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Isocarbonyl complexes of divalent samarium and ytterbium. The molecular structures of [{Ln($Tp^{tBu,Me}$)(THF)(μ-CO)$_2$Mo(η-C_5H_4Me)(CO)}$_2$] (Ln = Sm, Yb)

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The reaction of [Ln($Tp^{tBu,Me}$)I(THF)] (**1a** Ln = Sm, **1b** Ln = Yb) with Na[Mo(η-C_5H_4Me)(CO)$_3$] gives good yields of [{Ln($Tp^{tBu,Me}$)(THF)(μ-CO)$_2$Mo(η-C_5H_4Me)(CO)$_3$}$_2$], **2a** (Ln = Sm), **2b** (Ln = Yb). The low temperature X-ray crystal structures of **2a** and **2b** have been determined. The structures contain a 12-membered ring of samarium/ytterbium and molybdenum atoms with isocarbonyl groups linking the metal centres. **2a** represents the first example of an isocarbonyl bound to samarium(II). Addition of pyridine results in the breakup of the tetramer to give [{Ln($Tp^{tBu,Me}$)(py)$_n$(μ-CO)Mo(η-C_5H_4Me)(CO)$_2$}$_2$].

Introduction

The reactivity of samarium(II) iodide towards a wide range of saturated and unsaturated organic molecules is now widely applied in organic synthesis.[1] A detailed understanding of such reactions is gradually being built up thanks to careful work involving stoichiometric reactions of samarium complexes bearing suitable ancillary ligands, which allow the isolation of 'intermediates' containing the substrate bound to the metal centre. Samarocene and its derivatives in particular have been widely explored in Evans' group and have yielded a wealth of unusual reactions.[2]

However, bis-cyclopentadienyls of divalent lanthanides effectively offer only neutral binding sites for incoming substrates and attempts to prepare heteroleptic complexes have been hampered by ligand redistribution reactions. Alternative ancillaries such as alkoxides and hydrocarbyls, even when quite sterically demanding, invariably yield dimeric heteroleptic complexes.[3]

The use of tris(pyrazolyl)borate (Tp) ligands confers considerable control over a metal centre and is now being applied to lanthanide centres.[4] We and others have been interested in the exploration of divalent chemistry of samarium and ytterbium where the steric control offered by the non-planar Tp ligands should allow us to generate asymmetrical mononuclear TpMLX-type species capable of accommodating additional neutral L ligands *cis* to the X group.[5,6] A trivalent system of this type has also been reported recently.[7] It also provides a system in which to test the stability of anionic ligands beside a reducing metal centre. Carbon monoxide is an intriguing substrate in lanthanide chemistry because of its inertness in the absence of backbonding. Thus what little is known of its reactivity appears to be associated with electron transfer leading to the formation of ketenes and accompanied by CO bond cleavage— Evans has shown that decamethylsamarocene reacts with neutral CO at high pressure to give an unusual ketene-carboxylate.[8]

The preparation of heterobimetallics of the lanthanides with d-block transition metals has been carried out in two ways: by reductive cleavage of metal–metal bonds and by reaction of lanthanide halides with carbonyl metalates.[9] Here, we describe application of the latter method to the preparation of isocarbonyl complexes of divalent samarium and ytterbium.

Results and discussion

Addition of Na[Mo(η-C_5H_4Me)(CO)$_3$] to a solution of [Ln($Tp^{tBu,Me}$)I(THF)] (Ln = Sm **1a** or Yb **1b**) gave a deep blue–green (Ln = Sm) or bright yellow solution (Ln = Yb). Extraction into diethyl ether and cooling to −20 °C yielded deep blue or canary yellow blocks of **2a** and **2b** respectively as their diethyl ether solvates which were found to desolvate fairly quickly upon removal from the mother liquors [eqn. (1)].

$$[Ln(Tp^{tBu,Me})I(THF)] + Na[Mo(\eta\text{-}C_5H_4Me)(CO)_3] \longrightarrow$$

$$[\{Ln(Tp^{tBu,Me})(THF)Mo(\eta\text{-}C_5H_4Me)(CO)_3\}_2] + NaI\downarrow$$

(Ln = Sm, **2a**; Ln = Yb, **2b**)

Both compounds are quite air and moisture sensitive, the solids decomposing within a few seconds of exposure to air. They dissolve easily in hydrocarbon and ether solvents. The solid state infrared spectra show the expected B–H stretching absorption around 2555 cm^{-1}, compared with 2463 cm^{-1} in $KTp^{Me,Me}$, consistent with a tridentate Tp ligand bound to a lanthanide.[10] A number of intense bands appear in the carbonyl region corresponding to the stretches of the terminal CO groups at approximately 1920 and 1834 cm^{-1} and low energy bands at 1745 and 1687 cm^{-1} diagnostic of bridging isocarbonyl groups. This compares with 1654 cm^{-1} observed, for example, in the related trivalent complex [Sm($Tp^{Me,Me}$)$_2$(μ-OC)Mo(η-C_5H_4Me)(CO)$_2$][11] which is in a range similar to those observed by others previously. That the complexes retain their integrity in toluene solution is suggested by the presence of three IR bands at closely similar wavenumbers to those recorded in the solid state. Both compounds gave readable ^{1}H NMR spectra, that of **2b** being sharp, consistent with the diamagnetic f^{14} metal centre. No significant changes were observed in the spectra of either compound on cooling the sample.

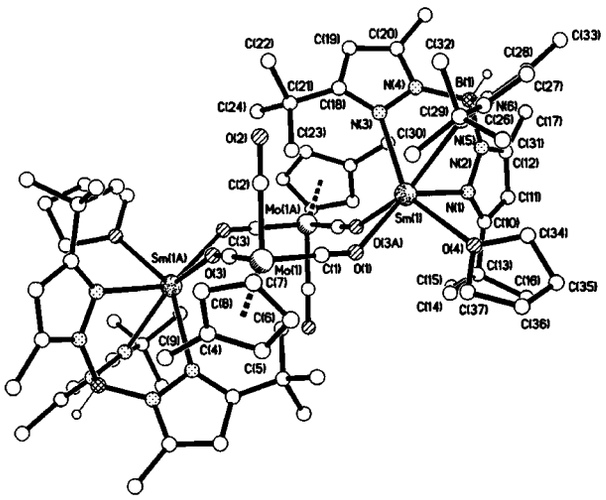

Fig. 1 Molecular structure of **2a** with the atom numbering scheme defined. H-atoms, and diethyl ether molecule of crystallization omitted for clarity.

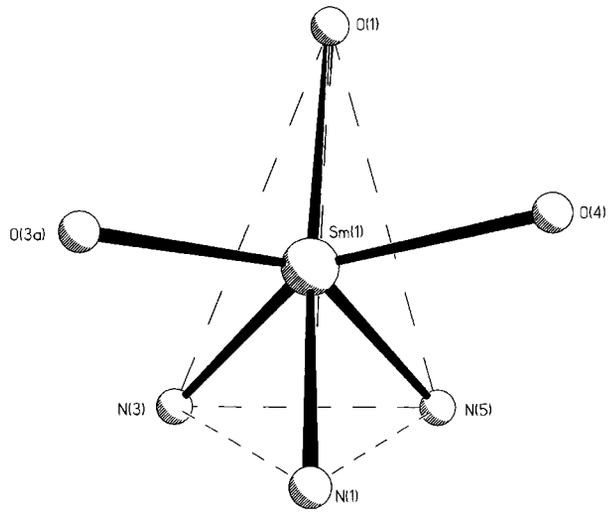

Fig. 2 The inner coordination sphere of **2a** showing the bicapped trigonal pyramidal geometry around the metal.

Table 1 Selected distances (Å) and angles (°)

2a		**2b**	
Sm(1)–O(1)	2.524(2)	Yb(1)–O(1)	2.390(3)
Sm(1)–O(3A)	2.577(2)	Yb(1)–O(3A)	2.449(3)
Sm(1)–O(4)	2.617(2)	Yb(1)–O(4)	2.510(3)
Sm(1)–N(1)	2.616(2)	Yb(1)–N(1)	2.494(3)
Sm(1)–N(3)	2.605(2)	Yb(1)–N(3)	2.494(3)
Sm(1)–N(5)	2.588(2)	Yb(1)–N(5)	2.478(3)
C(1)–O(1)	1.194(3)	C(1)–O(1)	1.195(4)
C(2)–O(2)	1.160(3)	C(2)–O(2)	1.155(5)
C(3)–O(3)	1.181(3)	C(3)–O(3)	1.184(5)
Mo(1)–C(1)	1.899(3)	Mo(1)–C(1)	1.900(4)
Mo(1)–C(2)	1.955(3)	Mo(1)–C(2)	1.960(5)
Mo(1)–C(3)	1.897(3)	Mo(1)–C(3)	1.905(4)
Mo(1)–Cp(av)	2.380(7)	Mo(1)–Cp(av)	2.383(9)
O(1)–Sm(1)–O(3A)	87.46(6)	O(1)–Yb(1)–O(3A)	83.91(9)
O(1)–Sm(1)–O(4)	74.66(6)	O(1)–Yb(1)–O(4)	75.38(9)

Compounds **2a** and **2b** crystallized from diethyl ether as isomorphous triclinic blue–green or yellow blocks respectively (which tended to lose solvent) in the space group $P\bar{1}$, incorporating two molecules of diethyl ether in the lattice for each Mo_2Sm_2 unit. A view of the molecule of **2a** is shown in Fig. 1 with the numbering scheme for the atoms. Selected bond lengths and angles for both complexes are given in Table 1. The molecules consist of 'molecular squares' lying on an inversion centre, making half of each molecule unique. The two lanthanide centres are linked to the molybdenum atoms *via* isocarbonyl bridges. The overall structure therefore resembles those observed before with trivalent lanthanides such as $[\{(\eta\text{-}C_5H_3R_2)_2CeW(\eta\text{-}C_5H_5)(CO)_3\}_2]$ (R = $SiMe_3$)[12] and $[\{(\eta\text{-}C_5H_5)_2SmFe(\eta\text{-}C_5Me_5)(CO)_2\}_2]$.[13] The core of the molecule is puckered, the central 12-membered ring adopting a 'deck-chair' conformation, with two coplanar $Mo(CO)_2$ units facing each other and the two lanthanide atoms closing the ring at either end. The cyclopentadienyl ring centroids lie in equatorial positions and the terminal carbonyls axial to the ring.

Each lanthanide atom is six coordinate with a geometry best described as bicapped trigonal pyramidal. The tridentate tris(pyrazolyl)borate ligand defines the base of the pyramid with the oxygen atoms of the bridging carbonyl groups defining the apex and capping a face (Fig. 2). The THF molecule caps a second face, binding in the cleft between two pyrazolyl groups of the $Tp^{t\text{-}Bu,Me}$ ligand. The geometry is therefore very similar to that seen in the divalent starting material **1a** with the two capping ligands effectively perpendicular to the apical carbonyl [OC at 87.46(6)°, **2a**; 83.91(9)°, **2b** and the THF at 74.66(6)°, **2a**; 75.38(9)°, **2b**]. As expected the average metal–nitrogen distance, in **2a**, 2.603(3) Å, is similar to that in **1a**, 2.637(9) Å. The metal–oxygen distances to the isocarbonyls are significantly different. The apical oxygen lies 2.524(2) Å (**2a**), 2.390(3) (**2b**) from the metal atom while the face-cap is longer at 2.577(2) Å (**2a**), 2.449(3) (**2b**). These are markedly longer than those observed both in trivalent samarium isocarbonyls, such as $[(Tp^{Me,Me})_2SmI_2(\mu\text{-}OC)Mo(\eta\text{-}Cp)(CO)_2]$, 2.335(4) Å,[11] $[SmI_2(\mu\text{-}OC)Mo(\eta\text{-}Cp)(CO)_2]$ 2.41(2) Å,[14] and the tetrametallic complex $[\{(\eta\text{-}Cp^*)_2Sm(\mu\text{-}OC)_2Fe(\eta\text{-}Cp^*)\}_2]$[13] as well as in four-coordinate samarium(II) alkoxides 2.339(9) Å.[15]

The corresponding distances in the ytterbium complex **2b**, Yb–O 2.390(3) Å (apical) and 2.449(3) Å (face-cap) are comparable to those observed in the Yb(II) compounds $[Yb(HMPA)_4\{(\mu\text{-}OC)MoCp(CO)_2\}_2]$ [HMPA = $P(NMe_2)_3O$],[16] 2.47(2) Å, $[\{[(MeCN)_3YbFe(CO)_4]_2\cdot MeCN\}_\infty]$, 2.389(5) and 2.374(5) Å and $[\{(MeCN)_3YbFe(CO)_4\}_\infty]$ 2.444(8), 2.541(6) and 2.459(6) Å.[17] As one might expect, these distances are somewhat longer than the Yb–O (isocarbonyl) bond lengths in trivalent ytterbium complexes, *e.g.* 2.268(Å) Å in the structurally similar $[\{Yb(Cp^*)_2(\mu\text{-}OC)_2Mn(CO)_3\}_2]$[18] and 2.258(2) Å in $[Yb(Cp^*)_2(THF)(\mu\text{-}OC)Co(CO)_3]$.[19]

The isocarbonyl C–O distances in **2a** and **2b** [1.194(3) and 1.195(4) Å (apical); 1.181(3) and 1.184(5) Å (face-cap)], are significantly longer than those in the terminal carbonyls, 1.160(3) and 1.155(5) Å respectively. In trivalent samarium isocarbonyls the analogous C–O (isocarbonyl) distances are generally at least 1.20 Å, for example 1.22(2) Å in $[SmI_2(THF)_4(\mu\text{-}OC)Mo(\eta\text{-}Cp)(CO)_2]$[14] and 1.206(7) Å in $[(Tp^{Me,Me})_2Sm(\mu\text{-}OC)Mo(\eta\text{-}Cp)(CO)_2]$[20] consistent with the fact that the divalent lanthanide centre may be considered a somewhat weaker Lewis acid. The bridging C–O separations in $[Yb(HMPA)_4\{(\mu\text{-}OC)MoCp(CO)_2\}_2]$ [1.14(4) and 1.20(3) Å],[16] $[\{[MeCN)_3YbFe(CO)_4]_2\cdot MeCN\}_\infty]$[1.198(8) Å] and $[\{(MeCN)_3YbFe(CO)_4\}_\infty]$[1.17(1), 1.20(1) and 1.19(1) Å][17] are, on the whole, comparable. Shorter C–O distances have also been observed for trivalent ytterbium with other transition metal systems, such as the average C–O separations of 1.186 Å in $[\{Yb(Cp^*)_2(\mu\text{-}OC)_2Mn(CO)_3\}_2]$[18] and 1.188(3) Å in $[Yb(Cp^*)_2(THF)(\mu\text{-}OC)Co(CO)_3]$.[19] A short C–O bond of 1.182 Å has also been noted in $[\{(\eta\text{-}C_5H_3R_2)_2Ce(\mu\text{-}OC)_2W(\eta\text{-}C_5H_5)(CO)\}_2]$.[12] The attendant shortening of the Mo–C (isocarbonyl) distances [1.897(3) (apical) and 1.899(3) Å (face-cap), **2a**; 1.900(4) and 1.905(4) Å, **2b**] compared to the terminal Mo–C bonds [1.955(3) Å, **2a**; 1.960(5) Å, **2b**] is as expected for the more 'carbene-like' nature of the isocarbonyls.[21]

The fact that the ^1H NMR spectra of **2a** and **2b** are temperature invariant implies that there is very rapid interconversion of the pyrazolyl environments in solution. This behaviour has

also been observed for $[Ln(Tp^{tBu,Me})I(L)_n]$ (Ln = Sm, n = 2; Ln = Yb, n = 1, L = 3,5-dimethylpyridine).[5] Since the IR spectra in solution and in the solid state are closely similar this is unlikely to occur by breakage of the isocarbonyl links. It is more probable that dissociation of one arm of the Tp ligand occurs allowing the resulting five-coordinate intermediate to rearrange by pseudo-rotation or related process. Such dissociations are presumed to be facile in view of the known fluxionality of $[Sm(Tp^{tBu,Me})_2]$ in which the two Tp ligands are tridentate and bidentate respectively.[22]

Nevertheless, the lanthanide to isocarbonyl interaction may be presumed to be fairly weak. Addition of pyridine to solutions of **2a** and **2b** results in deep blue–green and red solutions respectively. The infrared spectra of these solutions are essentially identical to each other, with three bands in the carbonyl region at 1910, 1810 and 1660 cm^{-1} consistent with a break up of the tetramer, probable displacement of THF, and the coordination of one or more pyridine ligands in the lanthanide coordination sphere as was seen for **1a** and **2a**.[5,23] The CO region of the IR spectra is essentially superimposable with those of $[Sm(Tp^{Me,Me})_2(\mu\text{-}OC)Mo(\eta\text{-}MeCp)(CO)_2]$. The compounds could not however, be isolated in pure form, possibly as a result of partial pyridine dissociation.

The preparations of complexes **2a** and **2b** are further examples of how polynuclear conjugated systems can be built up using carbonyls to bridge between both lanthanides and transition metals. The presence of the ancillary ligands serves to constrain the oligomerization. This is the first example of an isocarbonyl bound to samarium(II) and only the third to a divalent ytterbium centre. Dimeric species have been obtained from the reaction of ytterbium metal with $[\{CpMo(CO)_3\}_2]$ in HMPA[16] and an infinite polymer $YbFe(CO)_4$ from the reaction of $Fe(CO)_5$ with ytterbium in liquid ammonia.[17] The carbonyl groups appear resistant to electron transfer; this is to be expected in view of the back-bonding from the transition metal centre. In the present case calculations suggest that a partial negative charge is localized on the oxygens of the $MeCpMo(CO)_3$ units.[24] We are currently exploring further reactions of this type in the hopes of observing unusual reactivity of the carbonyl groups.

Experimental

Preparation of $[\{Sm(Tp^{tBu,Me})(THF)Mo(\eta\text{-}C_5H_4Me)(CO)_3\}_2]$ 2a

A solution of $[\{Mo(\eta\text{-}C_5H_4Me)(CO)_3\}_2]$ (37 mg, 0.057 mmol)[25] in THF (15 cm^3) was stirred over excess 1% Na/Hg amalgam for 5 min until the red colour had disappeared. The resulting yellow solution was filtered directly onto a green–black solution of **1a** (100 mg, 0.115 mmol) in THF (20 cm^3) at −78 °C and the mixture stirred for 12 h while warming to room temperature. The solvent was removed under reduced pressure from the dark green solution and the green residue extracted into diethyl ether (30 cm^3). The volume of solvent was reduced slightly and slow cooling to −20 °C gave large deep blue crystals of **2a**. Yield: 32 mg (22%). Analysis. Calc. for $C_{74}H_{110}B_2Mo_2N_{12}O_8Sm_2$: C, 49.1; H, 6.13; N, 9.2. Found: C, 48.35; H, 6.20; N, 9.09%. ^1H NMR (C_6D_6, 298 K), δ 1.25 (s, 3H, MeCp), 1.32 (s, 27H, Bu^t), 2.19 (s, 9H, 5-Me), 5.69 (s, 6H, pz CH), 4.48 (s, 2H, Cp), 4.63 (s, 2H, Cp). IR (KBr disk, cm^{-1}) 2555 (ν_{B-H}), 1914 (s, ν_{CO}), 1828 (s, ν_{CO}), 1630 (br, $\nu_{\mu\text{-}CO}$).

Preparation of $[\{Yb(Tp^{tBu,Me})(THF)Mo(\eta\text{-}C_5H_4Me)(CO)_3\}_2]$ 2b

The preparation of **2b** was carried out analogously to that described above using $[Yb(Tp^{tBu,Me})I(THF)]$ (100 mg, 0.126 mmol) and $[Mo(\eta\text{-}C_5H_4Me)(CO)_3]_2$ (34 mg, 0.066 mmol) to give yellow crystals of **2b**. Yield: 50 mg (46%). Analysis. Calc. for $C_{74}H_{110}B_2Mo_2N_{12}O_8Yb_2$: C, 45.67; H, 6.43; N, 9.83. Found: C, 45.45; H, 5.57; N, 9.65%. ^1H NMR (C_6D_6, 298 K), δ 1.35 (s, 27H, Bu^t), 1.16 (s, 3H, MeCp), 2.16 (s, 9H, 5-Me), 5.62 (s, 3H, pz CH), 4.50 (m, 2H, Cp), 44.65 (m, 2H, Cp). IR (KBr disk, cm^{-1}) 2552 (ν_{B-H}), 1920 (s, ν_{CO}), 1835 (s, ν_{CO}), 1647 (br, $\nu_{\mu\text{-}CO}$).

Crystallography

Crystal data for 2a. $C_{74}H_{110}B_2Mo_2N_{12}O_8Sm_2\cdot 2C_4H_{10}O$, blue crystal of dimensions 0.65 × 0.46 × 0.44 mm, M = 1958.18, triclinic space group $P\bar{1}$, a = 13.6825(5), b = 13.7204(5), c = 15.1643(6) Å, α = 63.455(2), β = 67.914(2), γ = 88.812(2)°, U = 2322.26(15) $Å^3$, Z = 1, $F(000)$ = 1004, D_c = 1.400 g cm^{-3}, μ(Mo-Kα) = 1.567 mm^{-1}, $2\theta_{max}$ = 57.96°, T = 160(2) K.

Data collection, structure solution and refinement. 17258 reflections (10241 unique with R_{int} = 0.0201). Final $wR_2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}$, w = 0.0641 for 512 refined parameters, conventional R = 0.0252 [for F values of 10241 data with $F^2 > 4\sigma(F^2)$]. Goodness of fit = 1.046 on F^2 for 512 refined parameters. The largest features in the final difference synthesis were within 1.233 e $Å^{-3}$, close to the metal atoms.

Crystal data for 2b. $C_{74}H_{110}B_2Mo_2N_{12}O_8Yb_2\cdot 2C_4H_{10}O$, yellow crystal of dimensions 0.25 × 0.13 × 0.04 mm, M = 2003.56, triclinic space group $P\bar{1}$, a = 13.6797(7), b = 13.7364(8), c = 15.1241(8) Å, α = 63.213(2), β = 67.115(2), γ = 89.525(2)°, U = 2288.6(2) $Å^3$, Z = 1, $F(000)$ = 1020, D_c = 1.454 g cm^{-3}, μ(Mo-Kα) = 2.351 mm^{-1}, $2\theta_{max}$ = 57.20°, T = 160(2) K. 15610 reflections collected (9993 unique with R_{int} = 0.0277) Final $wR_2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{\frac{1}{2}} = 0.0698$, conventional R = 0.0368 [for F values of 9993 data with $F^2 > 4\sigma(F^2)$]. Goodness of fit = 1.066 on F^2 for 512 refined parameters. The largest features in the final difference synthesis were within 0.706 e $Å^{-3}$, close to the metal atoms.

All data were collected on a Bruker SMART CCD area detector diffractometer with narrow frames (0.3°) and three dimensional profile fitting using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for absorption and other effects by a semi-empirical method based on the high degree of data redundancy. Cell parameters were refined by locally written software from the positions of a large number of reflections. The structures were solved by Patterson methods and refined by full-matrix least squares on F^2 values. All non-H atoms were refined anisotropically, H atoms were constrained. Programs: Bruker SMART, SAINT, and SHELXTL software for data collection and reduction and local programs.

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See http://www.rsc.org/suppdata/dt/1998/3871/ for crystallographic files in .cif format.

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