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Bis(perchlorocatecholato)germane: Hard and Soft Lewis Superacid with Unlimited Water Stability

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Abstract: Previously described Lewis superacids are moisture sensitive and predominantly hard in character - features that are severely limiting their widespread use in orbital controlled reactions and under non-inert conditions. Herein, we describe adducts of bis(perchlorocatecholato)germane, the first hard and soft Lewis superacid based on germanium. Remarkably, the synthesis of this compound is performed in water, and the obtained H₂O-adduct constitutes a strong Brønsted acid. If applied as adduct with aprotic donors, it displays excellent activity in a diverse set of Lewis acid catalvzed transformations, covering hydrosilvlation. hydrodefluorination, transfer hydrogenation, and carbonyl-olefin metathesis. Given the very straightforward synthetic access from two commercially available precursors, the unlimited water stability and the soft Lewis acidic character, it promotes the transfer of Lewis superacidity into organic synthesis and materials science.

Lewis acids play a vital role in all domains of chemistry.^[1] For the most efficient and broad applicability of an ideal Lewis acid, two features are critical to be upheld simultaneously: 1) high affinity toward a full range of hard and soft Lewis basic substrates and 2) high stability against external stress such as temperature, moisture, or redox events.^[2] The most comprehensive value to scale the hard Lewis acidity is the fluoride ion affinity (FIA).^[3] Lewis acids that are exceeding the FIA of SbF₅ are considered Lewis superacids (LSA).^[2, 4] A value that reflects the soft Lewis acidity is the hydride ion affinity (HIA), and Lewis acids that are exceeding the HIA of $B(C_6F_5)_3$ have been classed as soft Lewis superacids (sLSA).^[2] Overall, Lewis superacids promise the extra portion of strength but have been used only to a limited extend.^[2] Their hesitant use is directly connected to the second feature: stability. In this regard, significant improvements have been made during the last decade. The daunting oxidizing and corrosive power of the prototypical SbF5 has been tamed by Krossing's hallmark Lewis acid Al(OC(CF₃)₃)₃, among others.^[4-5] The limited thermal stability of aluminum-based Lewis acids has been tackled by an evolved ligand design in Al(OC(C₆F₅)₃)₃.^[6] Still, most LSA suffer from high oxophilicity and the lability of M-O bonds, making them highly prone to hydrolysis. Hence, not only the requirement for strictly inert conditions but also the incompatibility with released water during Lewis acid-mediated condensation reactions and poor functional group tolerance are still major obstacles. Indeed, an entirely water-stable neutral LSA is unknown, but to the best of our knowledge, only approximated with the air-stable $Sb(C_6F_5)_4^+$.^[7]

a) Limitations with previous Lewis superacids (LSA)

• high oxophilicity • moisture intolerance • excessive hard Lewis acidity while limited *soft* Lewis acidity





Scheme 1. a) Previous limitations for the broad applicability of Lewis superacids (LSA) and b) the herein described bis(perchlorocatecholato)germane 1.

Although some water-compatible metal triflates also reach considerable Lewis acidities, this class suffers from poorly defined compositions.^[8] Moreover, the limitation to one type of ligand (OTf in this case) prevents any steric or electronic tuning. We recently emphasized the influence of perhalogenated catecholate ligands on the Lewis acidity of silicon and introduced the first neutral silicon LSA.^[9] However, like virtually all other LSA, bis(catecholato)silanes are highly sensitive towards moisture. In stark contrast, germanium catecholates have been known to be stable against moisture since their first isolation in 1954, but were never considered as Lewis acids.^[10] In general, germanium Lewis acids are only little explored, and a germanium LSA is unknown.[11] Herein, we describe the first germanium LSA, and the first LSA which offers unlimited water stability. Importantly, the compound qualifies not only as hard LSA (FIA > SbF₅) but also as soft LSA (HIA > $B(C_6F_5)_3$).

Heating two equivalents of perchlorocatechol (Cat^{CI}H₂) with GeO₂ in water leads to the dissolution of all insoluble starting materials (Figure 2a). Reaction monitoring via ¹H NMR spectroscopy indicated the disappearance of the OH-signals of Cat^{CI}H₂ and the simultaneous formation of a characteristic ¹³C NMR signal set of a new catecholate species. The product Ge(cat^{CI})₂-(H₂O)₄ (**1**-(H₂O)₄) was isolated upon vacuum removal of the solvent and washing with dichloromethane in 94% yield at 5 g scale.^[12] The isolated compound was recrystallized from water and analyzed by single-crystal X-ray diffraction (SCXRD, Figure 2b). The unit cell contains the bis-aqua adduct of **1** with four additional hydrogenbonded water molecules. The coordination geometry around Ge is almost ideally octahedral, with the two catecholates lying coplanar and the two (H₂O)₃ clusters in *trans* orientation.

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Figure 2. a) Synthesis of selected adducts of 1, together with the molecular structures of b) $1-(H_2O)_6$ (only two water molecules of the second coordination sphere are depicted, Ge-O1 184.5(3) pm, Ge-O3 195.7(3) pm) and c) [NEt₄]₂[*trans*-1-Cl₂] (cation omitted for clarity, Ge-O1 187.6(4) pm, Ge-Cl 235.3(2) pm).

Interestingly, the structure of the nonhalogenated derivative, *trans*-Ge(cat^H)₂-(H₂O)₂, was derived by vibrational spectroscopy in 1970,^[13] but an SCXRD confirmation remained elusive. **1**-(H₂O)_n not only represents a rare LSA-water adduct (*vide infra* for proof),^[14] but a LSA which does not reveal any signs of decomposition over months under bench-top conditions.

Storing 1-(H₂O)₄ in a mixture of CH₃CN/CH₂Cl₂ or acetone in the presence of molecular sieves (3 Å) leads to the replacement of bound H_2O_1 , and the isolation of $1-(CH_3CN)_2$ or $1-(acetone)_2$ in 95% or 91% yield, respectively. The composition of the two adducts was confirmed by elemental analysis and NMR spectroscopy. The binding of CH₃CN was corroborated by the blue shifting of the C=N stretching mode (2324 cm⁻¹, cf. 2253 cm⁻¹ in free CH₃CN). 1-(acetone)₂ possesses decent solubility in non-polar solvents such as CH₂Cl₂ or toluene. The addition of other neutral Lewis bases such as DMSO, Et₃PO, or (*n*-BuO)₃PO to $1-(CH_3CN)_2$ or $1-(H_2O)_6$ resulted in the formation of the respective Lewis adducts. All compounds were fully characterized. including SCXRD (see SI). The addition of one eq. of KF/18crown-6 to 1-(CH₃CN)₂ furnished the mono-fluorido adduct [K@18-crown-6][1-F], constituting a square-pyramidal structure with the two catecholates in the basal positions.^[15] Interestingly, also crystals of the octahedral mixed fluoride-aqua adduct [K@18-crown-6][trans-H2O-1-F] were obtained and analyzed crystallographically (see SI). Upon reaction with two equivalents of NEt₄Cl, the formation of octahedral [NEt₄]₂[trans-1-Cl₂] readily occurred (Figure 2c). The two chloride substituents are arranged in trans-fashion, with Ge-Cl bond lengths of 235 pm, slightly longer compared to GeCl62- or GeCl5- (229 - 232 pm).[16] It represents, beyond GeCl62-, only the second dianionic chlorido germanate and, to the best of our knowledge, the first dianionic GeO₄Cl₂ structural motif.^[17] Next, we sought after a donor-free variant of Lewis acid 1. Spontaneous hydroboration of both acetones in 1-(acetone)₂ with 9-BBN granted access, but a very poor solubility prevented NMR spectroscopy in non-donor solvents or crystallization of 1. Yet, IR spectroscopy, elemental analysis, and a clean NMR-spectrum after dissolving the powder in DMSO-d₆ supported its pristine composition as donor-less 1. Having various forms of 1 in hand, we considered its Lewis acidity and its hydrolytic stability by quantum chemical methods. The

fluoride ion affinity (FIA) and the hydride ion affinity (HIA) were computed first and compared with those of other literature-known germanium and silicon Lewis acids (Figure 3a). Notably, it exceeds the FIA and HIA of all previously reported germaniumbased Lewis acids by more than 100 kJ mol⁻¹. The FIA of 1 is very close to the value determined for its silicon counterpart and exceeds that of SbF₅, thus meeting the criteria for hard Lewis superacidity. Excitingly, the HIA of 1 sharply exceeded the HIA of Si(cat^{Cl})₂ and that of $B(C_6F_5)_3$, rendering this new compound also a soft Lewis superacid. The COSMO-RS corrected FIAsolv revealed the expected decrease in affinities by solvation damping.^[2, 3b] The hydrolytic stability was considered by comparing the computed enthalpies of the hydrolysis steps of 1 with those of the moisture-sensitive Si(cat^{Cl})₂ (Figure 3b). Indeed, the hydrolytic opening of the first M-O-C-C-O five-membered ring is thermodynamically more favorable by 43 kJ mol⁻¹ for silicon as the central atom. Similar trends exist for the remaining steps, making the total hydrolysis of Si(cat^{Cl})₂ more exothermic by about 70 kJ mol⁻¹. This difference can be explained as the result of diminished ring-strain in the five-membered ring of 1 in comparison to Si(cat^{Cl})₂ (Figure 3c), exemplified by comparison of the molecular structures of Si(cat^{Cl})₂-(OPEt₃)₂^[9b] with the one of Ge(cat^{Cl})₂-(OPEt₃)₂ (see SI for full comparison). The longer Ge-O bonds (186 pm) in comparison to Si-O (176 pm) cause less deviation from the preferred 120° O-C-C valence angle in the parent catecholate moiety (see SI, section 4).

(a)			(b) $M(cat^{Cl})_2 \xrightarrow{4 H_2O} M(OH)_4 + 2 Cat^{Cl}H_2$
Compound	FIA (solv) [kJmol ⁻¹]	HIA (solv) [kJmol-1]	- 63.4 - 69.2
GeF ₄	360 (244)	407 (427)	- 20.8 M = Si, Ge
GeF(CF ₃) ₃	373 (224)	437 (420)	H ₂ O Luchause a Cha
Ge(CF ₃) ₄	355 (197)	416 (387)	$(cat^{C})M(cat^{C}H)(OH) (cat^{C})M(OH)_2 + Cat^{C}H_2$
Ge(C(CF ₃) ₂ OC ₆ H ₄) ₂	321 (148)	458 (402)	- 2.2
Ge(cat ^{CI}) ₂	504 (304)	555 (485)	(c) CI $M = 4 C_2 C_1 O' d(M-O)$
Si(cat ^{CI}) ₂	507 (315)	491 (429)	RM ["] [pm]
$B(C_6F_6)_3$	453 (259)	515 (448)	0-C ₂ Ge 116.41(9) 186.47(9)
SbF ₅	501	-	ĊI Si 114.1(1) 176.6
			$R = Cat^{Cl}$, (OPEt ₃) ₂

Figure 3. Computational evaluation of a) the ion affinities of 1 in comparison to other strong Lewis acids (DLPNO-CCSD(T)/aug-cc-pVQZ//PW6B95-D3(BJ)/def2-TZVPP and COSMO-RS) and b) the reaction enthalpies in kJ mol⁻¹ of hydrolysis in comparison to Si(cat^{Cl})₂ (PW6B95-D3(BJ)/def2-TZVPP). c) Comparison of relevant bond lengths and angles in Si(cat^{Cl})₂-(OPEt₃)₂ and 1-(OPEt₃)₂.

Subjecting 1-(CH₃CN)₂ in CD₂Cl₂ to Et₃PO provided an estimate of Lewis acidity according to the Gutmann-Beckett method.^[18] As pentacoordination is rather uncommon for neutral germanium complexes,^[19] the formation of the respective bis-adduct 1-(OPEt₃)₂ was strongly favored.^[20] Interestingly, both the *cis* and *trans* bis-adducts were observed by NMR spectroscopy in a 1:1.3 ratio. The chirality in the C₂-symmetric *cis* adducts leads to strong diastereotopic splitting of the CH₂-proton signals. Hence, the preferential coordination state in 1-(OPEt₃)₂ differs in solution and the solid-state, for which SCXRD illustrated only the *trans* adduct. The induced ³¹P NMR chemical shift upon binding of the Lewis acid (δ ⁽³¹P) = 75.1 and 70.6 ppm, *cis* and *trans*) is significantly more downfield shifted compared to that of GeF₄-(OPEt₃)₂ (60.1 ppm),^[21] and in the range of the respective silicon bis-adduct Si(cat^{Cl})₂-(OPEt₃)₂ (73.1 ppm).^[9b]

While 1 does not exist in the condensed phase as soluble 'free' Lewis acid, the adduct with acetonitrile still exhibits Lewis superacidic behavior. In the reaction of $1-(CH_3CN)_2$ with [PPh4][SbF₆], rapid formation of the mono-fluorido adduct [1-F]⁻ was detected by ¹³C and ¹⁹F NMR spectroscopy, as well as ESI

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mass spectrometry. No defined reaction product was isolated due to follow-up reactions initiated by the strong oxidant SbF₅. Treating a solution of the hydridoborate salt [tBu₃PH][HB(C₆F₅)₃] with **1**-(CH₃CN)₂ led to hydride abstraction and formation of the adduct CH₃CN-B(C₆F₅)₃, experimentally supporting also the soft Lewis superacidic character of **1**.

With an established picture of the features of $1-(CH_3CN)_2$ concerning Lewis acidity and stability, the utility in Lewis acid catalysis was probed. First, the hydrosilylation of aldehydes was tested with 0.5 - 5 mol% of $1-(CH_3CN)_2$ as the catalyst. Aliphatic, electron-rich, and electron-poor aromatic aldehydes were cleanly hydrosilylated with Et₃SiH as reducing agent (Figure 4a). The feasibility of this process for electron-rich aromatic aldehydes outperforms the catalytic aptitude of Si(cat^X)₂ or electrophilic phosphonium cations.^[9a, 22] Those *harder* Lewis acids tolerate only electron-poor aromatic aldehydes in stoichiometric fashion.

The catalytic hydrodefluorination of an aliphatic C-F bond was successfully achieved for 1-adamantyl fluoride in CD₂Cl₂ (Figure 4b). An exceptionally high TON of >1900 (0.05 mol% cat, loading) was determined, underpinning the robustness of the catalyst towards eventual trace impurities or moisture. The intermediate detection of a signal corresponding to the mono-fluorido adduct [1-F]⁻ indicated C-F bond activation over Si-H bond activation as a more likely pathway for the reaction. Despite the outstanding activity with 1-fluoroadamantane as a substrate, no reaction could be observed for other C-F bonds. This lack of reactivity is attributed to the relatively strong binding of acetonitrile to 1-(CH₃CN)₂ and the inability of weaker donor substrates to displace the ligand for subsequent activation of the substrate by the Lewis acid. The significant computed hydride ion affinity of 1 tempted us to probe the catalytic activity in transfer hydrogenation reactions. Using 1,4-cyclohexadiene as hydrogen surrogate, the hydrogenation of 1,1-diphenylethylene (1,1-DPE) proceeded smoothly under full conversion at room temperature employing 10 mol% catalyst (Figure 4c). In the absence of a reductant, 1-(CH₃CN)₂ catalyzes the Friedel-Crafts dimerization of 1,1-DPE in typical Lewis acid fashion (Figure 4d). After heating at 50 °C for 24 h. 48 % conversion to the dimer was observed, very similar to the value previously reported for B(C₆F₅)₃.^[23] Interestingly, 1-(CH₃CN)₂ was also found to catalyze the intramolecular carbonylolefin metathesis of the β -ketoester **A**, which presents a powerful method for the formation of carbon-carbon bonds.^[24] The reaction proceeds with 5 mol% catalyst at room temperature, where full conversion of the substrate is achieved within 20 h. The formation of the byproduct acetone did not preclude catalytic turnover. Contrastingly, direct use of the acetone adduct 1-(acetone)₂ does not lead to any visible reaction even after prolonged heating. This observation emphasizes the critical role of displacement of the first Lewis base in a bis-adduct of 1. Several tests on the potential involvement of hidden proton catalysis were performed for the mentioned reactions (see supporting information). The outcome of those tests corroborated true Lewis acid catalysis of 1-(CH₃CN)₂ under the above-described conditions. Although, 1-(H₂O)_n was either inactive or considerably slower, a background reactivity by Brønsted acid catalysis was indicated in some reactions. Hence, the catalytic activity of the water adducts 1-(H₂O)_n itself was inspected. With 10 mol% of 1-(H₂O)₆ and Et₃SiH as the hydride source, clean transfer hydrogenation of 1,1diphenylethylene was achieved (Figure 4c).

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Figure 4. Catalytic applications of 1-(donor) in a) the hydrosilylation of aldehydes, b) the hydrodefluorination of 1-adamantylfluoride, c) the transfer hydrogenation of DPE, d) Friedel-Crafts dimerization of 1,1-DPE and e) the intramolecular carbonyl-olefin metathesis. The conversion was determined by ¹H NMR integration against an internal standard.

Control experiments using 1-(CH₃CN)₂ and D₂O verified that the transferred deuterium originates from bound water. Transfer hydrogenation combining water as a proton source and Et₃SiH as a hydride source was reported only recently for the first time, using an iridium catalyst.^[25] Yet, it is unprecedented for a main group catalyst. This reactivity renders aprotic adducts of 1 not only active in Lewis acid catalysis but qualifies protic adducts of 1 as easily accessible Brønsted acids for proton-driven catalysis. A quantitative description of the Brønsted acidity of 1-(H₂O)₂ was obtained by the computed gas-phase acidity (GA = standard Gibbs energy of deprotonation in the gas phase). For 1-(H₂O)₂, a GA value of 1168 kJ mol⁻¹ was calculated at the BP86/def2-TZVP level of theory.^[26] This acidity exceeds the computed values of HSO_3F (1233 kJ mol⁻¹) or H_2SO_4 (1272 kJ mol⁻¹),^[27] and approaches the strength of the Lewis superacid - water adduct H₂O-Al(OC(CF₃)₃)₃, for which a GA of 1148 kJ mol⁻¹ was calculated at the same level of theory.[14c] Indeed, the Brønsted acidity of a 0.1 mM solution of 1 in water was assessed qualitatively, in which the measured pH value of ≈4 corresponds to complete dissociation. It is worth reiterating that this Brønsted superacidic system is obtained simply by heating commercially available perchlorochatechol and GeO₂ in water.

In conclusion, adducts of bis(perchlorocatecholato)germane **1** were prepared as the first neutral Lewis superacid that is entirely stable under aqueous conditions, compellingly emphasized by its preparation *in* water. The Lewis superacidity of **1** and the hydrolytic stability was proven and rationalized by theory and experiment. If **1** is used as an adduct of aprotic donors, it serves as a versatile Lewis acid catalyst. As complex with protic donors, it promises applications in the field of Brønsted superacids. The robustness allows handling and catalytic transformations under standard bench-top conditions. The *soft* Lewis superacidic features of **1** might enable high activity in orbital controlled processes. Ultimately, it will allow to merge **1**) the activity

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expected from a Lewis superacid, 2) the selectivity achievable with a Lewis acid that is easy to derivatize, and 3) the robustness of an entirely water-stable species. Given those desirable features paired with its straightforward synthesis, we foresee many potential applications in organic synthesis and materials science.

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Bis(perchlorocatecholato)germane is a hard and soft Lewis superacid with unlimited water stability. Its utility in catalysis as both Lewis and Brønsted acid was demonstrated by application to a variety of catalytic transformations, such as hydrodefluorination, hydrosilylation, transfer hydrogenation and carbonyl-olefin metathesis.

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