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Calcium stilbene complexes: structures and dual reactivity[†]

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Addition of a calcium hydride complex to diphenylacetylene gave a complex in which the stilbene dianion symmetrically bridges two Ca^{2+} ions. DFT calculations discuss the effect of the metal stilbene coordination. The stilbene complex reacts as a base (with H₂) or an electron donor (with I₂) and catalyzes the reduction of diphenylacetylene.

The stilbene dianion $[Ph(H)C-C(H)Ph]^{2-}$, abbreviated here as SD, was synthesized already more than 100 years ago by Wilhelm Schlenk,¹ an extraordinary chemist who should not only be regarded as the father of Schlenk techniques but also as a pioneer of early main group organometallic chemistry.² Schlenk and coworkers reacted stilbene with metallic sodium to obtain Na₂(SD) in the form of an extremely air-sensitive brown-violet powder that in reaction with air emits a cloud of stilbene vapor (Scheme 1).

The latter reactivity nicely demonstrates the electron storage properties of this highly-charged dianion. The compound $Na_2(SD)$ can be seen as a hydrocarbon-soluble form of sodium metal³ that can be used as a tuneable reducing agent for the degradation of halogenated organic pollutants (Scheme 1).⁴ Additionally, this multipurpose reagent may function as a double nucleophile⁵ or a Brønsted base.⁶

Only a handful of metal stilbene complexes have been structurally characterized. These have been obtained by four different routes (Scheme 2) which include: (i) deprotonation of 1,2-diphenylethane (*e.g.* by BuLi-TMEDA),⁷ (ii) reduction of stilbene (*e.g.* by $Cp*_2Sm^{II}$ or $[ArNC(Me)C(Me)NAr]Al^{II})$,^{8,9} (iii) combined stilbene reduction and salt-metathesis (*e.g.* by successively adding Na and a lanthanide chloride complex)^{10,11} or (iv) double addition of a metal hydride complex to diphenyl-acetylene (*e.g.* by lanthanide hydride complexes).^{12,13} Herein we



Scheme 1 Synthesis and reactivity of Na₂(SD).



describe the synthesis, structure and reactivity of a calcium

stilbene complex by application of route (iv).

We recently reported the solvent-free amidinate calcium hydride complex $[tBuAm^{DIPP}CaH]_2^{14}$ (1, Fig. 1a) in which (N, aryl)coordination of the amidinate ligand saturates the large Ca²⁺ coordination sphere to stabilize the complex; $tBuAm^{DIPP} = tBuC[N(2,6-iPr-phenyl)]_2$. Reaction of 1 with diphenylacetylene in benzene at 80 °C led to a color change from white to brown-red and gave precipitation of a dark-red microcrystalline product

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Fig. 1 (a) Synthesis of $[tBuAm^{DIPP}Ca]_2(SD)$ (2). (b) Crystal structure of $[tBuAm^{DIPP}Ca]_2(SD)$; hydrogen atoms have been omitted for clarity (except those at the stilbene dianion). Selected bond distances (Å): Ca-N2 2.384(1), Ca-C30 2.617(2), Ca-C30' 2.591(2), Ca-C31 2.616(1), Ca-C36 2.860(2), and Ca-Ar 2.750(1)-2.922(2) (average: 2.839(1)). (c) Comparison of bond distances (Å) for $[tBuAm^{DIPP}Ca]_2(SD)$ (red), $[tBuAm^{DIPP}Yb]_2(SD)$ (blue) and $[AdAm^{DIPP}Ca]_2(SD)$ (green). (d) Selected bond distances for an Al stilbene complex.

 $[tBuAm^{DIPP}Ca]_2(SD)$. This synthetic route is comparable to that for the analogue Yb^{II} complex, $[tBuAm^{DIPP}Yb]_2(SD)$,¹² underscoring the great similarity between Ca^{II} and Yb^{II} chemistry.¹⁵

Due to the nearly equal ionic radii for Ca²⁺ and Yb^{2+,16} the Ca and Yb stilbene complexes crystallize isomorphically with closely related geometries. The centrosymmetric dimer $[tBuAm^{DIPP}Ca]_2(SD)$ is composed of two $tBuAm^{DIPP}Ca^+$ units that are symmetrically bridged by a stilbene dianion (Fig. 1b): the Ca-C distances range from 2.591(2) to 2.617(2) Å. There are additional attractive interactions between Ca2+ and the ring Cipso and Cortho atoms. The H atoms at the stilbene dianion have been refined and the sum of the valence angles of $352(1)^{\circ}$ at C30 indicates an essentially flat structure with sp²-hybridized carbon atoms. The double negative charge is significantly delocalized over the Ph substituents resulting in nearly equal C30-C30' (1.453(2) Å) and C30-C31 (1.437(2) Å) bond distances. Also the very acute C-C-C angle at Cipso (115.4(1)°) and elongated Cipso-Cortho bonds (1.423(2)-1.426(2) Å) are tell-tales for the extensive delocalization of electron density into the Ph rings.^{17,18} The slightly different complex with an adamantyl substituent in the backbone of the amidinate ligand, $[AdAm^{DIPP}Ca]_2(SD)$, shows an essentially similar geometry (Fig. 1c and ESI;† AdAm^{DIPP} = $(1-adamantyl)C[N(2,6-iPr-phenyl)]_2)$.

Apart from the Yb stilbene complex, not many structures are known for comparison. Crystal structures of $[Li(TMEDA)]_2(SD)$ and $[Li(PMDTA)]_2(SD)$ show similar connectivities.⁷ The metals bridge the stilbene dianion with equal Li–C bond distances but standard deviations are high on account of disorder. Also lanthanide(III) metals show symmetrical bridging but an exact bond analysis is plagued either by poor crystal quality $(Sm)^8$ or stilbene disorder (La, Y).¹⁰ A singular example of a bis-amide Al complex in which stilbene bridges between Al centers shows unequal Al–C distances (Fig. 1d).⁹ The stilbene fragment should be described as the dianion PhC[–](H)–(H)C[–]Ph with sp³-hybridized C atoms that form 2-center–2-electron C–Al bonds of considerable covalent character. Charge-localization on the central C atoms by Lewis acidic Al³⁺ is also evident from long C–C and C–Ph bonds.

The few available crystal structures of stilbene complexes suggest that SD in predominantly ionic compounds interacts symmetrically with metal cations and are highly delocalized whereas more covalent complexes contain SD fragments with localized negative charges. Given the lack of reliable structural data, a series of metal stilbene complexes was studied by computational methods. Centrosymmetric stilbene complexes with group 1–3 metals of increasing electronegativity have been optimized at the B3PW91//6-311++G** level (see the ESI† for calculations on the full complex). Selected geometric parameters and NPA charges are compared with the two extremes: SD and PhCH₂CH₂Ph (Table 1).

The C–C bond in SD is extremely short (1.388 Å) and close to that of a standard C=C double bond (1.337(6) Å).²⁰ Short Ph–C bonds indicate a considerable transfer of electron density from the benzylic Cs to the Ph groups which is supported by NPA charge analysis. In fact, the Ph groups carry more than 90% of the negative charge: q(Ph) = -0.904. Coordination of alkali metal cations leads to elongation of the C–C bond. This is due to the localizing effect of these cations that increases along the row K⁺ < Na⁺ < Li⁺ (*i.e.* with decreasing size and increasing Lewis acidity). NPA analysis indeed shows a strong increase of the negative charge on C with a concomitant decrease of q(Ph) along the same row K⁺ < Na⁺ < Li⁺. The bonding between SD and the alkali metals is quite ionic (80–90%) and metals bridge the C–C bond symmetrically (Q defined as M–C/M–C' \approx 1).

Bonding with group 2 metal cations Be^{2+} , Mg^{2+} and Ca^{2+} gives a larger variation in geometries. It is peculiar that although the ionicity of the metal-SD bonds and the negative charge on SD increase along the row $Be^{2+} < Mg^{2+} < Ca^{2+}$, the highest q(C) is found in the Be complex. This rather unusual situation is due to the very strong localizing effect of the small and highly Lewis-acidic Be^{2+} cation that, like Al^{3+} , polarizes electron density from the Ph rings towards the central Cs. This leads to extensive repulsion and a very long C–C bond of 1.570 Å.

Hybridization at these C atoms is quantified by the sum of the non-metal valence angles (Σ_{angles}) and changes from sp² (Ca) to sp³ (Be). The latter is also strongly reflected in the Ph–C

 Table 1
 Comparison of stilbene geometries (distances in Å and angles in °) and NPA charges (q)

Complex	X ^a	C-C'	Ph-C	$\Sigma_{\mathrm{angles}}{}^{b}$	M-C/M-C' = Q	$q(\mathbf{M})$	q(SD)	q(C)	q(Ph)
SD	_	1.388	1.428	360.0	_	_	-2	-0.272	-0.904
$K_2(SD)$	0.91	1.459	1.414	358.2	2.763/2.843 = 0.972	0.905	-1.810	-0.558	-0.543
$Na_2(SD)$	0.93	1.467	1.426	354.6	2.472/2.560 = 0.965	0.791	-1.582	-0.560	-0.432
Li ₂ (SD)	0.97	1.488	1.433	354.4	2.053/2.088 = 0.983	0.809	-1.618	-0.645	-0.388
$(HCa)_2(SD)$	1.04	1.487	1.437	354.7	2.548/2.565 = 0.990	1.513	-1.614	-0.695	-0.337
$(HMg)_2(SD)$	1.23	1.543	1.466	341.3	2.168/2.439 = 0.888	1.266	-1.436	-0.759	-0.186
(HBe) ₂ (SD)	1.47	1.570	1.506	332.2	1.698/2.591 = 0.655	1.152	-1.368	-0.853	-0.062
$(H_2AI)_2(SD)$	1.47	1.529	1.503	335.2	1.994/2.973 = 0.671	1.344	-1.192	-0.764	-0.069
$(H_2B)_2(SD)$	2.01	1.531	1.526	332.2	1.564/2.659 = 0.588	0.233	-0.294	-0.283	+0.022
PhCH ₂ CH ₂ Ph	2.20	1.543	1.507	331.4	1.095/2.162 = 0.506	0.211	-0.422	-0.396	-0.026

^{*a*} Allred–Rochow electronegativity of the metal (or B or H).^{19 *b*} Sum of the Ph–C–C, Ph–C–H and H–C–C valence angles defining the planarity/ hybridization of the C atom (360° is planar/sp² and 327° is tetrahedral/sp³).

and C–C bond lengths as well as in the metal–SD bonding which becomes less symmetric along the row Ca^{2+} (Q = 0.990) > Mg^{2+} (Q = 0.888) > Be^{2+} (Q = 0.655). Bonding of the SD unit with group 3 elements B and Al is considerably more covalent with ionicities of 15% (B) and 60% (Al). Both B and Al bridge asymmetrically with Q values of 0.588 (B) and 0.671 (Al). In agreement with the long (essentially single) C–C bonds, the central Cs are hybridized close to sp³.

The geometry of the calcium model complex $(HCa)_2(SD)$ closely resembles that of $[tBuAm^{DIPP}Ca]_2(SD)$ (Fig. 1b). Although the diagonal relationship²¹ between Li and Mg would predict close similarities between Li₂(SD) and $(HMg)_2(SD)$, Table 1 clearly shows that the Li and Ca stilbene complexes match better.

The highly air-sensitive complexes $[tBuAm^{DIPP}Ca]_2(SD)$ and [AdAm^{DIPP}Ca]₂(SD) are poorly soluble in C₆D₆ and partially decompose into homoleptic species (see the ESI[†]). Addition of hexane, however, regenerated crystals of the [RAm^{DIPP}Ca]₂(SD) complexes, demonstrating that decomposition is indeed due to ligand scrambling. In contrast, attempted NMR measurements of [tBuAm^{DIPP}Yb]₂(SD) resulted in exclusive hydrolysis of PhCH₂CH₂PH and the amidine *t*BuAm^{DIPP}H and therefore no further reactivity has been described.¹² The C₆D₆ solution of [*t*BuAm^{DIPP}Ca]₂(SD) shows a characteristic triplet at 5.88 ppm that may be assigned to the para-H of the SD ion. Its unusually high-field shift is comparable to that in benzyl alkali metal complexes²² and signifies considerable charge delocalization into the Ph ring. The ambivalent nature of SD, which can be seen as either the dianion PhC⁻(H)-(H)C⁻Ph or the delocalized dianion [Ph(H)C=C(H)Ph]²⁻, is also clear from its reactivity. In reaction with I₂, SD acts as an electron reservoir leading to the formation of Ph(H)C=C(H)Ph (cis/trans: 10/90) and a calcium iodide complex (Scheme 3). The latter crystallized as $[tBuAm^{DIPP}CaI \cdot (THF)_2]_2$ (3) in 40% yield (see the ESI[†] for details and crystal structures). In reaction with H₂, however, SD acts as a strong base yielding PhCH₂CH₂Ph and [tBuAm^{DIPP}CaH]₂ which could be isolated in a crystalline yield of 36%. Although the reaction with I₂ at low temperature $(-30 \,^{\circ}\text{C})$ is also very fast, the latter reaction with H₂ is much slower (6 bar, 80 °C, 2 days). The high temperature needed results in a partial ligand exchange (Schlenk equilibrium) to give $Ca(tBuAm^{DIPP})_2$ as a side product. The double addition of a calcium hydride complex to diphenylacetylene to give [tBuAm^{DIPP}Ca]₂(SD) and



Scheme 3 Reactivity of $[tBuAm^{DIPP}Ca]_2(SD)$ with I_2 and H_2 and the catalytic cycle for alkyne hydrogenation.

its further reaction with H_2 back to the initial calcium hydride complex suggests that Ca-catalyzed alkyne hydrogenation may be possible (Scheme 3). With few exceptions,²³ the latter process is generally catalyzed by noble transition metals (Ru, Os, Ir, Rh).²⁴ Indeed, nearly quantitative conversion of diphenylacetylene into 1,2-diphenylethane could be achieved: C₆D₆, 80 °C, 6 bar H₂, 10 mol% cat, 48 h, 97% conversion (see the ESI†). Considering the stoichiometric reactions discussed above, a likely catalytic cycle involves double hydride addition followed by double H₂ deprotonation (Scheme 3, right). Although there is precedence for a frustrated Lewis pair catalyzed alkyne-toalkene reduction,²⁵ the current Ca-catalyzed conversion represents the first transition metal-free alkyne-to-alkane reduction. The further substrate scope and selectivity of this catalytic procedure are currently under investigation.

In summary, double addition of a calcium hydride complex to diphenylacetylene gave the calcium stilbene complex $[tBuAm^{DIPP}Ca]_2(SD)$ that closely resembles its Yb analogue $[tBuAm^{DIPP}Yb]_2(SD)$. The crystal structure of this compound contains a highly delocalized stilbene dianion that is symmetrically bridged by Ca²⁺ ions. This bonding situation compares well to that in ionic alkali metal stilbene complexes. DFT-calculations demonstrate close similarities of electronics and structures in di-lithio stilbene complexes Li₂(SD) and (HCa)₂(SD). The ambivalent nature of the Ca stilbene complex is demonstrated by its reactivities with I₂ and H₂. In reaction with I₂, the stilbene dianion functions as an electron reservoir for the reduction of I₂ to 21⁻, giving stilbene as a side product. In this case, the Ca stilbene complex can be seen as a Ca(1) synthon, *i.e.* it reacts similar to the hitherto hypothetical *t*BuAm^{DIPP}Ca^I. Given the very negative reduction potential of SD (-2.72 V),²⁶ its reducing power is similar to that of Na. We are currently exploring the use of 2 as a synthon in organocalcium chemistry. In reaction with H₂, however, it reacts as a double Brønsted base that deprotonates H₂ giving the initial calcium hydride reagent [*t*BuAm^{DIPP}CaH]₂ and the side product 1,2-diphenylethane. The latter reactivity is the key to catalytic alkyne hydrogenation. The first Ca-catalyzed alkyne-to-alkane reduction demonstrates the growing scope and possibilities of alkaline-earth metal catalysis.²⁷

Conflicts of interest

There are no conflicts to declare.

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