Arene complexation of Sm, Eu, Tm and Yb atoms: a variable temperature spectroscopic investigation

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Abstract

Codeposition of a monatomic lanthanide vapour (Sm, Eu, Tm or Yb) and tri-*tert*-butylbenzene $C_6H_3-{}^tBu_3$-1,3,5 onto a cold (77 K) surface affords matrices that contain zerovalent bis(η-arene)lanthanide complexes of the form $[Ln(\eta^6-C_6H_3-{}^tBu_3-1,3,5)_2]$ as formed in macroscale co-condensation reactions using metal vapour synthetic (MVS) techniques. The reproduction of the experiments in the 77 K matrix allows the detailed characterization of thermally unstable members of the series that were previously not possible. The bis(arene) sandwich complexes $[Ln(\eta^6-C_6H_3-{}^tBu_3-1,3,5)_2]$ (Ln = Sm, Eu) are stable at low temperatures, but may not be the only products of the cocondensation reactions, while the analogues $[Ln(\eta^6-C_6H_3-{}^tBu_3-1,3,5)_2]$ (Ln = Tm or Yb) cannot be made at liquid nitrogen temperatures. By replacement of tri-*tert*-butylbenzene with N- and P-substituted heteroarenes $NC_5H_2-{}^tBu_3$-2,4,6 and $PC_5H_2-{}^tBu_3$-2,4,6, the relative stabilities of these zerovalent complexes have been determined. Lanthanum vapour was also cocondensed with the arenes using MVS techniques, and the crude product extracted directly from the machine was analysed in solution at −78 °C. There is very little difference in thermal stability between carbocyclic and heteroaromatic sandwich derivatives of an individual metal.
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1. Introduction

A number of unusual f-element complexes in unprecedented, formally low-valent, oxidation states have been reported recently, including divalent lanthanum, lanthanide, thorium and uranium cations in the +1 and +2 oxidation states [1]. Many of these show electrostatic interactions with aromatic ligand groups such as five-membered ring heterocycles, or commonly, arene solvent molecules. These reduced electropositive metal complexes show fascinating reductive chemistry, and

have opened a new area of chemistry for these electropositive metals [2]. We have previously used the technique of metal vapour synthesis (MVS) to generate bis(η^6-arene) f-element complexes, in which the spectroscopic and magnetic properties of the complexes support the formulation of the zerovalent oxidation state of the lanthanide [3]. A metal vapour formally provides the simplest source of zerovalent lanthanide 'starting material' for the synthesis of molecular zero- or low-oxidation state lanthanide organometallic complexes [4]. Kinetic stabilisation of the complexes using bulky ligands, e.g. 1,3,5-tri-*tert*-butylbenzene (Bz*) allows the isolation of a range of complexes such as $[Gd(\eta^6-C_6H_3-{}^tBu_3-1,3,5)_2]$ (1), for which a significant metal arene bond enthalpy has been measured [5]. However, the largest metals, La and Ce, and those with a high one-

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electron f→d promotion energy, including Sm, Eu, Tm and Yb, did not give complexes that were isolable at −78 °C—the lowest convenient temperatures at which products can be extracted from the MVS apparatus [6] (Fig. 1).

In order to understand further the factors affecting the stability of these complexes, we have used specially developed cryostats to study the low-temperature syntheses of the sandwich arene complexes. In this paper we report the results of a spectroscopic investigation of the formation and decomposition of different arene sandwich complexes of the four metals Sm, Tm, Eu and Yb. We have also prepared the unstable La complex and analysed the crude product at low temperatures. The study of the analogous lanthanide complexes of the heteroatom-substituted arenes 2,4,6-tri-*tert*-butylpyridine (NBz*) and 2,4,6,-tri-*tert*-butylphosphorin (PBz*), has also been undertaken, to investigate the influence of the heteroatom on complex stability (Fig. 2).

2. Experimental

All metals were used as purchased except lanthanum which was degassed before use (99.9%). The ligands 1,3,5-tri-*tert*-butylbenzene, 2,4,6-tri-*tert*-butylpyridine, and 2,4,6-tri-*tert*-butylphosphorin were synthesised according to literature procedures and were recrystallised from pentane, then sublimed (10^{-3} mbar) before use.[7] In the synthesis of PBz* the final step differed from that described in the literature: Under an inert atmosphere, a stirred yellow solution of 2,4,6-tri-*tert*-butylpyrillium tetrafluoroborate (18 g, 0.06 mol) and Li[P(SiMe$_3$)$_2$] (22 g, 0.086 mol) in THF (400 ml) was heated to reflux for 96 h. After this time, volatiles were removed under reduced pressure and a yellow solution extracted with hexanes and filtered through a bed of Celite. Removal of volatiles under reduced pressure afforded a yellow waxy solid from which PBz* could be isolated as an air stable white precipitate after dissolution in a minimum volume of ethanol and dropwise addition of water. Yield 75%, 11.75 g. The synthesis of Li[P(SiMe$_3$)$_2$] is outlined in the literature [8].

The cocondensation of lanthanum vapour with 2,4,6-tri-*tert*-butylphosphorin was performed according to a
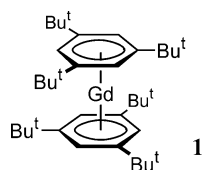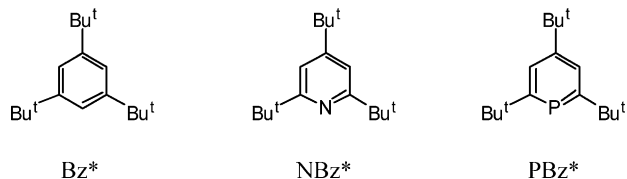
Fig. 2.

modification of the method used to prepare bis(η-2,4,6-tri-*tert*-butylphosphorin)holmium [9]. However, the matrix was only allowed to warm to ca. −78 °C before being extracted with cold (−78 °C) hexanes, and collected in a cooled Schlenk flask. Subsequent filtration through a bed of celite, or teflon powder, to remove unreacted metal particles, and concentration of the solutions for spectroscopic analyses were performed at −78 °C.

The cryostats used were specially developed in the Low Temperature Chemistry Laboratory of Moscow State University; the construction of these has been described in detail elsewhere.[10] The apparatus allows IR and UV–vis. spectroscopic characterisation of the matrix formed in situ under vacuum at 77–300 K. A typical cocondensation experiment involved evacuation of the system to below 10^{-4} mbar then simultaneous evaporation of the metal (from a resistively-heated alumina crucible) and ligand (from a needle-valve controlled, water-cooled inlet) to form a co-condensate film on a cooled spectroscopic window, to known thickness. Deposition rates were adjusted to ensure an excess of ligand, thus minimising the formation of metal clusters in the matrix. Matrices were deposited onto the window of a cooled (77 K) quartz cuvette suitable for transmission UV–vis spectroscopy and spectra recorded after rotating the window by 90°. IR spectra were obtained by reflective methods on a matrix deposited onto a cooled (77 K) polished copper block, after a 90° rotation of the block. The deposition conditions employed for metals and ligands were the same for each experiment, and the spectroscopic apparatus of comparable geometry so comparisons of the matrices formed can be made with confidence.

3. Results and discussion

3.1. Cocondensation experiments

Macroscale cocondensation experiments were used to study lanthanum complexes, and a mixture of macro and microscale cocondensation experiments were used to study samarium, europium, thulium and ytterbium complex formation and stability.

Fig. 1.

(1)
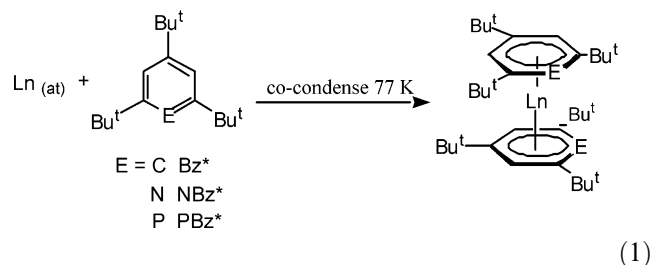
Both macroscale and microscale co-condensation reactions were carried out for Sm and Bz* or NBz*. From the physical and spectroscopic properties we infer that the thermally unstable π-complexes formed in the matrix are the same as those formed in the macroscale MVS experiments (Eq. (1)).

The MVS reactions of La and Sm vapours with 2,4,6-tri-*tert*-butylarenes were all performed analogously to the syntheses of the thermally stable bis(η-2,4,6-tri-*tert*-butylarene) Group 3 and Ln complexes, Eq. (1). However, the matrices were only allowed to warm sufficiently to allow the compounds to be washed out of the reactor with hexanes. Subsequent manipulations were performed at or below −78 °C. The cryostats used in the microscale co-condensation reactions contain either a cooled quartz spectrophotometric cell, or a cooled copper cube as a surface for the co-condensate. This allows either transmission UV–vis or reflectance IR spectroscopic investigations to be carried out. The metal:ligand ratio used in each of the experiments was approximately equal, and excess in ligand.

Matrix spectra were recorded from 77 K, upwards in increments of 10 K. The results are collated in Table 1.

The deposition of either Bz* or NBz* in the absence of metal afforded a colourless glassy film on both the copper block and the quartz cell at 77 K.

3.1.1. Lanthanum complexes

The lanthanum complexes are sufficiently thermally stable to be extracted from the MVS machine. The expansion of the arene ring arising from substitution of one C with a P atom is depicted in Fig. 3, drawn to scale [12]. It was considered that lanthanum bis(η-arene) sandwich complexes with these larger ligands might be kinetically more stable, and perhaps even isolable at room temperature. The co-condensate formed between La vapour and PBz*, and its solutions, are brown. Unfortunately, the hexanes extract of the complex is only stable at temperatures up to 283 K, so the complex formed is more stable than the carbocyclic analogue, but only slightly.

However, the effect on the λ_{max} of the La/arene matrix upon changing from Bz* to PBz* is an order of magnitude larger for La than any of the other lanthanides studied, and also the Group 4 bis(η-arene) sandwiches [13]. The very low λ_{max} value for the complex assumed to be [La(PBz*)$_2$] could be due to the charge transfer taking place between different frontier orbitals; it is conceivable that the metal size
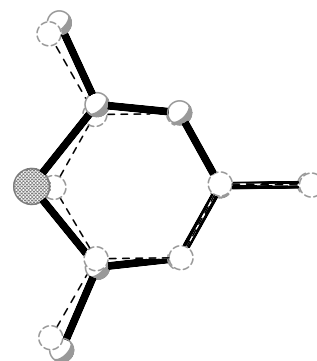

Fig. 3. Scale overlay ORTEP picture of the core C$_5$P and C$_6$ rings from crystallographic data [15].

Table 1
Properties of cocondensates between La, Sm, Eu, Tm and Yb and bulky aromatic ligands

Metal	Ligand	Degradation temperature (K)	IR absorption bands (cm^{-1})	UV–vis absorption bands at 80 K (nm)
La	Bz*	273	–	637 [a]
	PBz*	283	–	417
Sm	Bz*	225	967 and 973, 1280	653, 690.6
	NBz*	220	943, 1290	715
	PBz*	200	–	713.0
Eu	Bz*	200	969	581.4/714.3
Tm	Bz*	140	–	(410)
	NBz*	140	–	(450)
Yb	Bz*	–	–	(693)
	NBz*	–	–	(490)
	Bz*	–	898, 1120, 1246, 1358–1450, 1472, 1593 [b]	230.6, 260.1(sh)
	NBz*	–	1250, 1356, 1407, 1472, 1541, 1559, 1597	224.2, 227.2(sh)

[a] Ref. [11].
[b] Full assignment (ab initio calculations) 715, δ_{CH} ring (out of plane) 874, δ_{CC} ring(out of plane) 898, δ_{CC} (ring) 931, δ_{CC} (*tert*-butyl, rotational) 1020, δ_{CH} (CH$_3$) 1120, δ_{CH} (ring) 1198, ν_{CC} (*tert*-butyl) 1246, ν_{CC} (ring, *tert*-butyl) 1358–1450, δ_{CH} (CC$_3$) 1472, δ_{CH} (CC$_3$, bending) 1593, ν_{CC} in ring.

and dipolar contributions favour a bent sandwich complex for this metal. Several groups have reported calculations on the actinide system $[An(\eta^6\text{-}C_6H_3R_3)_2]$ (An = Th, U, Pu; R = Me, tBu); these molecules have yet to be isolated. They tentatively conclude that the bis(η-arene) actinide complexes will be bent, rather than coplanar sandwich complexes, if electronic factors dominate the bonding [14].

3.1.2. Samarium complexes

The codeposition of samarium vapour with Bz* or with NBz* afforded a dark blue–green coloured film. New bands observed in the IR spectrum at 77 K (Table 1) in each experiment indicate the formation of a metal–ligand adduct assigned as the bis(η^6-arene) sandwich complex (the assumed product of the macroscale co-condensation), by comparison with IR spectra of thermally stable analogues. The unsymmetrical band in the UV–vis spectrum of the SmBz* matrix compares closely with that obtained from the macroscale experiment (691 nm in pentane solution recorded at 180 K). Both IR and UV–vis spectroscopic monitoring of the annealed matrix showed decomposition of the complexes at 210 K.

The characteristic intense band in the visible region of the spectra of bis(η-arene) complexes of lanthanides are assigned to a ligand-to-metal charge transfer (LMCT) transition [6]. Matrices of Sm/NBz* or Sm/PBz* impart a visibly greener hue to the co-condensate film, indicative of a LMCT charge transfer band of lower energy.

Fig. 4(a) shows a basic MO scheme suggested for an yttrium (f^0) bis-arene sandwich complex. It is suggested that a lanthanide atom with a d^{1}s^2 (or f^{n-1}d^{1}s^2) configuration can form a bis(η-arene) sandwich complex, by analogy with transition metal sandwich com-

plexes, with three electrons in the e$_{2g}$ ([Y(Bz*)$_2$] has a ^{2}E ground state). Fig. 4(b) is a correlation diagram between the experimental EAs and IPs of benzene and Group 15 heterobenzenes [16]. In the frontier MOs of these complexes there are a number of orbitals that could receive charge donation from ligand-based orbitals. Most importantly, the incorporation of the pnictogen atom lifts the degeneracy of the two e sets in Bz*, Fig. 4(b), suggesting that these remain unpaired in orbitals of different energies. The transitions measured in these heteroarene complexes must arise from electron donation into the lowered of the split π* set of the manifold of available frontier orbitals. Of less importance, the frontier a$'_{1g}$ MO should be at a slightly higher energy in the bis(η-NBz*) and bis(η-PBz*) complexes than in the bis(η-Bz*) complexes, leading to in an increased partial positive charge on the metal, a contraction of the metal d$_{z^2}$ orbital, and a decreased metal–ligand orbital overlap.

There appeared to be more than one unstable species in the Sm–Bz* matrix, so the product decomposition in the matrices have been investigated further over the range 100–240 K. The UV–vis. spectra recorded between 95 and 215 K are shown in Fig. 5; above these temperatures the spectra lose all structure. During the annealing process, no change in intensity of any absorption bands in the IR- and UV–vis. spectra of the matrix was observed until 160 K. At this temperature a decrease in intensity of the band at 967 cm^{-1} was detected (spectra are in the supplementary information). Above 180 K the intensity of the band at 973 cm^{-1} started to decrease; both bands had decreased to baseline by 200 K. Both spectroscopies suggest that the matrix contains two compounds, one of which is less thermally stable than the other.
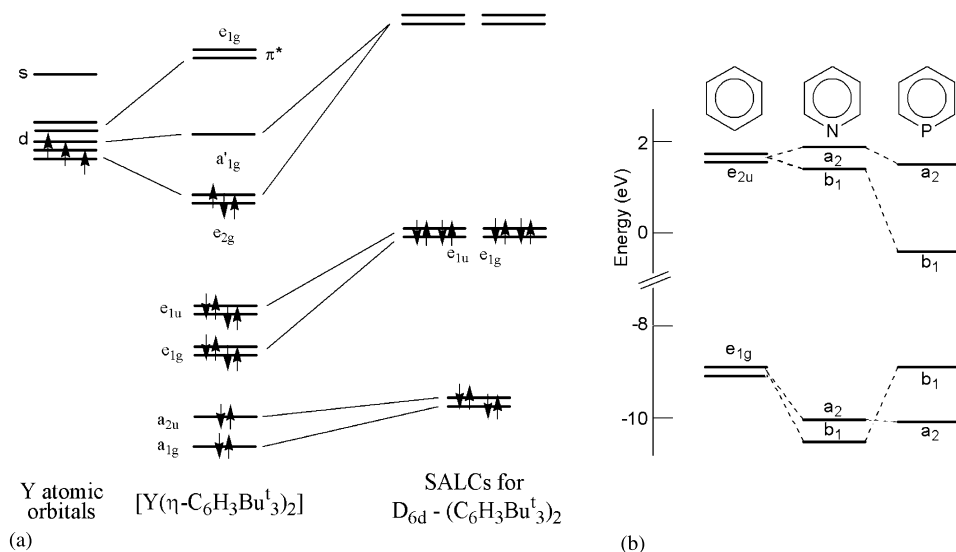

Fig. 4. (a) Basic MO scheme for a zerovalent arene yttrium sandwich complex (b) correlation diagram between the experimental EAs and IPs of benzene and Group 15 heterobenzenes.
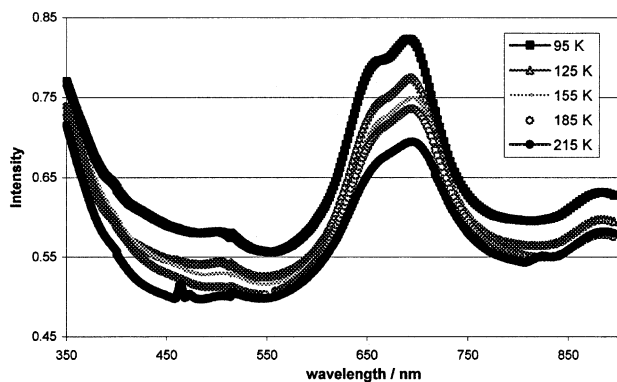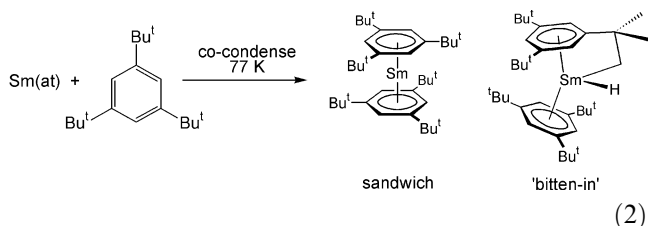
Fig. 5. UV–vis spectra of Sm/Bz* matrix recorded at intervals on warming the matrix from 95 to 215 K.

Two possible processes might account for this unanticipated observation:

(2)

The first possibility is that a 'bitten in' complex, as shown in Eq. (2), is being generated in addition to the sandwich, as has been observed by EPR for a scandium/Bz* matrix [17]. The Sc(0) and Sc(II) derivatives could not be interconverted post-synthesis, and only the Sc(0) complex could be isolated pure, always at the expense of the putative 'bitten-in' hydride. The particular stability of the divalent state for Sm supports this possibility, and since loss of the neutral arene still leads to complex degradation, the similarity in decomplexation temperature seems reasonable [18]. The intense absorption maxima of the two also compares favourably with the UV–vis. spectra of the scandium complex mixtures. A samarium hydride band, expected around 1140 cm^{-1} in the IR spectrum, was not observed, although this is often difficult to see [19].

The second is the formation of two complexes in the matrix that differ simply in metal:ligand ratio, Fig. 6. Previously, measurement of the analogous Sc complex product ratios from co-condensates formed at different temperatures, and unsuccessful experiments to interconvert the Sc(0) and Sc(II) complexes suggest that the
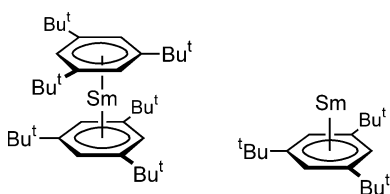

Fig. 6.

species [Sc(η-C$_6$H$_3^t$Bu$_3$)] is the most likely stable intermediate; this matrix may thus contain a mixture of [Sm(η-C$_6$H$_3^t$Bu$_3$)] and [Sm(η-C$_6$H$_3^t$Bu$_3$)$_2$]. The decomposition of one complex at 160 K corresponds to an activation energy of 7–10 kJ mol^{-1} for the process. This value is characteristic for a diffusion-controlled process, suggesting sufficient mobility in the matrix for the monoarene fragment to come into contact with a second arene in the correct geometry to form the sandwich complex, which itself decomposes at 200 K.

3.1.3. Europium complexes

The codeposition of Eu with Bz* results in blue–green matrices that retain their colour to 140 K. If the *tert*-butyl C–H activation process described above is occurring to yield two complexes in the matrix, we cannot rule out the possibility that two Eu complexes have also been formed. However, the very low stability of this complex did not allow for a detailed study of decomplexation.

3.1.4. Thulium and ytterbium matrices

All co-condensations involving Tm/Bz*, Tm/NBz*, Yb/Bz* and Yb/NBz* gave only grey (Tm) or red–brown (Yb) matrices with broad, low intensity absorbance bands in the visible region at 80 K, indicative of colloidal metal. In the macroscale co-condensation experiment this same red colour was also observed. The colloid colour is not uncommon in matrix isolation work of this nature, and does not require the occurrence of any orbital overlap between the metal and ligand [20].

3.2. Trends in stability

Table 2 summarises the promotion energy for the configuration change to (s^{2}d^1) for these lanthanides [21]. It also shows the available radius data of selected neutral metal atoms (no standard data are available for covalent lanthanide compounds).

3.2.1. Promotion energy

The promotion energy to the f^{n-1}d^{1}s^2 configuration (from f^{n}s^2 in the ground state) is notably higher for Eu and Yb, increasing in the order Tm < Sm < Yb $\sim$ Eu. (The electronic configuration of Sc and La is f^{0}d^{1}s^2). In general, the thermal instability of the sandwich complexes shows a correlation with a high value of the promotion energy to form a bonding electron configuration. This is presumably not sufficiently offset by the metal–arene bond enthalpies to afford stable complexes.

However, from promotion energy considerations, the putative Yb complex should be as stable as the Eu complex we observed, and a Tm complex more stable than one of Sm. Our failure to observe these complexes cannot simply be due to a discrepancy between the energy required to generate a Ln (s^{2}d^1) configuration and the energy gained from the formation of two arene–

Table 2

Metal	Promotion energy [a] to $f^{n-1}d^1s^2$/ 10^3cm^{-1}	Atomic radius (empirical) [b]	Atomic radius (calculated) [c]	Atomic radius (metallic) [d]	Covalent radius (empirical) [d]
La	− 15	1.95	None available	1.870	1.69
Sm	15	1.85	2.38	1.790	None available
Eu	26	1.85	2.31	1.995	None available
Tm	12	1.75	2.22	1.724	None available
Yb	25	1.75	2.22	1.940	None available
Sc	–	1.60	1.84	1.606	1.44

[a] Ref. [21].
[b] Radii defined from measurement in ionic, covalent and metallic compounds and crystals, Ref. [22].
[c] Ref. [23].
[d] Ref. [24].

Ln bonds. This suggests that the bonding model originally proposed for these bis(η-arene) complexes may be too simple. Further experiments to clarify the electronic configuration of the perdeuterated dysprosium complex [Dy(η-Bz*-d$_{30}$)$_2$] are in progress [25].

3.2.2. Size

The lanthanum complex is assumed to be kinetically reactive towards decomposition processes involving attack at the large metal, but is stable to temperatures as high as 273 K. This compares with the stable, sublimeable (10^{-5} mbar, ca. 100 °C) yttrium and scandium complexes.

If another reason for instability lies in the fact that covalent radius of zerovalent Tm or Yb is too small to bond two tri-*tert*-butyl arenes, it is only a contributing factor, since the titanium sandwich complexes of all these arenes are kinetically stable molecules [13].

4. Conclusions

The less thermally stable members of the family of zerovalent arene–lanthanide complexes have proven amenable to study by matrix isolation techniques. However, it is not possible to make all members of the series of zerovalent bis(arene) or bis(heteroarene) lanthanides at 77 K. The large, early metals form complexes which are characterised as bis(η-arene) complexes, but incorporation of the heteroatom is insufficient to stabilise the La complex at room temperature. The change from carbocyclic to Group 15 heterocyclic ligands does not appreciably affect the thermal stability of the resultant arene sandwich complexes, so long as the arene is sufficiently bulky kinetically to stabilise the metal and prevent reactions of the pnictogen lone pair.

Of the metals for which the s–d promotion energy is too high, namely Sm, Eu, Tm, and Yb, only the two larger (Sm and Eu) form complexes. The simple Sm and Eu bis(arene) sandwich complexes [Ln(η^6-C$_5$H$_2$E^{t}Bu$_3$)$_2$] (E = CH, N, P) may not be the only products of the

cocondensation reactions. Surprisingly, the Tm and Yb analogues cannot be made even at liquid nitrogen temperatures. The arguments for stability based on the metal radius, and electronic promotion energy, are still valid for the complexes that are stable above 77 K, but our inability to make Tm and Yb complexes in the matrix suggests that the bonding model originally proposed for these bis(η-arene) complexes may be too simple.

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