ga2−Au 118.04(14), N22−Ga2−Au 118.75(14), Cl−Ga2−Au 121.13(5).

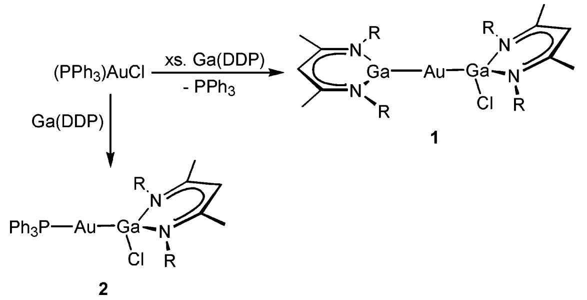
177.88(2)°). The Au−Ga bond lengths are almost equal (Au−Ga1 = 2.4125(7) Å; Au−Ga2 = 2.4117(7) Å).

The direct Ga−Cl interaction is also reflected by the slightly distorted tetrahedral environment of Ga2. Thus, N21−Ga2−Au (118.04(14)°) and N22−Ga2−Au (118.75(14)°) are slightly smaller than Cl−Ga2−Au (121.13(5)). Yet, the Ga2−Cl bond length (2.2837(16) Å) is significantly longer than in (DDP)$GaCl_2$ (2.22 Å), reflecting the weaker acidic character of the coordinated Ga^I ligand compared to a Ga^{III} center.

Performing the reaction of $(PPh_3)AuCl$ with stoichiometric amounts rather than with an excess of Ga(DDP) allows us to isolate the intermediate of the formation of **1**. Thus, treatment of $(PPh_3)AuCl$ with 1 equiv of Ga(DDP) in toluene and recrystallization of the raw product from toluene/hexane at −30 °C gives [(PPh_3)Au{Ga(DDP)Cl}] (**2**) in a yield of 76% (Scheme 1).[18]

The ^1H NMR spectrum of **2** in C_6D_6 is similar to that of **1**, showing only one DDP signal set with C_s symmetry and additional signals for the PPh_3 ligand. The ^{31}P NMR signal of **2** is found at 54.7 ppm, which is strongly downfield shifted relative to $(PPh_3)AuCl$ (34.2 ppm)[19] or even the cation $[(PPh_3)_2Au]^+$ (42.6 ppm).[20]

Scheme 1. Reaction of $(PPh_3)AuCl$ with Ga(DDP)



Compound **2** crystallizes in the monoclinic space group $P2_1/c$ (Figure 2).[21] The molecular structure of **2** consists of a linearly coordinated Au center (P−Au−Ga = 174.64(5)°). The geometric parameters of the coordinated {Ga(DDP)Cl} moiety are overall very similar to those in **1**, with a slightly shorter Au−Ga bond length (2.411(1) Å).

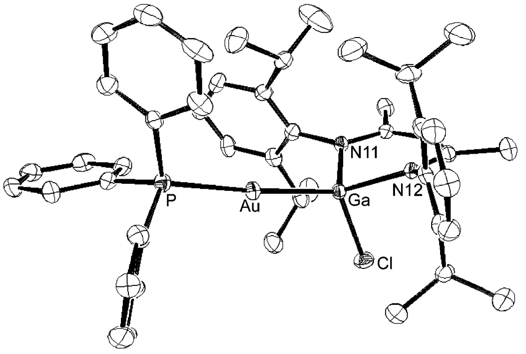


Figure 2. Molecular structure of **2**; hydrogen atoms have been omitted for clarity. Selected bond length (Å) and angles [deg]: P−Au 2.344(2), Au−Ga 2.411(1), Ga−N11 1.984(6), Ga−N12 1.978(5), Ga−Cl 2.290(2); P−Au−Ga 174.64(5), Au−Ga−Cl1 119.94(6), Au−Ga−N11 114.13(2), Au−Ga−N12 124.35(2), N11−Ga−Cl1 98.99(2), N12−Ga−Cl1 99.98(2), N11−Ga−N12 93.9(2).

Interestingly, the GaN_2C_3 ring systems of all (DDP)Ga moieties in both compounds **1** and **2** do not adopt planar geometries. Thus, the GaN_2 and the C_3N_2 planes of this ring system intersect each other by angles of 164.38° [Ga(DDP)] and 156.95° [Ga(DDP)Cl] in **1** and 150.74° [Ga(DDP)Cl] in **2**, respectively. This is a rather common geometrical feature for E(III) compounds E(DDP)X_2 (E = Al, Ga, In).[22] In contrast, the GaN_2C_3 ring in Ga(DDP) is almost planar.[15] This effect is best explained by sterics, as considerable repulsion should exist between the large DDP ligand and the groups X in Ga(DDP)X_2. This situation is further

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(17) Crystallographic data for [{Ga(DDP)}Au{Ga(DDP)Cl}] (**1**): $C_{58}H_{82}AuClGa_2N_4$ (1207.13), orthorhombic $P2_12_12_1$, $a = 13.788(2)$ Å, $b = 17.9638(18)$ Å, $c = 25.485(2)$ Å. $V = 6312.1(12)$ Å^3, $Z = 4$, $D_{calc} = 1.270$ Mg m^{-3}, $T = 105$ K, λ(Mo Kα) = 0.71073 Å, R1 = 0.0362 ($I > 2\sigma(I)$), wR2 = 0.0781 (all data). The contribution of a disordered hexane molecule within the asymmetric unit to the structure factors was taken into account by back-Fourier transformation using PLATON/SQUEEZE. measurements: Oxford Excalibur 2 diffractometer; programs used, SHELXS-97 and SHELXL-97. CCDC-253792 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

(18) [(PPh_3)Au{Ga(DDP)Cl}] (**2**): pale yellow crystals. Yield: quantitative (NMR), 76% isolated yield. Anal. Calcd for $AuGaN_2C_{47}H_{56}PCl$: C, 56.77; H, 5.82; N, 2.61. Found: C, 57.49; H, 5.71; N, 2.85. ^1H NMR (C_6D_6, RT): δ 7.15 (arom, 21H); 5.08 (s, CH, 1H); 4.31 (sept, MeC*H*Me, 2H); 3.61 (sept, MeC*H*Me, 2H); 1.70 (s, C*Me*, 6H); 1.64 (d, MeCH*Me*, 6H); 1.30 (d, MeCH*Me*, 6H); 1.27 (d, MeCH*Me*, 6H); 1.16 (d, MeCH*Me*, 6H). ^{13}C NMR (C_6D_6, RT): δ 167.4 (CN); 147.0 (Ar); 143.6 (Ar); 143.6 (Ar); 134.7 (Ar); 134.4 (Ar); 129.2 (Ar); 129.1 (Ar); 126.8 (Ar); 125.2 (Ar); 123.6 (Ar); 98.1 (γ-C); 29.6 (C*Me*); 28.4 (*C*H(CH$_3$)$_2$); 28.3 (*C*H(CH$_3$)$_2$); 25.3 (CH(*C*H$_3$)$_2$); 25.0 (CH(*C*H$_3$)$_2$); 24.4 (CH(*C*H$_3$)$_2$); 24.3 (CH(*C*H$_3$)$_2$). ^{31}P NMR (C_6D_6, RT): δ 54.74 (s).

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(21) Crystallographic data for [(PPh_3)Au{Ga(DDP)Cl}] (**2**): $C_{47}H_{56}AuClGaN_2P{\cdot}C_6H_6$ (1059.09), monoclinic, $P2_1/c$, $a = 22.708(8)$ Å, $b = 13.753(5)$ Å, $c = 15.900(6)$ Å, $\beta = 101.593(9)°$, $V = 4864(3)$ A^3, $Z = 4$, $D_{calc} = 1.448$ Mg m^{-3}, $T = 203$ K, λ(Mo Kα) = 0.71073 Å, R1 = 0.0560 ($I > 2\sigma(I)$), wR2 = 0.1451 (all data). Measurements: Bruker SMART CCD 1000 diffractometer; programs used, SHELXS-97 and SHELXL-97. CCDC-253793 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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aggravated by the fact that the stronger polarized Ga−N bonds in Ga(III) compounds are considerably shortened with respect to Ga(I). This concept is also able to explain well the molecular geometries of **1** and **2**. Thus, the deviation of the GaN_2/C_3N_2 angle is significantly larger for the chloro-substituted {Ga(DDP)Cl} ligands in **1** and **2**, respectively, than for the Ga(DDP) ligand in **1**.

Notably, the Ga−N bond lengths in **1** and **2** are distinctly shortened with respect to free Ga(DDP), indicating the strong σ-donor character of Ga(DDP) and the increased positive polarization of the Ga center upon coordination. Comparable Ga−N bond lengths were found in the acid base adduct $Ph_3B-Ga(DDP)$ (1.94 Å average).[23] The {Ga(DDP)Cl} moiety in **1** can also be described as a chloride stabilized acidic Ga center of the hypothetical cation $[Au\{Ga(DDP)\}_2]^+$, which is isolobal to the known cation $[(PPh_3)_2Au]^+$:

$$\{Ga(DDP)\}Au\{Ga(DDP)Cl\} \leftrightarrow [\{Ga(DDP)_2\}Au]^+Cl^-$$

This is consistent with our observation that insertion reactions of ECp* into the M−Cl bonds of $[(RhCp^*Cl_2)_2]$ and $[(Ru(p\text{-cymene})Cl_2)_2]$ typically lead to products exhibiting E−Cl−E bridging motifs.[11−13] However, as indicated by NMR spectroscopy (vide supra), the Ga−Cl bond is rather strong and no Cl^- exchange between the two Ga centers in **1** is observed at room temperature. Thus, a direct Ga−Cl bond remains also in solution rather than the formation of a contact ion pair $[\{Ga(DDP)_2\}Au]^+Cl^-$.

Notably, the effect of Ga−N bond shortening is much weaker in complexes of other d^{10} metal centers such as [Pd(dvds){Ga(DDP)}] (dvds = tetramethyldivinyldisiloxane), $[Pd(CO)\{Ga(DDP)\}]_2$, or $[Pt(1,3\text{-cod})\{Ga(DDP)\}_2]$, which contain the neutral metal centers Pd(0) or Pt(0), respectively.[24]

The insertion reaction of Ga(DDP) is not only restricted to Au−Cl bonds. Reaction of $[(PPh_3)AuMe]$ with Ga(DDP) yields the colorless complex $[\{Ga(DDP)\}Au\{Ga(DDP)(CH_3)\}]$ (**3**) as indicated by ^1H NMR spectroscopy of the crude reaction product.[25] Despite several attempts, no single crystals of **3** suitable for X-ray analysis could be obtained. However, **3** can also be prepared independently starting from **1** by reaction with MeLi in THF at −30 °C, pointing to the structural analogy of compounds **1** and **3**.

In summary, we found that Ga(DDP) indeed is a suitable ligand for stabilizing transition metal centers, showing chemical reactivities different from those of the well studied ligand class ECp*. We have prepared and characterized the first molecular compounds with Au−Ga bonds, by using Ga(DDP) as a ligand for Au(I) centers. The reactivity of the new complexes, especially the preparation of the cationic species $[Au\{Ga(DDP)\}_2]^+$ by halide abstraction from **1** as well as the stabilization of other unsaturated transition metals by Ga(DDP), will be reported in due course.[24]

Acknowledgment. We gratefully thank Dr. Ned J. Hardman for helpful and inspiring discussions.

Note Added in Proof: During the proofreading of this Communication, the preparation and structural characterization of a AuGaCp* cluster was published: Anandhi, U.; Sharp, P. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6128. Due to the concomitance, this compound could not be discussed herein, nor the title of this Communication changed.

Supporting Information Available: Experimental details for the preparation of complexes **1**, **2**, and **3**. Crystallographic details in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) $[(Ph_3P)Au\{Ga(DDP)Me\}]$ (**3**). ^1H NMR (C_6D_6, RT): δ 7.3−6.7 (arom 6H); 4.94 (s, CH, 1H); 4.11 (sept, $C\mathit{H}Me_2$, 2H); 3.70 (sept, $C\mathit{H}Me_2$, 2H); 1.68 (s, $C\mathit{Me}$, 6H); 1.44 (d, $CH(\mathit{Me})_2$, 6H); 1.34 (d, $CH(\mathit{Me})_2$, 6H); 1.24 (d, $CH(\mathit{Me})_2$, 6H); 1.22 (d, $CH(\mathit{Me})_2$, 6H); 0.24 (s, $Ga\mathit{Me}$, 3H). ^{13}C NMR (C_6D_6, RT): δ 166.95 (CN); 144.88 (Ar); 144.44 (Ar); 134.78 (Ar); 134.54 (Ar); 126.08 (Ar); 124.28 (Ar); 124.19 (Ar); 96.22 (γ-C); 29.42 ($\mathit{C}H(CH_3)_2$); 28.80 ($\mathit{C}H(CH_3)_2$); 28.30 ($\mathit{C}H(CH_3)_2$); 26.66 ($CH(\mathit{C}H_3)_2$); 26.49 ($CH(\mathit{C}H_3)_2$); 24.88 ($CH(\mathit{C}H_3)_2$); 24.75 ($CH(\mathit{C}H_3)_2$); 24.15 ($C\mathit{Me}$); 23.62 ($C\mathit{Me}$); 21.60 ($Ga\mathit{Me}$). ^{31}P NMR (C_6D_6, RT): δ 56.40 (s).