ChemComm

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Group 3 metal stilbene complexes: synthesis, reactivity, and electronic structure studies†

Wenliang Huang, Paul M. Abukhalil, Saeed I. Khan and Paula L. Diaconescu*

Cite this: *Chem. Commun.*, 2014, **50**, 5221

Received 1st October 2013,
Accepted 15th November 2013

DOI: 10.1039/c3cc47505k

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Group 3 metal (*E*)-stilbene complexes supported by a ferrocene diamide ligand were synthesized and characterized. Reactivity studies showed that they behave similar to analogous naphthalene complexes. Experimental and computational results indicated that the double bond was reduced and not a phenyl ring, in contrast to a previously reported uranium (*E*)-stilbene complex.

Group 3 metals (scandium, yttrium, lanthanum, and lutetium) usually show chemistry representative of all rare earths and their compounds are easier to characterize because of their diamagnetic nature.[1,2] Their classification with lanthanides rather than with transition metals is supported by the fact that, with few exceptions,[2] their complexes contain the metal in the +3 oxidation state, while transition metals display multiple oxidation states. Recently, our group reported the synthesis of group 3 metal naphthalene[3–5] and biphenyl complexes[6] supported by a ferrocene diamide ligand (NN^{TBS} = 1,1′-fc(NSi^tBuMe_2)$_2$)[7] (Chart 1a). The metal naphthalene complexes, with the general formula $[(NN^{TBS})M(THF)_x](\mu\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8)$ (**M_2-naph**, M = Sc, x = 0; M = Y, La, Lu, x = 1), contain a naphthalene dianion bridging the two metal centers through different phenyl rings. The metal biphenyl complexes, with the general formula $([(NN^{TBS})M](\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_5Ph))$-$[K(solvent)]_2$ (**M_2K_2-biph**, M = Sc, Y, La, Lu, solvent = toluene, tetrahydrofuran, diethyl ether, or 18-crown-6), contain a biphenyl tetraanion bridging the two rare-earth centers through the same phenyl ring. While the negative charges in **M_2-naph** are equally distributed over the naphthalene fragment, the four electron reduction is mainly localized on the coordinating phenyl ring in **M_2K_2-biph** and results in a 6C,10π-electron aromatic system. DFT calculations on the naphthalene and biphenyl complexes showed π overlap for the former and δ overlap for the latter between the metal orbitals and arene π* orbitals.

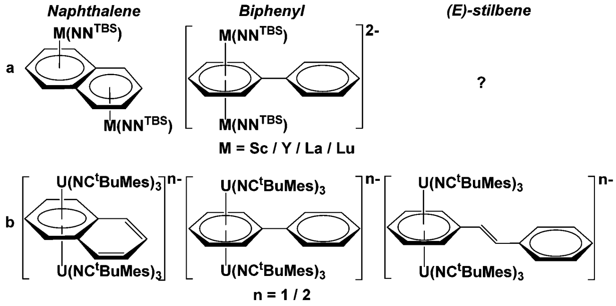

Chart 1 (a) Rare-earth arene complexes supported by a ferrocene diamide ligand; (b) uranium arene complexes supported by a ketimide ligand.

This bonding dichotomy is in sharp contrast to diuranium inverse sandwich arene complexes of biphenyl, *p*-terphenyl, naphthalene, and (*E*)-stilbene supported by a ketimide ligand (Chart 1b).[8] Despite the different nature of the arene, the resulting complexes shared analogous electronic structures, featuring δ overlap between LUMOs of one phenyl ring and the two uranium centers. The related diuranium inverse sandwich benzene or toluene complexes have been synthesized using various ancillary ligands and present a similar bonding character.[9–14] As mentioned, the δ interaction is also present in **M_2K_2-biph**,[6] but to a lesser extent than in the uranium compounds. Since group 3 metal arene complexes supported by the ferrocene diamide ligand showed discrepancy in the binding mode of naphthalene and biphenyl, we became interested in synthesizing the corresponding (*E*)-stilbene complexes; the presence of multiple sites for reduction and binding, *i.e.*, the C═C bond and the phenyl rings, will offer insight into the binding preference for rare-earths in comparison with uranium.

In spite of the abundance of rare-earth naphthalene complexes in the literature,[1,15,16] (*E*)-stilbene complexes are rare. Evans *et al.* reported the synthesis of $[(C_5Me_5)_2Sm]_2$((*E*)-stilbene) from $(C_5Me_5)_2Sm$ and (*E*)-stilbene.[17] The structure of $[(C_5Me_5)_2Sm]_2$-((*E*)-stilbene) was established based on connectivity data derived from X-ray crystallography; however, the poor quality of the data

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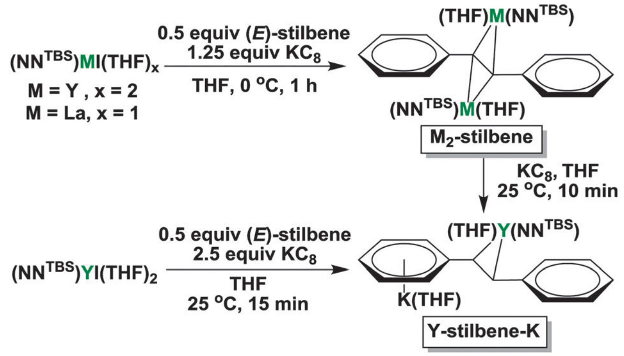
Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, USA. E-mail: pld@chem.ucla.edu

† Electronic supplementary information (ESI) available: Synthesis, characterization, NMR spectra, X-ray crystallographic data and DFT calculations. CCDC 963318–963320, 963896, 963897 and 969772. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc47505k



Scheme 1 Synthesis of **M_2-stilbene**, **Y-stilbene-K**, and transformation of **Y_2-stilbene** to **Y-stilbene-K**.

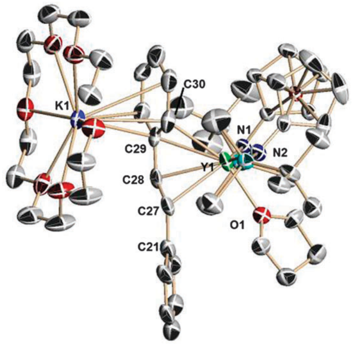


Fig. 2 Molecular structure of **Y-stilbene-K-crown**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and disordered counterparts were omitted for clarity.

prevented an accurate interpretation of the structural parameters. The analogous samarium styrene and butadiene complexes showed two electron reduction of the C=C bond and concomitant oxidation of Sm(II) to Sm(III).[18] Related yttrium and lutetium complexes of the readily available tetraphenylethylene dianion have been reported with similar structural features.[19,20]

Addition of 1.25 equiv. KC_8 to a pre-mixed THF solution of $(NN^{TBS})YI(THF)_2$ and 0.5 equiv. (*E*)-stilbene at −78 °C resulted in an immediate color change to dark green (Scheme 1). After stirring at 0 °C for 1 h, the color gradually changed to red. The ^1H NMR spectrum of the crude reaction mixture indicated the formation of a single product. Crystals suitable for single X-ray diffraction were grown from a toluene solution layered with hexanes. The molecular structure (Fig. 1) unambiguously established the formation of a yttrium (*E*)-stilbene complex with the formula $[(NN^{TBS})Y(THF)]_2(\mu\text{-}\eta^3{:}\eta^3\text{-}(E)\text{-stilbene})$ (**Y_2-stilbene**). The analogous lanthanum complex was synthesized following the same protocol and structurally characterized (see the ESI† for details, Fig. SX4). The synthesis of **M_2-stilbene** (M = Y and La) mimics that of **M_2-naph**: when excess KC_8 was used, the formation of a heterobimetallic complex, $[(NN^{TBS})Y(THF)][(E)\text{-stilbene}][K(THF)]$ (**Y-stilbene-K**), took place (Scheme 1). This is different from the synthesis of **M_2K_2-biph**: **M_2K_2-biph** was the only observed rare-earth product regardless of the KC_8 stoichiometry employed. It is interesting to note that adding KC_8 to isolated **Y_2-stilbene** did not afford further reduction but rather exclusion of one $(NN^{TBS})Y(THF)$ fragment to form **Y-stilbene-K** (Scheme 1). In addition, **Y-stilbene-K** could be generated from the reaction of **Y_2K_2-biph** and (*E*)-stilbene (see the ESI† for details). Attempts to obtain single crystals of **Y-stilbene-K** were not successful due to incorporation of labile potassium ions. However, by using 18-crown-6, single crystals of $[(NN^{TBS})Y(THF)](E\text{-stilbene})[K(18\text{-crown-}6)]$ (**Y-stilbene-K-crown**) were grown from a hexane solution and its molecular structure was determined by X-ray crystallography (Fig. 2).

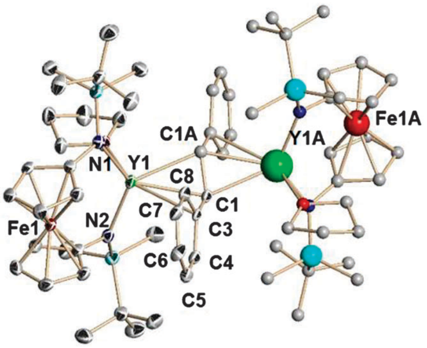
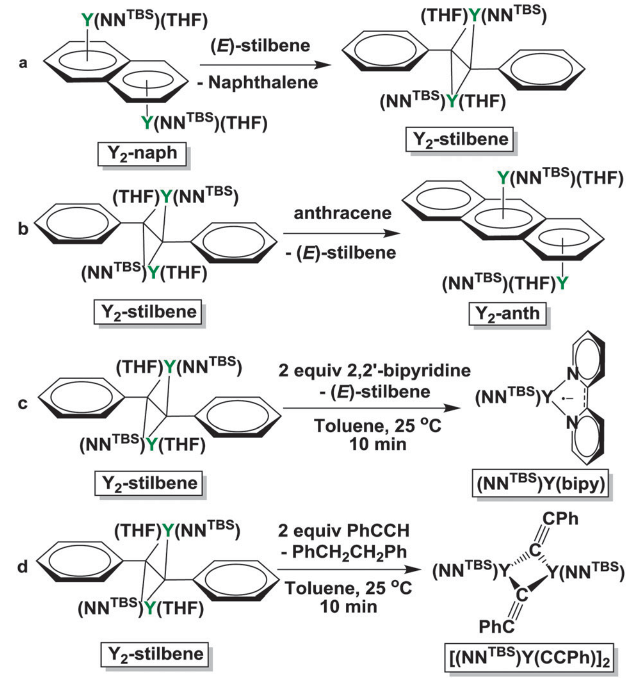


Fig. 1 Molecular structure of **Y_2-stilbene**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and disordered counterparts were omitted for clarity.

Disorder in the molecular structures of **M_2-stilbene** (M = Y, La) is caused by flipping the central C–C bond; the resulting two conformations were solved separately and only one is shown in Fig. 1 (see the ESI† for details and additional parameters). Since they are isostructural, **Y_2-stilbene** will be discussed as a representative. The bridging (*E*)-stilbene ligand coordinates equally to the two yttrium centers in an η^3-fashion through the central C–C bond and one *ipso*-carbon, with Y–C distances of 2.60, 2.58, and 2.74 Å, respectively. An additional contact between Y and one *ortho*-carbon of 2.99 Å is also present but is longer than the sum of the covalent radii of yttrium and carbon.[21] This symmetrical coordination mode is different from the asymmetrical coordination mode suggested for $[(C_5Me_5)_2Sm]_2((E)\text{-stilbene})$,[17] but is reasonable with the less sterically demanding NN^{TBS}. The C1–C1A distance of 1.52 Å is consistent with the single bond character, while the shortened C1–C3 distances of 1.43 Å and the elongated C3–C4 distance of 1.46 Å indicate charge delocalization. **Y-stilbene-K-crown** exhibits a similar coordination mode for yttrium as **Y_2-stilbene**, while K^+ is η^6-coordinated to one of the phenyl rings (Fig. 2).

Since the synthesis of **Y_2-stilbene** echoed that of **M_2-naph**, we were interested to determine the relative reducing strength of **Y_2-stilbene** with respect to that of the other rare-earth arene complexes. Based on arene exchange experiments (Schemes 2a and b), we found that the reducing power decreases in the order **Y_2-naph** > **Y_2-stilbene** > **Y_2-anth**. Compound **Y_2-anth** ($[(NN^{TBS})Y(THF)]_2(\mu\text{-}C_{14}H_{10})$) was synthesized from $(NN^{TBS})YI(THF)_2$ and anthracene following a similar protocol to that reported for the corresponding scandium complex.[5]

The arene exchange results prompted us to explore the reactivity of **Y_2-stilbene** toward organic substrates to compare its behavior



Scheme 2 Relative reducing strength of **Y_2-stilbene** (a, b) and its reactivity with organic substrates (c, d).

with that of **M_2-naph**. The reaction of **Y_2-stilbene** and 2,2′-bipyridine (bipy) or phenylacetylene (PhCCH) resembled the reactivity of **Sc_2-naph** and yielded $(NN^{TBS})Y(THF)(bipy)$ and $[(NN^{TBS})Y(THF)]$-$[(NN^{TBS})Y](CCPh)_2$ with the concomitant formation of (*E*)-stilbene and bibenzyl, respectively (Scheme 2c and d).[5] However, addition of excess pyridine did not yield the corresponding C–C coupled complex but rather an intractable mixture of products; no formation of (*E*)-stilbene was observed by ^1H NMR spectroscopy. This suggests that the dianion of (*E*)-stilbene is not innocent in this reaction.

The ^1H and ^{13}C chemical shifts of **M_2-stilbene** ($M = Y, La$) are consistent with the reduction of the C=C bond instead of the phenyl ring as indicated by their molecular structure and reactivity behavior. Group 3 metals prefer binding to the central C–C bond rather than to an aromatic ring as observed for uranium.[8] This difference in the binding mode prompted us to investigate the electronic structure of **M_2-stilbene** by DFT calculations. The computed molecular parameters matched well with the experimental structure (Table S1 in the ESI†). The HOMOs of **M_2-stilbene** were found to be comprised of the π* orbitals of the central C–C bond and are stabilized by a π interaction with the metal ions and delocalization to adjacent phenyl rings (Fig. 3). This π interaction is similar to that observed for **Sc_2-naph**[5] but different from the δ interaction observed in uranium arene complexes.[8,10,22] These results suggest that, while uranium forms relatively strong δ interactions with the π* orbitals of arenes, likely because of the involvement of f orbitals, rare-earths prefer π binding over δ binding. Only in the case of **Y_2K_2-biph**, where no π* orbitals with π symmetry are available, the δ interaction dominates to afford an unprecedented 6C,10π-electron aromatic system.[6]

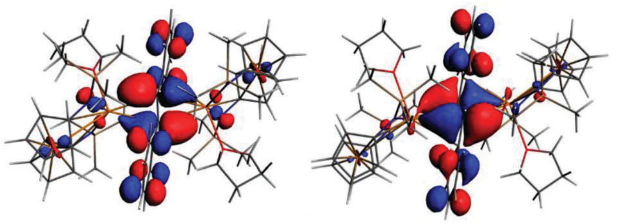


Fig. 3 HOMO plot for **Y_2-stilbene** (left) and **La_2-stilbene** (right).

In summary, we successfully synthesized group 3 metal (*E*)-stilbene complexes through reduction of (*E*)-stilbene by the (NN^{TBS})-$MI(THF)_x$–KC_8 system. The resulting complexes, **M_2-stilbene**, showed similar reactivity to **M_2-naph** complexes. Both experimental and computational data suggest that the reduction takes place at the C=C bond instead of the phenyl ring. This contrasts the case of uranium and indicates different binding preferences for rare-earths that are similar to those of transition metals and not actinides. Our synthetic route also allows access to rare-earth alkene complexes, which were previously limited to samarium.[23]

This work was supported by NSF (CAREER Grant 0847735 to PLD and CHE-1048804 for NMR spectroscopy). The authors thank the Kaner group (UCLA) for generous gifts of KC_8.

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