Linear Coinage Metal Complexes Stabilized by a Group 13 Metalloid Ligand

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The synthesis and structural characterization of the linear, cationic complex [{(DDP)Ga}_2Cu][OTf] $\cdot 2C_6H_5F$ (2, Tf = O_2SCF_3) stabilized by the monodentate, gallium-based ligand Ga(DDP) (DDP = [HC{(CMe)N(2,6-*i*Pr₂C₆H₃)}₂]⁻), as well as NMR spectroscopic evidence for the formation of the

Introduction

The chemistry of coinage metal complexes has attracted a lot of attention in the past few years, due to their interesting bonding, structural properties and diverse applications.^[1] Particularly, gold complexes bearing monodentate ancillary ligands such as N-heterocyclic carbenes or phosphanes have been in the focus of extensive research in recent years, with regard to their application as homogeneous catalysts for organic synthesis,^[2] where the importance of cationic complexes has been highlighted.^[3] Complexes of the d¹⁰ ions of the group 11 transition metals present variable coordination numbers. CuI and AgI complexes most commonly exhibit coordination numbers of three or four, while Au^I compounds are mostly linear, two-coordinate species. It has been suggested that this difference may be ascribed to relativistic effects, which allow the efficient hybridization of s, p and d orbitals of gold atoms.^[4] In 2004, the first examples of complexes containing Au-Ga bonds were reported, namely the trinuclear cluster [Au₃(µ-GaI₂)₃-(Cp*Ga)₅]^[5a] and the mononuclear, linear complexes [Ph₃PAu–Ga(Cl)DDP] and [DDPGa–Au–Ga(Cl)DDP] $(DDP = [HC{(CMe)N(2,6-iPr_2C_6H_3)}_2]).^{[5b]}$ Despite the extensive work that has been done on the study of the coordination chemistry of gallium-based ligands, only a handful of complexes of the coinage metals have been isolated. Both neutral GaCp* and Ga(DDP), and anionic [Ga{[N(Ar)- $C(H)_{2}^{-}$ (Ar = 2,6-*i*Pr₂C₆H₃) ligands have been used to stabilize such species.^[6] All low-valent RGa compounds are strong σ -donors, but the nature of the R groups influences their steric and π -acceptor properties strongly, leading to distinctly different coordination behaviours. Therefore, the

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corresponding silver compound $[{(DDP)Ga}_2Ag][Al(hfip)_4]$ (3, hfip = $[OC(H)(CF_3)_2]$), are reported. The remarkable steric properties of this gallium-based ligand permit the stabilization of 2, which exhibits an unusual linear geometry and a coordination number of two.



Figure 1. Coinage metal complexes stabilized by gallium-based ligands.

nature of the RGa–M (Cu, Ag, Au) complexes characterized so far is very different from one another (Figure 1).^[5-7]

SHORT COMMUNICATION

During our studies on the coordination chemistry of Ga(DDP), we have tried to obtain cationic transition metal complexes only with limited success. Attempts to abstract the chlorine atoms of $[(Ph_3P)_2Rh{Ga(DDP)}(\mu-Cl)]$ and $[(COE)(benzene)Rh-\{(DDP)GaCl\}]$ (COE = cyclooctene) with TlBAr^F (BAr^F = B[3,5-(CF₃)₂C₆H₃]₄) to produce the corresponding cationic species did not lead to stable products that could be isolated. However, their formation was confirmed by means of ¹H NMR spectroscopy. Only the linear, symmetrical, cationic species [{(DDP)Ga}₂Au]- $[BAr^{F}]$ (1a) and $[{(DDP)Ga \cdot THF}_{2}Au][BAr^{F}]$ (1b) have been fully characterized so far.^[6a] Herein, we report on the synthesis of analogous complexes [{(DDP)Ga}₂Cu][OTf]· $2C_6H_5F$ (2) and [{(DDP)Ga}_2Ag][Al(hfip)_4] (3, hfip = $[OC(H)(CF_3)_2]$), by treatment of the appropriate metallic precursor directly with Ga(DDP).

Results and Discussion

The wide variety of available Ag^{I} and Cu^{I} starting materials allowed us to try the direct reaction of Ga(DDP) with metal salts containing weakly coordinating anions, such as TfO⁻, BAr^{F-}, SbF₆⁻ and [Al(hfip)₄]⁻, to obtain the corresponding ionic complexes. As previously reported,^[6c] we have also observed that the nature of the anion has a strong influence on the formation of the desired species. Most of the attempted reactions led to decomposition products, as evidenced by the formation of metallic films on the walls of the reaction flasks or precipitation of grey metallic solids. However, we were able to isolate ionic complexes **2** and **3** (Scheme 1).



Scheme 1. Synthesis of 2 and 3.

$[{(DDP)Ga}_{2}Cu][OTf] \cdot 2C_{6}H_{5}F(2)$

Reduction of Cu(OTf)₂ with 4 equiv. of Ga(DDP) in fluorobenzene afforded bimetallic complex **2** as colourless crystals in 53% yield. Compound **2** is stable under an inert atmosphere and soluble in polar organic solvents such as THF and fluorobenzene. It has been characterized by IR and NMR (¹H, ¹³C and ¹⁹F) spectroscopy, elemental analysis and single-crystal X-ray diffraction. The ¹H and ¹³C{¹H} NMR spectra in [D₈]THF solution show signals associated with the DDP ligand, which are in the expected range when compared to Ga(DDP)-supported metal complexes.^[5b,6a] It is noteworthy that the triflate carbon atom of the counterion is not observed in the ¹³C{¹H} NMR spectroscopic time scale. However, the ¹⁹F NMR spectrum presents a sharp single signal at $\delta = -80.5$ ppm for the fluorine atoms of the triflate group. Moreover, the NMR spectra of **2** clearly indicate that **2** is stable in solution for several hours. The triflate stretching absorptions [1261(s), 1230(m), 1163(m), 1015(s) cm⁻¹] in the infrared spectrum suggest the presence of a non-coordinating triflate anion.^[8]

To elucidate the nature of the metal-ligand bonding and the solid-state structure of 2, we carried out a single-crystal X-ray diffraction study. Single crystals suitable for X-ray structural determination were obtained from a fluorobenzene/hexane solution at -30 °C over a period of 24 h. The X-ray structure, selected bond lengths and bond angles for 2 are shown in Figure 2. Complex 2 crystallizes in the space group C_2/m .^[12–14] Molecule 2 contains a linear Ga–Cu–Ga linkage [180.0(1)°] with a non-coordinating OTf group. The Me₂C₃N₂ backbone of Ga(DDP) ligands are nearly coplanar with the Ga–Cu–Ga chain. The $2,6-iPr_2-C_6H_3$ groups attached to the DDP nitrogen atoms lie perpendicular to the $Me_2C_3N_2$ framework. It is noteworthy that there is a limited number of known examples of linear coordination geometry around copper centres.^[4b] Furthermore, no linear copper compounds stabilized by group 13 ligands have been reported so far. Hence, compound 2 represents the first example of a linear copper(I) compound supported by the Ga(DDP) ligand.



Figure 2. Molecular structure of **2**. Hydrogen atoms attached to carbon, the disordered anionic ligand OTf and two disordered fluorobenzene molecules are omitted for clarity. Selected bond lengths [Å] and angles [°] for **2**: Ga–Cu 2.3157(10), Ga–N 1.930(5), Ga–Cu–Ga 180.0(1), N–Ga–N 94.9(3).

The Ga–Cu bond length is 2.3157(10) Å, which is remarkably shorter than the average Ga–Cu distance found in dimeric complexes [{(DDP)GaCu(OTf)}_2] (av.: 2.4605 Å), [Cu₂(GaCp*)(μ -GaCp*)₃Ga(OTf)₃] (av.: 2.412 Å) and [Cu₂(GaCp*)₃(μ -GaCp*)₂][OTf]₂ (av.: 2.4189 Å),^[7] while it is comparable with that in [LCu–GaR] {2.3066(6) and 2.2807(5) Å with R = {N(C₆H₃-2,6-*i*Pr₂)CH}₂, L = {N(2,4,6-Me₃–C₆H₂)CH}₂C and L = {N(2,6-*i*Pr₂-C₆H₃)-CH}₂C, respectively} and [Cu(GaCp*)₄]⁺[BAr^F] [2.3517(5)



and 2.3496(5) Å] (BAr^F = B[3,5-(CF₃)₂C₆H₃]₄).^[6b,6c] The coordination environment around gallium centres is satisfied with Cu^I atoms and nitrogen atoms from the DDP ligand. The Ga-N bond lengths and N-Ga-N angles of 2 are typical for (DDP)Ga-supported metal complexes.^[5b] The analogous silver compound 3 can be obtained by treatment of Ag[Al(hfip)₄] with 2 equiv. of Ga(DDP) in fluorobenzene. The product is very light-sensitive, and all attempts to obtain satisfying elemental analysis data or single crystals suitable for X-ray analysis failed. However, 3 was characterized by NMR spectroscopy in solution. Its ¹H NMR spectrum exhibits signals corresponding to two symmetrically coordinated Ga(DDP) moieties (γ -CH, δ = 5.45 ppm in $[D_8]$ THF, $\delta = 5.34$ ppm in C_6F_5/C_6D_6) as well as a signal for the [Al(hfip)₄] anion in a 2:1 ratio (δ = 4.54 ppm in $[D_8]$ THF, $\delta = 5.13$ ppm in C_6F_5/C_6D_6). The observed chemical shifts are in good agreement with those reported for 1a.[5b,6a]

Conclusions

Reduction of copper(II)triflate with an excess of Ga(DDP) afforded the first copper(I) cationic complex **2** supported by a main group metalloid ligand. Similarly, the reaction of Ag[Al(hfip)₄] and Ga(DDP) is also likely to yield the corresponding compound **3**, which, however, could only be characterized by NMR spectroscopy in solution. It is noteworthy that the cationic part of **2** can be regarded as being isostructural to copper(I) cationic complexes [NHC–Cu–NHC]⁺[Anion]⁻ stabilized by *N*-heterocyclic carbenes [NHC, NHC = N,N'-bis(aryl)imidazol-2-ylidene], which are known to be potential catalysts for hydrosilylation, carbonylation and coupling reactions.^[9]

Experimental Section

General Considerations: All manipulations were carried out in an atmosphere of purified argon by using standard Schlenk and glove box techniques. The solvents were dried by using an mBraun Solvent Purification System. Ga(DDP)^[10] and Ag[Al(hfip)₄]^[11] were prepared according to previously reported methods. 2,6-Diisopropylaniline (Aldrich), 2,4-pentanedione (Aldrich), gallium (Aldrich), potassium hydride (Acros), iodine (Aldrich), copper(II) triflate (ABCR), LiAlH₄ (Aldrich), (CF₃)₂CHOH (ABCR) and AgF (ABCR) were purchased from commercial sources. IR measurements (neat) were carried out with a Bruker Alpha-P Fourier transform spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the Ruhr University of Bochum. NMR spectra were recorded with a Bruker Avance DPX-250 spectrometer at 25 °C unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. The X-ray crystal structure of 2 was determined with an Oxford Excalibur diffractometer. The structure was solved by direct methods using SHELXS-97 and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.^[12] Two severely disordered fluorobenzene molecules and the triflate anion (apart from the sulfur) had to be "squeezed" out by using the program "Platon 1.13"[13] The fluorobenzene molecules and a triflate anion are included in the empirical formula. CCDC-779125 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[{(DDP)Ga}₂Cu][OTf]·2C₆H₅F (2)

Method A: To a mixture of Ga(DDP) (0.1 g, 0.206 mmol) and $Cu(OTf)_2$ (0.019 g, 0.052 mmol) was added fluorobenzene (3 mL) under vigorous stirring at room temp. The clear pale yellow solution was heated at 60 °C for 1 h, filtered, layered with hexane (2 mL) and stored at -30 °C for 24 h to afford colourless crystals of **2**. Yield: 53% [based on Cu(OTf)].

Method B: Cu(OTf)·4CH₃CN (0.05 g, 0.132 mmol) was added to a pale yellow solution of Ga(DDP) (0.129 g, 0.265 mmol) in fluorobenzene (3 mL). The resultant slurry was heated at 60 °C for 1 h. The tan-coloured insoluble solid formed was filtered off, and the colourless filtrate was layered with hexane to isolate colourless crystals of **2** at -30 °C over a period of one week. Yield: 61% [based on Cu(OTf)·4CH₃CN].

The samples used for elemental analysis and spectroscopic characterization were washed with hexane and completely dried under vacuum. This procedure removes all solvents from the synthesis, especially fluorobenzene. C59H82CuF3Ga2N4O3S (1187.36 without solvent): calcd. C 59.68, H 6.96, N 4.71, S 2.70; found C 59.54, H 6.05, N 4.48, S 2.88. ¹H NMR ([D₈]THF, 250 MHz): δ = 7.30–7.07 (m, 12 H, Ar), 5.35 (s, 2 H, γ -CH), 2.92 (sept, ${}^{3}J_{HH} = 7$ Hz, 8 H, CHCH₃), 1.73, 1.70 (s, 12 H, CCH₃), 1.10 (d, ${}^{3}J_{HH} = 6.5$ Hz, 24 H, CHCH₃), 0.89 (d, ${}^{3}J_{HH}$ = 6.5 Hz, 24 H, CHCH₃) ppm. ${}^{13}C$ NMR ([D₈]THF, 62.9 MHz): δ = 168.2 (CN), 144.4 (Ar), 142.0 (Ar), 124.8 (Ar), 116.1, 115.7 (Ar), 100.7 (γ-CH), 28.8 (CHCH₃) ppm. ¹⁹F NMR ([D₈]THF, 235.3 MHz): δ = -80.5 (OTf) ppm. IR: $\tilde{v} = 2961$ (w), 2869 (w), 1594 (s), 1528 (m), 1495 (m), 1460 (m), 1438 (m), 1360 (s), 1317 (s), 1261 (s), 1230 (m), 1199 (m), 1176 (m), 1163 (m), 1101 (w), 1055 (m), 1015 (s), 935 (w), 867 (w), 798 (s), 753 (m), 709 (w), 684 (w), 662 (vs), 632 (w), 572 (w), 531 (w), 516 (w), 498 (m), 439 (w), 403 (w) cm⁻¹.

Analogous Ga-Ag Complex (Attempted Synthesis of 3): A solution of Ga(DDP) (0.245 g, 0.50 mmol) in toluene (5 mL) was added to Ag[Al(hfip)₄] (0.2 g, 0.25 mmol) in fluorobenzene (10 mL) at -30 °C. The reaction mixture was warmed slowly to room temperature and stirred overnight. After filtration, all volatiles were removed to leave an oily, clear residue, which was washed twice with hexane to yield a white powder. The product was filtered and dried in vacuo. Yield: 0.27 g {61% based on Ag[Al(hfip)₄]}. ¹H NMR $(C_6H_5F/C_6D_6, 250 \text{ MHz}): \delta = 5.34 \text{ (s, 2 H, } \gamma\text{-CH}), 5.13 \text{ [sept, } {}^3J_{\text{HF}}$ = 6.3 Hz, 4 H, (CF₃)₂C(H)O], 2.54 (sept, ${}^{3}J_{HH}$ = 6.7 Hz, 8 H, CHCH₃), 1.68 (s, 12 H, CCH₃), 1.13 (d, ${}^{3}J_{HH} = 6.8$ Hz, 24 H, CHCH₃), 0.85 (d, ${}^{3}J_{HH}$ = 6.8 Hz, 24 H, CHCH₃) ppm. ${}^{13}C$ NMR $([D_8]THF, 62.9 \text{ MHz}): \delta = 169.2 (CN), 144.3 (Ar), 141.5 (Ar), 128.2$ (Ar), 125.2 (Ar), 100.6 (γ-CH), 29.3 (CHCH₃), 26.3 (CHCH₃), 24.4 (CCH₃) ppm. ²⁷Al NMR (C₆H₅F/C₆D₆, 65.2 MHz) δ = 61 ($\bar{\omega}_{1/2}$ = 130 Hz) ppm.

Supporting Information (see footnote on the first page of this article): IR and NMR spectra of **2** and **3**.

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- [14] X-ray crystal structure analysis of **2**: $C_{71}H_{92}CuF_5Ga_2N_4O_3S$, M = 1379.53, Monoclinic, space group C2/m, a = 19.6816(13) Å, b = 18.2169(6) Å, c = 11.9282(8) Å, $\beta = 121.448(9)^\circ$, V = 3648.5(4) Å³, Z = 2, $\rho_{calcd.} = 1.256$ g/cm³, T = 112(2) K, F(000) = 1444, μ (Mo- K_{α}) = 1.108 mm⁻¹, block, 6717 reflections measured, 3321 unique ($R_{int} = 0.0217$), 160 parameters, $R_1 = 0.0937$ [$I > 2\sigma(I$]], $wR_2 = 0.2808$ [$I > 2\sigma(I$]], GOF = 1.109.

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