Preliminary communication

Reactivity of pyrazolylborate complexes of samarium with transition metal carbonyls [1]

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Abstract

The reaction of $[Sm(Tp^{Me,Me})_2]$ with $[M(\eta-C_5H_4R)(CO)_3]_2$ (M = Cr, R = H; M = Mo, R = Me, ^tBu; M = W, R = H) gives good yields of $[Sm(Tp^{Me,Me})_2(\mu-OC)M\{(\eta-C_5H_4R)(CO)_2\}]$. The crystal structure of the complex for which M = Mo and R = Me has been determined (triclinic, $P\bar{1}$, $a = 10.4106(6)$, $b = 14.1022(8)$, $c = 18.6974(11)$ Å, $\alpha = 71.579(2)$, $\beta = 88.751(2)$, $\gamma = 85.095(2)°$ and $V = 2594.8(3)$ Å^3) confirms the seven coordinate samarium centre with the expected bridging isocarbonyl. In contrast, the reaction of $[Sm(Tp^{Me,Me})_2]$ with $[Co_2(CO)_8]$ gives the salt $[Sm(Tp^{Me,Me})_2][Co(CO)_4]$ together with $[Co_4(CO)_{12}]$.

Keywords: Samarium; Isocarbonyl; Heterobimetallics; Metal carbonyl anions

1. Introduction

We and others have recently prepared divalent complexes of the elements samarium, europium and ytterbium with two tris-pyrazolylborate (Tp) groups as ancillary ligands [1]. These complexes react in one-electron transfer reactions with a wide variety of reagents such as oxygen [2], nitric oxide [3], azobenzenes [4], halogens and halocarbons [5], and dichalcogenides [6]. However, in contrast to the behaviour of the corresponding metallocene complexes, the steric requirements of the ancillary ligand system are such that tractable products have tended to be favoured by reagents which yield essentially planar or very narrow ligands upon reduction, and the di- or oligomeric products seen with cyclopentadienyl ancillaries have yet to be observed. In order to explore further the steric definition provided by these ligands, we have begun to examine the reaction with transition metal compounds containing metal–metal single bonds.

Reactions of this type are well-precedented with metallocene compounds. Thus the reaction of [Yb(η-

$C_5Me_5)_2(OEt_2)]$ with $Fe_3(CO)_{12}$ and $[Co(\eta-C_5H_5)(CO)_2]$ yields the structurally-related clusters $[Yb_2(\eta-C_5Me_5)_4Fe_3(CO)_{11}]$ [7] and $[Yb_2(\eta-C_5Me_5)_4Co_3(\eta-C_5H_5)_2(CO)_4]$ [8] respectively. In contrast, the reactions with $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ yield complexes of formula $[Yb(\eta-C_5Me_5)_2Mn(CO)_5]$ and $[Yb(\eta-C_5Me_5)_2Co(CO)_4(THF)]$ [9] respectively. Decamethylsamarocene reacts with $Co_2(CO)_8$ to give $[(\eta-C_5Me_5)_2Sm(THF)][Co(CO)_4]$ and with $[Fe(\eta-C_5Me_5)(CO)_2]_2$ to give the tetranuclear complex $[(\eta-C_5Me_5)_2Sm(\mu-OC)_2Fe(\eta-C_5Me_5)]_2$ [10]. In this work we set out to compare the behaviour of the metallocenes with their pyrazolylborate analogues.

2. Results and discussion

The reaction of two equivalents of $[Sm(Tp^{Me,Me})_2]$, 1, with $[M(\eta-C_5H_4R)(CO)_3]_2$ (M = Cr, Mo, W) in toluene [2] at low temperature resulted in the gradual dissolution of the purple samarium starting material and gave yellow or orange solutions which, after filtration and cooling to $-30°C$, yielded analytically pure yellow to orange crystals of 2 (M = Cr, R = H), 3a (M = Mo,

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R = Me), **3b** (M = Mo, R = ^{t}Bu) and **4** (M = W, R = H) as their toluene solvates.

$$2\left[\mathrm{Sm}(\mathrm{Tp}^{\mathrm{Me,Me}})_2\right] + \left[\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_4\mathrm{R})(\mathrm{CO})_3\right]_2$$

$$\rightarrow 2\left[\mathrm{Sm}(\mathrm{Tp}^{\mathrm{Me,Me}})_2\mathrm{M}(\eta\text{-}\mathrm{C}_5\mathrm{H}_4\mathrm{R})(\mathrm{CO})_3\right]$$
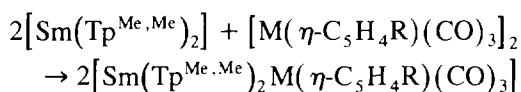
Compound **2** is significantly more oxygen sensitive than the others. All dissolve easily in THF and warm toluene but decompose in wet or chlorinated solvents. The solid-state IR spectra show the expected B–H stretching absorption at $2555\,\mathrm{cm}^{-1}$. Three very intense bands also appear in the carbonyl region corresponding to the stretches of the terminal CO groups at approximately 1910 and $1810\,\mathrm{cm}^{-1}$ and a very low energy band around $1650\,\mathrm{cm}^{-1}$ which we ascribe to a bridging isocarbonyl group, in a range similar to those observed by others previously [11]. That the complexes retain their integrity in toluene solution is suggested by the presence of three IR bands at closely similar wavenumbers. Preliminary experiments suggest that addition of acetonitrile to solutions of these complexes does not result in the break-up of the complexes, as has been seen for example in $[(\eta\text{-}\mathrm{C}_5\mathrm{H}_3\mathrm{R}_2)_2\mathrm{CeW}(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)\text{-}(\mathrm{CO})_3]_2$ [12].

Compound **3a** crystallized from toluene as triclinic red-orange blocks (which tended to lose solvent slowly) incorporating 1.5 molecules of toluene in the lattice in the space group $P\bar{1}$. A view of the molecule is shown in Fig. 1, which also shows the numbering scheme for the molecule. Fractional atomic coordinates are listed in Table 1. Selected bond lengths and angles are given in Table 2. The crystal structure confirms the structure proposed above. The samarium centre is seven-coordinate with two tridentate Tp ligands in an arrangement analogous to a metallocene and a bridging isocarbonyl ligand occupying the seventh site. The tightness of the bite angle of the $\mathrm{Tp}^{\mathrm{Me,Me}}$ ligands ensures that the geometry about samarium does not fit any of the 'regular' polyhedra particularly well. The two pyrazolylborates are staggered with respect to each other and bent back away from the bridge such that the B(1)–Sm(1)–B(2) angle is 149.8° as opposed to linear in **1**. The bending of the B–M–B vector is very similar to that observed in other seven-coordinate systems of this type, such as $[\mathrm{Nd}(\mathrm{Tp}^{\mathrm{Me,Me}})_2\mathrm{OTf}]$, 148° [13]. As expected, the average samarium–nitrogen distance, 2.513(9) Å, is significantly shorter than in the divalent starting material **1**, 2.617(4) Å, and consistent with seven-coordinate trivalent samarium. In the corresponding chloride $[\mathrm{Sm}(\mathrm{Tp}^{\mathrm{Me,Me}})_2\mathrm{Cl}]$ the average distance is 2.564(35) Å [14].

The samarium–oxygen distance is 2.335(4) Å, which is remarkably similar to those observed in the eight-co-ordinate $[\mathrm{SmTp}_2(\mu\text{-}\mathrm{O}_2\mathrm{CPh})]_2$ (2.34(5) Å) [15], suggesting that the lower coordination number in **3a** is compensated for by the presence of the additional methyl groups in the $\mathrm{Tp}^{\mathrm{Me,Me}}$ ligand. It is also similar to the
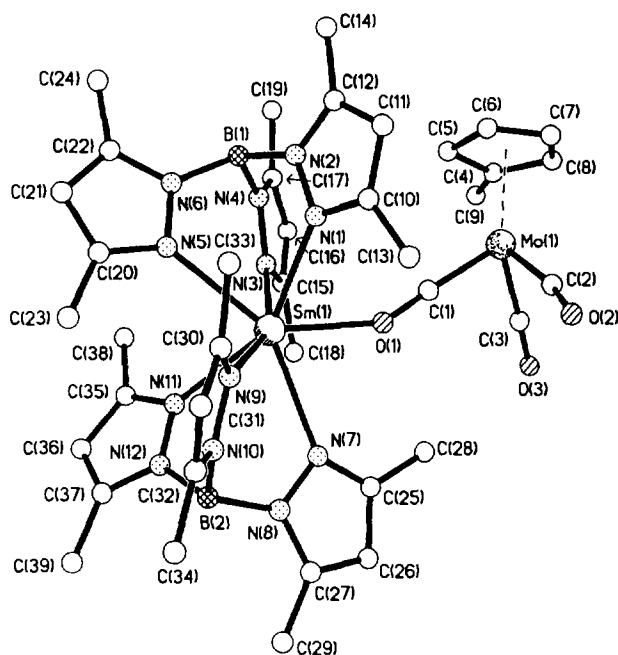

Fig. 1. Molecular structure of **3a** with the atom numbering scheme defined. H-atoms, disordered component of C(2) and toluene molecules of crystallization omitted for clarity.

samarium–oxygen distances in Sm(III) aryloxides such as $[\mathrm{Sm}(\mathrm{ArO})_2(\mathrm{THF})_3]$ 2.29(1)–2.35(1) Å [16].

The $\mathrm{Mo}(\eta\text{-}\mathrm{C}_5\mathrm{H}_4\mathrm{Me})(\mathrm{CO})_2$ unit lies with the Mo–C$_5$ centroid vector pointing approximately in the plane defined by the two boron atoms and the samarium. The $\mathrm{Mo}(\eta\text{-}\mathrm{C}_5\mathrm{H}_4\mathrm{Me})$ unit nestles in the cleft between the two pyrazolyl groups of the 'upper' $\mathrm{Tp}^{\mathrm{Me,Me}}$ ligand. At the same time, a methyl group (C(28)) from one of the pyrazolyl groups on the 'lower' $\mathrm{Tp}^{\mathrm{Me,Me}}$ ligand points up 'between the legs' of the molybdenum piano stool. The Sm–O–C–Mo vector is bent considerably away from linearity — this is commonly observed in such systems and this can be attributed to the significant steric congestion in **3a**. The bridging C(1)–O(1) bond length is significantly lengthened to 1.206(7) Å compared with the terminal C(3)–O(3) length 1.170(9) Å. This lengthening of the isocarbonyl compared with the terminal ligands is typical in this sort of system and is attributed to the increase in the carbenoid resonance form of the ligand as a result of the interaction of the oxygen with the Lewis acidic samarium centre [17].

The asymmetry of the $\mathrm{Mo}(\eta\text{-}\mathrm{C}_5\mathrm{H}_4\mathrm{Me})(\mathrm{CO})_3$ unit with respect to the $\mathrm{Sm}(\mathrm{Tp}^{\mathrm{Me,Me}})_2$ moiety implies that the methyl groups should appear in the $^1\mathrm{H}$ NMR spectrum as four sets of peaks in the ratio of 2:1. However, the $^1\mathrm{H}$ NMR spectra of **2**, **3** and **4** show three peaks in the ratio of 3:3:1 for the methyl and methine protons of the pyrazolyl groups, consistent with a fluxional system. We hoped that the paramagnetic samarium centre might enhance chemical shift differences between different environments at the low temperature limit. Variable-

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for **3a**

	x	y	z	U_{eq} [a]
Sm(1)	4685.5(2)	3605.3(2)	2277.68(13)	32.78(8)
Mo(1)	5592.4(5)	6939.2(5)	2796.7(3)	58.9(2)
C(1)	5576(5)	5778(5)	2520(3)	49.1(13)
O(1)	5631(4)	5009(3)	2363(2)	50.6(10)
C(2)	7187(7)	6325(7)	3315(4)	80(3)
O(2)	8146(21)	5603(53)	3709(19)	54(8)
O(2A)	8100(16)	6109(70)	3579(18)	77(12)
C(3)	6582(7)	7506(6)	1902(5)	67(2)
O(3)	7159(6)	7856(4)	1351(3)	86(2)
C(4)	3895(11)	8210(8)	2542(5)	115(4)
C(5)	3382(6)	7235(7)	2950(6)	83(3)
C(6)	3916(7)	6988(7)	3661(5)	81(2)
C(7)	4681(10)	7663(12)	3728(7)	126(5)
C(8)	4660(9)	8345(8)	3106(7)	100(3)
C(9)	3569(22)	8777(13)	1804(9)	269(13)
N(1)	3949(4)	3915(4)	3463(2)	45.3(11)
N(2)	2699(4)	4261(3)	3554(2)	38.9(10)
C(10)	4612(5)	3939(5)	4056(3)	55(2)
C(11)	3800(5)	4289(6)	4539(3)	59(2)
C(12)	2593(5)	4496(5)	4197(3)	47.8(14)
C(13)	6040(6)	3655(7)	4128(3)	76(2)
C(14)	1368(5)	4915(5)	4455(3)	53(2)
N(3)	2990(4)	4968(3)	1777(2)	34.7(9)
N(4)	1953(3)	5134(3)	2204(2)	32.6(8)
C(15)	2992(4)	5768(4)	1161(3)	35.6(10)
C(16)	1975(5)	6462(4)	1185(3)	39.3(11)
C(17)	1335(4)	6039(4)	1849(3)	35.4(10)
C(18)	4014(5)	5832(4)	571(3)	45.9(12)
C(19)	191(5)	6480(4)	2167(3)	47.4(13)
N(5)	2573(4)	2767(3)	2669(2)	41.0(10)
N(6)	1529(4)	3326(3)	2849(2)	35.1(9)
C(20)	2116(6)	1898(4)	2663(3)	46.3(12)
C(21)	814(5)	1905(4)	2831(3)	48.4(13)
C(22)	465(5)	2808(4)	2943(3)	40.5(11)
C(23)	2931(7)	1068(4)	2493(4)	66(2)
C(24)	−829(5)	3190(5)	3145(3)	51.9(14)
B(1)	1649(5)	4351(5)	2959(3)	37.7(12)
N(7)	6878(4)	3691(3)	1561(2)	32.0(8)
N(8)	7370(4)	2821(3)	1420(2)	33.4(8)
C(25)	7743(4)	4364(4)	1270(3)	33.3(10)
C(26)	8762(4)	3933(4)	956(3)	37.2(10)
C(27)	8504(4)	2971(4)	1055(3)	35.8(10)
C(28)	7657(5)	5421(4)	1295(3)	41.8(11)
C(29)	9294(5)	2166(4)	833(4)	49.8(13)
N(9)	5635(4)	1866(4)	2893(2)	53.0(13)
N(10)	6453(4)	1422(3)	2474(3)	51.3(12)
C(30)	5630(7)	1199(5)	3592(3)	71(2)
C(31)	6460(8)	366(6)	3627(4)	92(3)
C(32)	6958(7)	514(5)	2918(4)	74(2)
C(33)	4765(8)	1391(6)	4194(4)	88(3)
C(34)	7891(8)	−154(6)	2647(5)	101(3)
N(11)	4413(4)	2849(3)	1269(2)	34.4(8)
N(12)	5334(4)	2126(3)	1186(2)	37.7(9)
C(35)	3441(5)	2888(4)	790(3)	39.0(11)
C(36)	3745(6)	2214(4)	396(3)	50.5(14)
C(37)	4939(6)	1743(4)	654(3)	49.2(13)
C(38)	2251(5)	3574(5)	730(3)	48.6(13)
C(39)	5733(7)	976(6)	399(5)	80(2)
B(2)	6629(6)	1882(4)	1611(3)	40.2(13)
C(40)	−921(7)	1297(7)	5466(4)	86(3)
C(41)	−770(11)	1756(8)	6010(6)	115(5)
C(42)	293(13)	2254(7)	6002(5)	113(4)
C(43)	1241(10)	2316(6)	5474(5)	91(3)

Table 1 (continued)

	x	y	z	U_{eq} [a]	
C(44)	1104(8)	1875(7)	4938(4)	83(2)	
C(45)	21(8)	1353(7)	4934(4)	82(2)	
C(46)	−2101(8)	738(9)	5476(6)	126(4)	
C(47)	10155(9)	10031(8)	2(5)	134(5)	
C(48)	9277(8)	9474(7)	496(6)	73(4)	
C(49)	9525(12)	9141(9)	1267(6)	149(8)	
C(50)	10650(14)	9364(12)	1543(5)	119(6)	
C(51)	11528(11)	9920(10)	1049(7)	153(8)	
C(52)	11281(8)	10254(8)	279(6)	75(3)	
C(53)	9813(11)	10471(8)	−827(5)	69(3)	

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

temperature ^{1}H NMR spectra recorded in 4:1 toluene-d_8-benzene-d_6 down to −120 °C showed the expected Curie–Weiss shift in the position of the peaks due to the pyrazolyl groups. Below −80 °C the peak due to the 3-methyl groups broadened into the baseline but no low-temperature limit was reached.

In contrast to the Group 16 dimers, $Co_2(CO)_8$ reacted smoothly with 2 mol equivalents of [Sm-(Tp^{Me,Me})$_2$] to give a very dark solution, from which $Co_4(CO)_{12}$ could be isolated in 24% yield, together with an off-white precipitate, 5, which was insoluble in both hot toluene and THF, suggesting a salt-like formulation [13]. The IR spectrum of 5 shows the expected B–H stretch of the [Sm(Tp^{Me,Me})$_2$] together with a single sharp CO stretching band at 1839 cm^{-1} in the IR spectrum, consistent with the presence of the tetrahedral $Co(CO)_4^-$ anion unperturbed by the presence of the

lanthanide centre or by solid-state effects. Hence 5 may be formulated as [Sm(Tp^{Me,Me})$_2$][Co(CO)$_4$].

We note that while the {M(η-C$_5$H$_4$R)(CO)$_3$} unit coordinates to the samarium via an isocarbonyl bridge, the [Co(CO)$_4$]$^-$ anion remains isolated. Although Evans et al. have made a similar observation in the reaction of decamethylsamarocene, from which a salt is also obtained [18], decamethylytterbocene yields an isocarbonyl complex [9]. It is likely that the samarium isocarbonyl link is relatively weak and that the structure of the complex depends upon a number of factors, not least of which will be the charge to radius ratio of the metal and the lattice energy of the crystal. In the case of 5 the lattice energy may be maximized with a salt-like structure. Indeed, several complexes of this salt-like type have recently been isolated and crystallographically characterized, including [Sm(Tp^{Me,Me})$_2$][I] [19],

Table 2
Bond lengths (Å) and angles (deg) for 3a

Sm(1)–O(1)	2.335(4)	Sm(1)–N(1)	2.484(4)
Sm(1)–N(3)	2.458(4)	Sm(1)–N(5)	2.568(4)
Sm(1)–N(7)	2.614(4)	Sm(1)–N(9)	2.484(4)
Sm(1)–N(11)	2.473(4)	Mo(1)–C(1)	1.869(6)
Mo(1)–C(2)	1.933(8)	Mo(1)–C(3)	1.929(8)
Mo(1)–C(4)	2.349(8)	Mo(1)–C(5)	2.331(7)
Mo(1)–C(6)	2.364(7)	Mo(1)–C(7)	2.420(9)
Mo(1)–C(8)	2.361(8)	Mo(1)–Cp(centroid)	2.059
C(1)–O(1)	1.206(7)	C(2)–O(2)Av.	1.23(4)
C(3)–O(3)	1.170(9)		
O(1)–Sm(1)–N(1)	71.7(2)	O(1)–Sm(1)–N(3)	77.27(14)
O(1)–Sm(1)–N(5)	137.96(13)	O(1)–Sm(1)–N(7)	72.69(12)
O(1)–Sm(1)–N(9)	122.5(2)	O(1)–Sm(1)–N(11)	135.26(13)
N(1)–Sm(1)–N(5)	72.28(14)	N(1)–Sm(1)–N(7)	134.61(13)
N(1)–Sm(1)–N(9)	95.7(2)	N(3)–Sm(1)–N(1)	79.86(13)
N(3)–Sm(1)–N(5)	75.73(13)	N(3)–Sm(1)–N(7)	118.14(12)
N(3)–Sm(1)–N(9)	157.6(2)	N(3)–Sm(1)–N(11)	93.97(13)
N(5)–Sm(1)–N(7)	149.20(13)	N(9)–Sm(1)–N(5)	82.0(2)
N(9)–Sm(1)–N(7)	80.59(13)	N(11)–Sm(1)–N(1)	150.67(14)
N(11)–Sm(1)–N(5)	78.40(13)	N(11)–Sm(1)–N(7)	73.50(12)
N(11)–Sm(1)–N(9)	79.1(2)	C(1)–Mo(1)–C(2)	85.6(3)
C(1)–Mo(1)–C(3)	88.1(3)	C(3)–Mo(1)–C(2)	88.5(3)
O(1)–C(1)–Mo(1)	176.2(5)	C(1)–O(1)–Sm(1)	151.0(4)
O(2A)–C(2)–Mo(1)	171.0(50)	O(2)–C(2)–Mo(1)	162.0(20)
O(3)–C(3)–Mo(1)	178.6(6)		

$[Sm(Tp^{Me,Me})_2][Te_3Ph_3]$ and $[Sm(Tp^{Me,Me})_2][TCNE]$ [20], suggesting that the six-coordinate structure is favourable with a large anion. Secondly, the extent to which the negative charge is localized onto the CO groups can be expected to vary significantly. Fenske–Hall calculations by Bursten and Gatten suggest that in $[M(\eta\text{-}C_5H_5)(CO)_3]^-$ (M = Cr, Mo, W) systems, the negative charge is localized predominantly on oxygen, while in $[M(\eta\text{-}C_5H_5)(CO)_2]^-$ (M = Fe, Ru, Os) the negative charge lies predominantly on the metal [21]. This argument has been used by Beletskaya et al. to account for the close Ru–Lu interaction in $[(\eta\text{-}C_5H_5)_2LuRuCp(CO)_2]$ [22]. In the case of $Co(CO)_4^-$, this anion is known to be a poor nucleophile, as evidenced by its poor reactivity with alkyl halides [23].

3. Conclusions

We have shown that one-electron transfer reactions analogous to those of samarocene have been observed for its Tp analogue. The greater steric demand of the $Tp^{Me,Me}$ groups compared with Cp^* gives well-defined bimetallic species. The preparation of the isocarbonyl-bridged complexes suggests that it should be possible to introduce the isoelectronic alkynyl ligands into the coordination sphere of the metal, opening the possibility of preparing highly reactive hydrocarbyl and hydride species by σ-bond metathesis reactions.

4. Experimental

All preparations and manipulations were carried out using standard Schlenk line and dry box techniques in an atmosphere of dinitrogen [24]. Oxygen-free nitrogen was purified by passage over columns containing 3 Å molecular sieves and MnO [25]. All solvents were pre-dried over 5 Å molecular sieves or sodium wire and distilled under nitrogen from appropriate drying agents (Na (toluene), K (benzene, tetrahydrofuran), Na–K alloy (petroleum ether b.p. 40–60°C, pentane, diethyl ether)) before use.

$[Sm(Tp^{Me,Me})_2]$ was prepared from samarium diiodide and sodium hydro-tris-pyrazolylborate [26] as previously described [4]. $[M_2(\eta\text{-}C_5H_4R)_2(CO)_6]$ were prepared by literature methods [27].

IR spectra were recorded as KBr pellets or in solution in toluene using 0.1 mm CaF_2 solution cells on a Nicolet 205 FTIR spectrometer. ^1H NMR spectra in solution were recorded on Varian XL-200 and VXR-400 spectrometers at 200 MHz and 400 MHz respectively. Spectra were calibrated using residual proton resonances and are reported relative to tetramethylsilane. Elemental analyses were determined by Mr. Alan Stones of the UCL Analytical Services.

4.1. Preparation of $[Sm(Tp^{Me,Me})_2(\mu\text{-}OC)Cr(\eta\text{-}C_5H_5)-(CO)_2]$, 2

$Sm(Tp^{Me,Me})_2$ (0.09 g, 0.12 mmol) was suspended in toluene (25 cm^3) and cooled to $-78°C$ in a dry-ice–acetone bath. A solution of green $[Cr_2(\eta\text{-}C_5H_5)_2(CO)_6]$ (0.024 g, 0.06 mmol) in toluene (25 cm^3) was added dropwise and the solution allowed to warm slowly with stirring overnight. The yellow solution was filtered, the volume reduced to 10 cm^3 and cooled to $-30°C$ to give orange crystals of 2. Yield: 0.049 g (43%). Anal. Found: C, 53.58; H, 5.56; N 15.12. $C_{38}H_{37}B_2CrO_3N_{12}Sm \cdot 1.5(C_7H_8)$. Calc.: C, 53.73; H, 5.67; N, 15.50%. ^1H NMR $(C_6D_6$, 298 K) -1.68 (s, 18H, 3-Me); 3.20 (s, 18H, 5-Me); 5.38 (s, 6H, pz CH); 5.88 (s, 5H, Cp). IR (KBr disk, cm^{-1}) 2570 (ν_{B-H}), 1906 (s, ν_{CO}), 1813 (s, ν_{CO}), 1654 (s, $\nu_{\mu\text{-}CO}$).

4.2. Preparation of $[Sm(Tp^{Me,Me})_2(\mu\text{-}OC)Mo(\eta\text{-}C_5H_4\text{-}Me)(CO)_2]$, 3a

Preparations were carried out in analogous manner to that of 2. Red-orange crystals of the toluene solvate. Yield: 72%. Anal. Found: C, 47.77; H, 5.30; N, 17.60. $C_{39}H_{51}B_2MoN_{12}O_3Sm$. Calc.: C, 46.66; H, 5.08; N, 16.75%. ^1H NMR $(C_6D_6$, 298 K) -0.98 (s, 18H, 3-Me); 2.36 (s, 3H, Me–Cp); 3.06 (s, 18H, 5-Me); 5.53 (s, 6H, pz CH); 6.08 (m, 2H, Cp); 6.6.24 (m, 2H, Cp). IR (KBr disk, cm^{-1}) 2560 (ν_{B-H}), 1914 (s, ν_{CO}), 1825 (s, ν_{CO}), 1636 (s, $\nu_{\mu\text{-}CO}$).

4.3. Preparation of $[Sm(Tp^{Me,Me})_2(\mu\text{-}OC)Mo(\eta\text{-}C_5H_4\text{-}{}^tBu)(CO)_2]$, 3b

Preparations were carried out in analogous manner to that of 2. Red-purple crystals of the toluene solvate. Yield: 0.054 g (43%). Anal. Found: C, 51.03; H, 5.36; N, 14.98. $C_{42}H_{57}B_2MoN_{12}O_3Sm$. Calc.: C, 51.71; H, 5.76; N, 14.77%. ^1H NMR $(C_6D_6$, 298 K) -1.67 (s, 18H, 3-Me); 1.83 (s, 9H, ^tBu) 3.22 (s, 18H, 5-Me); 5.40 (s, 6H, pz CH); 6.14 (s, 2H, Cp_A), 6.33 (s, 2H, Cp_B). IR (KBr disk, cm^{-1}) 2555 (ν_{B-H}), 1910 (s, ν_{CO}), 1813 (s, ν_{CO}), 1650 (s, $\nu_{\mu\text{-}CO}$).

4.4. Preparation of $[Sm(Tp^{Me,Me})_2(\mu\text{-}OC)W(\eta\text{-}C_5H_5)_2-(CO)_2]$, 4

Preparations were carried out in analogous manner to that of 2. Orange crystals of the toluene solvate. Yield: 43%. Anal. Found: C, 46.21; H, 4.79; N, 13.40. $C_{38}H_{49}B_2N_{12}O_3SmW \cdot C_7H_8$. Calc.: C, 46.20; H, 4.91; N, 14.37%. ^1H NMR $(C_6D_6$, 298 K) -1.67 (s, 18H, 3-Me); 3.22 (s, 18H, 5-Me); 5.38 (s, 6H, pz CH); 6.27 (s, 5H, Cp). IR (KBr disk, cm^{-1}) 2555 (ν_{B-H}), 1910 (s, ν_{CO}), 1813 (s, ν_{CO}), 1650 (s, $\nu_{\mu\text{-}CO}$).

4.5. Preparation of [Sm(Tp^{Me,Me})$_2$][Co(CO)$_4$], 5

Sm(Tp^{Me,Me})$_2$ (0.09 g, 0.12 mmol) was suspended in toluene (25 cm^3) and cooled to $-78\,^\circ$C in a dry-ice–acetone bath. A solution of [Co$_2$(CO)$_8$] (0.021 g, 0.06 mmol) in toluene (25 cm^3) was added dropwise and the solution allowed to warm slowly with stirring overnight. The reaction mixture turned very dark with an off-white precipitate. The solution was filtered and the black solution reduced to 10 cm^3 and cooled to $-30\,^\circ$C to give flaky black crystals of Co$_4$(CO)$_{12}$. Yield: 4 mg (24% based on cobalt). The white residue was washed with toluene and dried in vacuo. Yield: 35 mg (32% based on Sm). Anal. Found: C, 42.49; H, 5.28; N, 17.68. C$_{34}$H$_{44}$B$_2$CoN$_{12}$O$_4$Sm. Calc.: C, 44.60; H, 4.84; N, 18.36%. IR (KBr disk, cm^{-1}) 2555 (ν_{B-H}), 1882 (s, ν_{CO}).

4.6. X-ray diffraction study of 3a

4.6.1. Crystal data for 3a

C$_{49.5}$H$_{63}$B$_2$N$_{12}$O$_3$Sm, yellow crystal of dimensions $0.40 \times 0.24 \times 0.22$ mm^3, $M = 1142.03$, triclinic, space group $P\bar{1}$, $a = 10.4106(6)$, $b = 14.1022(8)$, $c = 18.6974(11)$ Å, $\alpha = 71.579(2)$, $\beta = 88.751(2)$, $\gamma = 85.095(2)^\circ$, $U = 2594.8(3)$ Å^3, $Z = 2$, $F(000) = 1164$, $D_c = 1.462$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 1.415$ mm^{-1}, $2\theta_{max} = 56.90^\circ$, $T = 160$ K.

4.6.2. Data collection, structure solution and refinement

16 039 reflections (11 153 unique with $R_{int} = 0.0269$) were collected on a Siemens SMART CCD area detector diffractometer with narrow frames (0.3°) and three-dimensional profile fitting using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were corrected semi-empirically by ψ-scans. Cell parameters were refined by locally written software from the positions of 10 150 reflections in the range $2.18 \le \theta \le 28.33^\circ$ with $I > 10\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least squares on F^2 values. All non-H atoms were refined anisotropically, H atoms were constrained. The oxygen atom of one carbonyl group was modelled as disordered over two positions with refined occupancies O(2):O(2A) = 41(13):59(13)%. One toluene molecule (C(47)–C(53)) was disordered across a centre of symmetry and was refined as a rigid hexagon with restrained geometry for the methyl group (C(53)). Restraints were also placed on the anisotropic displacement parameters for this toluene molecule of crystallization. Final $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{-1} = 0.1172$ for 663 refined parameters, conventional $R = 0.0463$ (for F values of 9486 data with $F^2 > 4\sigma(F^2)$). The largest features in the final difference synthesis were within ± 2.18 e Å^{-3}, close to the metal atoms. Programs:

Siemens SHELXTL, SMART and SAINT software for data collection and reduction and local programs.

Atomic coordinates, bond lengths, bond angles and anisotropic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. Final atomic coordinates, selected bond lengths and bond angles are listed in Tables 1 and 2.

References

[1] I. Santos and N. Marques, New J. Chem., 19 (1995) 551.
[2] X.W. Zhang, G.R. Loppnow, R. McDonald and J. Takats, J. Am. Chem. Soc., 117 (1995) 7628.
[3] A. Sella, G.H. Maunder, J. Takats and X.W. Zhang, unpublished results.
[4] J. Takats, X.W. Zhang, V.W. Day and T.A. Eberspacher, Organometallics, 12 (1993) 4286.
[5] N. Marques, J. Takats, X.W. Zhang, V. Day, A. Sella and G.H. Maunder, in preparation.
[6] A.C. Hillier, S.Y. Liu, A. Sella and M.R.J. Elsegood, unpublished results.
[7] T.D. Tilley and R.A. Andersen, J. Chem. Soc. Chem. Commun., (1981) 985. T.D. Tilley and R.A. Andersen, J. Am. Chem. Soc., 104 (1982) 1772.
[8] J.M. Boncella and R.A. Andersen, J. Chem. Soc. Chem. Commun., (1984) 808.
[9] J.M. Boncella and R.A. Andersen, Inorg. Chem., 23 (1984) 432.
[10] A. Recknagel, A. Steiner, S. Brooker, D. Stalke and F.T. Edelmann, Chem. Ber., 124 (1991) 1373.
[11] Z. Hou, K. Aida, Y. Takagi and Y. Wakatsuki, J. Organomet. Chem., 473 (1994) 101 and references cited therein.
[12] P.N. Hazin, J.C. Huffman and J.W. Bruno, J. Chem. Soc. Chem. Commun., (1988) 1473.
[13] S.-Y. Liu, G.H. Maunder, A. Sella, M. Stevenson and D.A. Tocher, Inorg. Chem., 35 (1996) 76.
[14] V.W. Day, S.Y. Liu and A. Sella, unpublished results.
[15] D.L. Reger, S.J. Knox, J.A. Lindemann and L. Lebioda, Inorg. Chem., 29, (1990), 416.
[16] G.Z. Qi, Q. Shen and Y.H. Lin, Acta Crystallogr. Sect. C:, 50 (1994) 1456. Z. Hou, T. Miyano, H. Yamazaki and Y. Wakatsuki, J. Am. Chem. Soc., 117 (1995) 4421.
[17] C.M. Lukehart, Fundamental Transition Metal Organometallic Chemistry, Brooks Cole, Belmont, CA, 1985.
[18] W.B. Evans, I. Bloom, J.W. Grate, L.A. Hughes, W.E. Hunter and J.L. Atwood, Inorg. Chem., 24 (1985) 4620.
[19] N. Marques, personal communication.
[20] G. Maunder, A. Sella and M.R.J. Elsegood, unpublished results.

[21] B.E. Bursten and M.G. Gatten, *J. Am. Chem. Soc.*, *106* (1984) 2554.

[22] I.P. Beletskaya, A.Z. Voskoboynikov, E.B. Chuklanova, N.I. Kirillova, A.K. Shestakova, I.N. Parshina, A.I. Gusev and G.K.-I. Magomedov, *J. Am. Chem. Soc.*, *115* (1993) 3156.

[23] Y. Zhen, W.G. Feinberg, C.K. Lai and J.D. Atwood, *J. Am. Chem. Soc.*, *111* (1989) 7832.

[24] S. McNally and N.J. Cooper, in A.L. Wayda and M.Y. Darensbourg (eds.), *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*, ACS Symposium Series Vol. 357, American Chemical Society, Washington, DC, 1987.

[25] D.F. Shriver and M.A. Drezdzon, *The Manipulation of Air-Sensitive Compounds*, Wiley, New York, 2nd edn., 1986.

[26] S. Trofimenko, *J. Am. Chem. Soc.*, *89* (1967) 6288.

[27] A.R. Manning, P. Hackett, R. Birdwhistell and P. Soyer, *Inorg. Synth.*, *28* (1990) 148.