Available online at www.sciencedirect.com

SCIENCE DIRECT

Journal of Organometallic Chemistry 664 (2002) 298–305

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

The reaction of samarium(II) with manganese carbonyl: unexpected conversion of CO to formate. X-ray crystal structures of $[Sm(Tp^{Me2})_2]Mn(CO)_5$ and $\{[Sm(Tp^{Me2})_2]_2(\mu\text{-}HCO_2)\}Mn(CO)_5$ ($Tp^{Me2} = HB(3,5\text{-dimethylpyrazolyl})$)

Anna C. Hillier [a], Andrea Sella [a,*], Mark R.J. Elsegood [b]

[a] *Department of Chemistry, Christopher Ingold Laboratories, UCL, 20 Gordon Street, London WC1H 0AJ, UK*
[b] *Chemistry Department, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK*

Received 9 September 2002; accepted 29 September 2002

Abstract

The reaction of $[Sm(Tp^{Me2})_2]$ with Mn_2CO_{10} results in the reductive cleavage of the Mn–Mn bond and the formation of the salt $[Sm(Tp^{Me2})_2]Mn(CO)_5$ which has been characterized by X-ray diffraction ($Tp^{Me2} = HB(3,5\text{-dimethylpyrazolyl})_3$). In addition a second product, $[(Tp^{Me2})_2Sm(\mu\text{-}O_2CH)Sm(Tp^{Me2})_2]Mn(CO)_5$, was isolated and characterized crystallographically. Two mechanisms for the formation of this complex are proposed.

Keywords: Samarium; Lanthanide; Manganese; Formate; Pyrazolylborate; Hydrolysis

1. Introduction

As efforts to diversify the range of ancillary ligands available for the functionalization of lanthanide metal centres have intensified [1,2], polypyrazolylborate ligands have met with considerable success [3,4]. A range of homo and heteroleptic complexes of both the 2+ and 3+ oxidation states have been isolated. The divalent complexes in particular have been shown to have a diverse reactivity albeit somewhat suppressed relative to their metallocene analogues [5]. Steric effects have been found to be quite important. In the case of the simple Tp ligand ($Tp = HB(C_3H_3N_2)_3$), divalent complexes have been isolated as solvates [6]. The Tp^{Me2} analogues ($Tp^{Me2} = HB(C_5H_7N_2)_3$), with methyl substituents in the sterically critical three-position on the other hand are isolated solvent free [5,7,8], and have been shown to show suppressed, though complementary reactivity compared to their metallocene analogues. The redox chemistry of $[SmTp_2^{Me2}]$, **1**, with oxidizable substrates has led to the isolation of complexes with a wide range of ligands including superoxide [9], chalcogenolate [10,11], reduced quinones [12] and acetylide [13].

We have shown previously that reaction of binuclear transition metal carbonyls with **1** results in the cleavage of metal–metal bonds. In the case of $[CpM(CO)_3]_2$ (M = Cr, Mo, W) an isocarbonyl is isolated. When the negative charge is not as strongly delocalized onto the carbonyl groups, as with $[Co(CO)_4]^-$, salts are obtained, e.g. $[Sm(Tp^{Me2})_2][Co(CO)_4]$ [14]. The reducing nature of the lanthanide also provides mild routes to larger clusters as in the preparation of $[Re_4(CO)_{17}H]^-$ [15]. In this manuscript we report the reaction of **1** with $Mn_2(CO)_{10}$ and the isolation of an unexpected product resulting from adventitious hydrolysis.

2. Synthesis of $[Sm(Tp^{Me2})_2][Mn(CO)_5]$ (2)

Stirring a purple suspension of **1** with freshly recrystallized $[Mn_2(CO)_{10}]$ in toluene at −80 °C and allowing the reaction mixture to warm to room temperature overnight yielded a yellow/orange solution from which

---

* Corresponding author
E-mail address: a.sella@ucl.ac.uk (A. Sella).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(02)02026-0

yellow crystals, **$2\cdot C_7H_8$**, were isolated by cooling to low temperature. Small, variable amounts of a dark red material also formed. Elemental analysis of the yellow product, **2**, was consistent with the fomulation $[Sm(Tp^{Me2})_2][Mn(CO)_5]$. The solid state infrared spectrum displayed the expected ν_{BH} at 2564 cm^{-1} together with ν_{CO} at 1911, 1887 and 1854 cm^{-1}, consistent with terminal carbonyl groups on an anionic metal as opposed to the isocarbonyls seen previously for $[(C_5Me_5)_2YbMn(CO)_5]$ [16]. Spectra run in solution showed bands corresponding to the free $Mn(CO)_5^-$ anion, as well as a number of other bands which have been variously assigned to contact ion pairs and solvent-separated ions [17]. Analogous behaviour was observed for the more soluble samarium complex $[Sm(Tp^{Me,Me,4\text{-}Et})_2]$.[5] Finally it should be noted that the spectra of the material changed with time and aged samples gave evidence for the formation of an isocarbonyl (as evidenced by a band at 1736 cm^{-1}) and for decomposition (including formation of $Mn_2(CO)_{10}$). These processes were not explored further.

3. X-ray structure of $2\cdot C_7H_8$

Compound **$2\cdot C_7H_8$** crystallized from toluene at low temperature in the space group $P\bar{1}$ as yellow blocks. The asymetric unit comprises two half cations, one anion and one molecule of toluene. Although the crystals did not diffract strongly the resulting structure clearly showed the connectivity of the compound and confirmed it to be salt-like, $[Sm(Tp^{Me2})_2][Mn(CO)_5]$. The molecular structure is shown in Fig. 1. The cation is essentially identical to those observed by us and by others in $[Sm(Tp^{Me2})_2]I$, $[Sm(Tp^{Me2})_2]BPh_4$ [5], $[Sm(Tp^{Me2})_2](TePh)_3$ [18], with average Sm–N distance of 2.421 Å (range 2.406(9)–2.430(9) Å). The counterion is trigonal bipyramidal as expected [19,20]. No significant interionic interactions were observed. In this respect therefore the reaction proceeds analogously to the reaction with $Co_2(CO)_8$ which yields the salt-like $[Sm(Tp^{Me2})_2][Co(CO)_4]$ [21].

4. Isolation and X-ray structure of $[(Sm(Tp^{Me2})_2)_2(\mu\text{-}O_2CH)][Mn(CO)_5]\cdot 4(C_7H_8)$ ($3\cdot 4(C_7H_8)$)

During one synthesis of **2** yellow crystals were obtained which exhibited both BH and CO peaks in the infrared spectrum but which differed significantly from those of **2**. A yellow crystal of **$3\cdot 4(C_7H_8)$** crystallized in the orthorhombic space group $Pna2_1$ with four molecules of toluene included in the lattice. As for **2**, the structure is essentially salt-like with the surprising bimetallic cation, $[(Tp^{Me2})_2Sm(\mu\text{-}O_2CH)Sm(Tp^{Me2})_2]^+$, together with $[Mn(CO)_5]^-$ as counterion (Fig. 2). No significant interionic contacts were present.

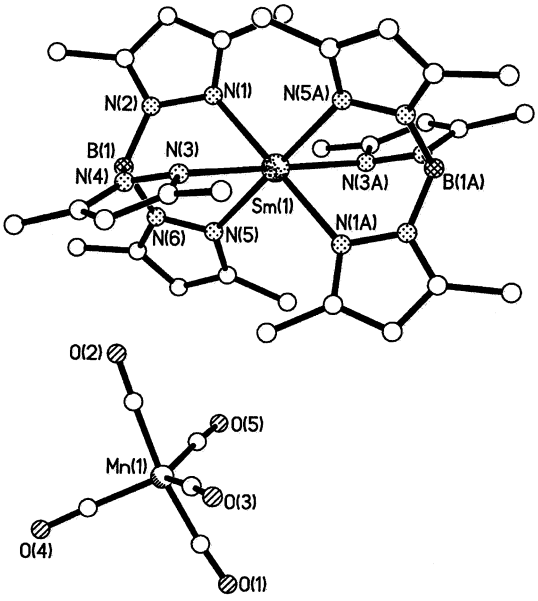


Fig. 1. The molecular structure of **2** (hydrogen atoms and toluene of crystallization omitted for clarity). Selected distances: Sm(1)–N(1) 2.406(9) Å, Sm(1)–N(3) 2.430(9) Å, Sm(1)–N(5) 2.427(7) Å, Mn(1)–C(31) 1.81(1), Mn(1)–C(32) 1.83(1) Å, Mn(1)–C(33) 1.79(1) Å, Mn(1)–C(34) 1.79(1) Å, Mn(1)–C(35) 1.80(1).

The cation consists of two essentially normal $[Sm(Tp^{Me2})_2]^+$ units linked by a single central formate group. Such an arrangment is rare in lanthanide chemistry. We are only aware of a single other example of a lanthanide complex with a single formate bridge [22] and a search in the Cambridge Databases indicates that analogous transition metal complexes are not common. This points towards an unusual formation mechanism for **3**.

The formate ligand lies directly between the two metal centres such that the samarium and oxygen atoms are approximately colinear. As a result the separation of the samarium atoms is unusually long, 6.888 Å, far greater than the 5.42 Å for the doubly bridged dimer $[SmTp_2(\mu\text{-}O_2CPh)]_2$ prepared previously by salt metathesis [23]. The Sm–O distances, on the other hand, (2.344(3) and 2.345(2) Å) are comparable to the average 2.33(4) Å observed in the dimeric samarium benzoate complex $[Sm(Tp)_2(\mu\text{-}O_2CPh)]_2$ [23], but shorter than those in other eight-coordinate trivalent samarium carboxylates, for example $[Sm(O_2CMe)_4(H_2O)_2]_2$ [24], (average Sm–O 2.43 Å) and $[Sm(O_2C\text{-}3\text{-}pyr)_2(\mu\text{-}O_2C\text{-}pyr)_2]_2$ [25] (average Sm 2.38 Å).

With C–O distances of 1.230(5) and 1.250(5) Å, the formate group deviates only very slightly from ideality— this is presumed to be a crystal packing effect. The distances are slightly longer than those in $[SmTp_2(\mu\text{-}O_2CPh)]_2$, 1.208 and 1.227 Å in one benzoate moiety and 1.218 and 1.261 Å in the second [23]. The

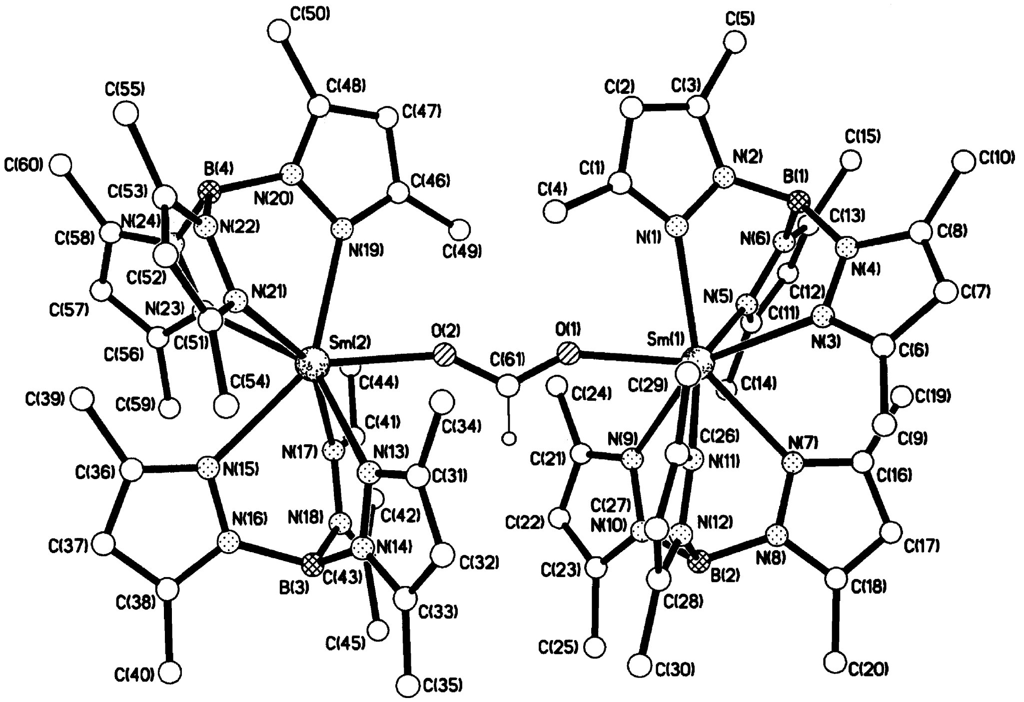


Fig. 2. The molecular structure of the cation in **3·4(C$_7$H$_8$)** (hydrogen atoms on the Tp ligands and the toluene molecules of crystallization omitted for clarity). Selected distances and angles: Sm(1)–O(1) 2.344(3) Å, Sm(2)–O(2) 2.345(2) Å, Sm(1)–N(1) 2.570(4) Å, Sm(1)–N(3) 2.493(4) Å, Sm(1)–N(5) 2.492(4) Å, Sm(1)–N(7) 2.601(3) Å, Sm(1)–N(9) 2.504(4) Å, Sm(1)–N(11) 2.435(3) Å, Sm(2)–N(15) 2.591(3) Å, Sm(2)–N(17) 2.441(3) Å, Sm(2)–N(19) 2.577(3) Å, Sm(2)–N(21) 2.486(3) Å, Sm(2)–N(23) 2.518(3) Å, O(1)–C(61) 1.230(5) Å, O(2)–C(61) 1.250(5) Å, Mn(1)–C(62) 1.823(5), Mn(1)–C(63) 1.804(6) Å, Mn(1)–C(64) 1.805(6) Å, Mn(1)–C(65) 1.808(6) Å, Mn(1)–C(66) 1.818(7) Å, Sm(1)–O(1)–C(61) 148.1(3)°, Sm(2)–O(2)–C(61) 150.0(3)°, O(1)–C(61)–O(2) 126.3(4).

O–C–O angle of 126.3(4)° is comparable to those observed in [SmTp$_2$(μ-O$_2$CPh)]$_2$, 124(2) and 121(2)° and to the angles of 124 and 127° in [Sm(O$_2$C-3-pyr)$_2$(μ-O$_2$C-3-pyr)$_2$]$_2$ [25].

The Tp^{Me2} ligands on each samarium are mutually staggered to minimize interligand interactions. The Sm–N distances are in the range 2.435(3) to 2.601(3)Å {Sm(1), average 2.516 Å} and 2.441(3) to 2.591(3) Å {Sm(2), average 2.522 Å), slightly shorter than those observed for [(Sm(Tp^{Me2})$_2$)$_2$(μ-C$_{14}$H$_8$O$_2$)] [12,26] and [Sm(Tp^{Me2})$_2$(O-C$_6$H$_4$-4-^{t}Bu)] [10] (average Sm–N 2.572 Å) but comparable to those observed for the dimeric benzoate bridged complex [SmTp$_2$(μ-O$_2$CPh)]$_2$ (2.527 and 2.523 Å) [23].

The pyrazolylborate groups on each samarium atom are bent away from the bridging formate group, as measured by the B–Sm–B angles of 147.4 and 149.3° for Sm(1) and Sm(2), respectively. The plane of the formate moiety is almost coplanar with the B–Sm–B planes, at 3.7° to the B–Sm(1)–B plane and at 6.3° to the B–Sm(2)–B plane, nestling between pyrazolyl groups 5 (N(9)N(10)) and 6 (N(11)N(12)) on Sm(1) and 7 (N(13)N(14)) and 9 (N(17)N(18)) on Sm(2). Four of the pyrazolyl rings are somewhat twisted relative to the ideal C$_3$ axis of the ligand, with torsion angles of 22.4, 20.4, 18.3 and 18.2°, respectively, presumably to accommodate the formate anion and to minimise interactions between the two halves of the dimer. The larger torsion angles for the pyrazolylborates attached to Sm(1) correlate with the shorter C(61)–O(1) and Sm(1)–N distances. Such twisting is quite common in lanthanide Tp^{Me2} systems [10,27].

The coordination geometry at each samarium atom is best described as distorted pentagonal bipyramidal, as has been found in related seven-coordinate systems [10,13,28]. N(5) and N(11) on Sm(1) and N(21) and N(17) on Sm(2) adopt axial positions, with the equatorial planes defined by O(1), N(1), N(3), N(7) and N(9), or O(2), N(13), N(15), N(23) and N(19), respectively. The arrangement of the ligands around Sm(1) is such that the axial nitrogens are bent away from linearity, with N(5)–Sm(1)–N(11) angle of 155.8° and the mean deviation from the equatorial plane is 0.3009 Å. The equivalent data at Sm(2) are closely similar, N(21)–Sm(2)–N(17) (155.3°) and mean deviation from equatorial plane (0.2701 Å).

5. Mechanism of formation of [{Sm(Tp^{Me2})$_2$}$_2$(μ-O$_2$CH)][Mn(CO)$_5$]

The formation of the carboxylate group in this reaction is rather unexpected. Formates are conventionally observed as a consequence of CO$_2$ reduction mediated by metal hydride complexes. Such reactions have been carried out both stoicheiometrically [29,30] and catalytically [31–34] by transition metal systems. In supercritical CO_2 spectacular conversions can be achieved in the presence of hydrogen [35].

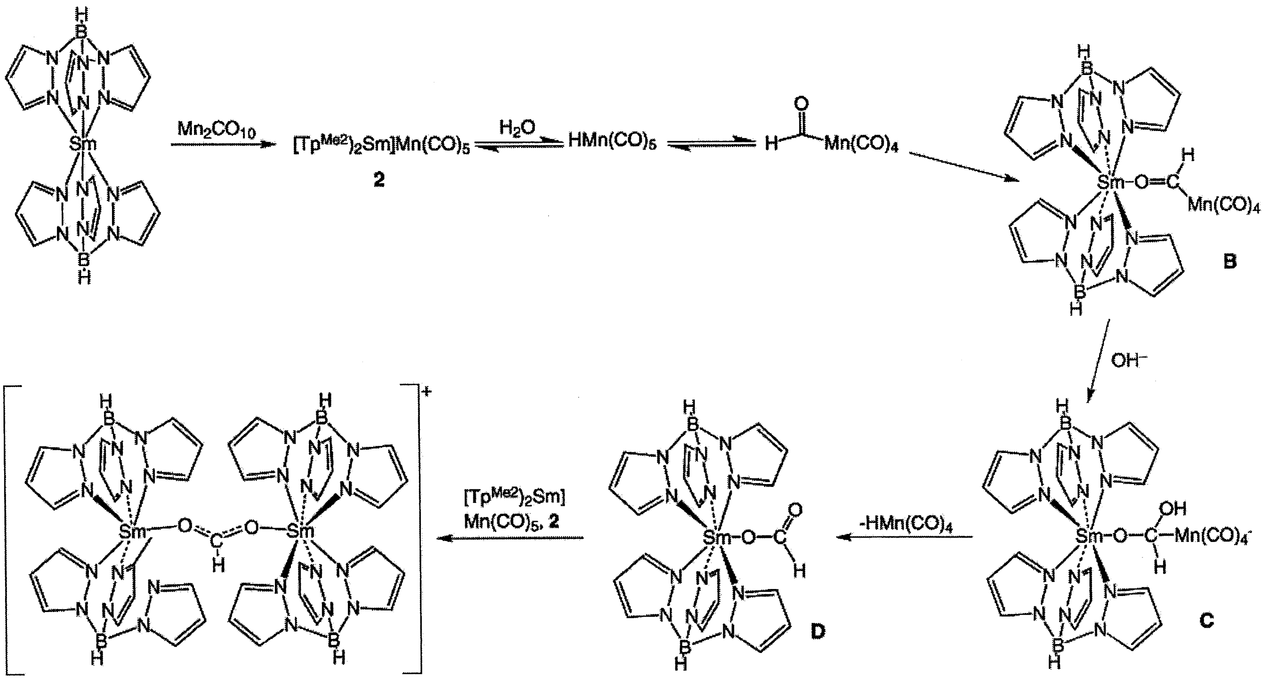
In the present case, we believe that a mechanism based on activation of CO_2, may be excluded on the basis of several observations. Lanthanide systems have previously been shown to reductively couple CO_2 to oxalate. Thus, exposing $[Sm(C_5Me_5)_2(THF)_2]$ at room temperature results in the formation of the oxalate-bridged complex $\{[Sm(C_5Me_5)_2]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2CCO_2)\}$ [36] while atmospheric CO_2 has been coupled by the complex $[Yb(N(SiMe_3)_3]$ in the presence of tetraphenylporphyrin [37]. Since in the present case reactions were carried out with fairly rigorous exclusion of air, the concentration of CO_2 should be extremely low. Nevertheless, accidental admission of air into the reaction flask might still seem a plausible means of introducing CO_2 into the system. We note, however, that Takats has shown that **1** reacts rapidly with O_2 at -78 °C to give side-bound superoxide [9]. On the other hand, exposure of **1** to an atmosphere of pure CO_2 resulted in very slow reactions at room temperature and mixtures of products were isolated [26]. Hence, we would expect products resulting from reaction with O_2 rather than with CO_2 had air been involved.

It seems more reasonable to invoke a pathway involving the reaction of a carbonyl with adventitious water. The direct reaction of CO and water to give formic acid is thermodynamically feasible but slow at room temperature ($\Delta H = -28$ kJ mol^{-1}). Only under forcing conditions, in the presence of a catalyst do appreciable conversions occur, though this process is not used industrially [38,39]. The dominant commercial method for the production of formic acid involves the carbonylation of methanol under basic conditions followed by hydrolysis [40]. The formation of the formate anion occurs with water gas shift (WGS) catalysts. In particular, reactions of hydroxides with metal carbonyls, the so-called oxidative hydrolysis step of the WGS reaction, gives formate in addition to carbonate and CO_2 [41,42]. The mechanism of this process is poorly understood. Nucleophilic attack by hydroxide on a metal carbonyl gives metallacarboxylates (hydroxycarbonyls) [43,44] which either decarboxylate giving CO_2 or can rearrange to give formate [41,45]. Such rearrangements have been postulated by a number of authors, for example by Darensbourg in phase-transfer-catalysed reactions of hydroxide with metal-bound carbon monoxide, which afford metal hydride as final organometallic product [46] and by Laine and coworkers in the homogeneously catalysed WGS reaction utilising $Ru_3(CO)_{12}$/KOH as catalyst [47]. It is interesting to note that although formates have been observed directly in heterogeneous systems, formates have very seldom been isolated from metal carbonyl reactions. Malatesta and coworkers reported that sodium reduction of $Ir_4(CO)_{12}$ in THF gave formates which the authors attributed to the presence of adventitious hydroxide [48].

To our knowledge, neither $Mn_2(CO)_{10}$ nor $Mn(CO)_5^-$ react directly with water to give formates. Hence we believe that the samarium ion plays a key role in driving the reaction. A mechanism may therefore be proposed for the formation of **3**, which requires combined interaction of the two metals to generate the product. Mechanism α is shown in Scheme 1. Initial reduction of $Mn_2(CO)_{10}$ by Sm^{2+} cleaves the Mn–Mn bond and affords the anion $Mn(CO)_5^-$. Under rigorously anhydrous conditions the expected salt **2** is obtained. However, the presence of adventitious moisture results in protonation of $Mn(CO)_5^-$ to give $HMn(CO)_5$. This is not unreasonable since the pK_a of $HMn(CO)_5$ is 15.1 compared to 15.7 for water [49]. Migratory insertion of the carbonyl into the Mn–H bond generates a manganese-bound formyl group, **A**. Whilst insertions of CO into metal–alkyl bonds are very common [50–52], the formation of formyls by this 'direct' method is rarely observed. External nucleophilic attack by reducing hydrides of, for example, Ti, Zr, B or Al is well-precedented [51]. If, on the other hand, the metal involved is sufficiently oxophilic to bind the formyl in the η^2 form, additional driving force for the reaction is provided. This has been found to be the case for the early d- [53] and the f-block [54] metals. The mechanism of the reaction of decamethyl zirconocene dihydride with CO is believed to involve initial insertion of CO into a Zr–H bond to afford an η^2-formyl. Related, intermolecular, conversions of coordinated CO to formyl have been reported [55,56]. A single example exists of such an insertion for a late transition metal [57].

The presence of an external Lewis acid is also known to facilitate CO insertion into metal alkyl bonds, presumably via a similar mechanism [58]. A number of steps in the homogeneously catalysed hydrogenation of CO to formaldehyde are believed to be facilitated by coordination of a metal carbonyl with Lewis acids through the oxygen [51,58]. Hence, if $HMn(CO)_5$ is indeed in equilibrium with the corresponding formyl, albeit with the equilibrium lying strongly to the left under normal conditions, binding the formyl to the Lewis acidic samarium centre (intermediate **B**) would drive the equilibrium toward the right.

The bridging formyl group in **B** can be expected to be activated towards nucleophilic attack by further water or hydroxide. β-Elimination from the resulting intermediate, **C**, releases the coordinatively unsaturated $[HMn(CO)_4]$ fragment, which would be expected to oligomerise and form hydrido-bridged carbonyl clusters such as $[H_3Mn_3(CO)_{12}]$ [59,60]. Small amounts of a red material were always obtained alongside the yellow



Scheme 1. Mechanism α for the formation of **2** and **3** (methyl groups Tp^{Me_2} ligands omitted for clarity).

product in the reaction of $[SmTp_2^{Me2}]$ with $[Mn_2(CO)_{10}]$. Unfortunately, it was not possible to isolate the red material in sufficient quantity or purity to make any claims. Mass spectrometry material enriched in the red materials showed only the parent ion, $[SmTp_2^{Me2}]^+$ and infrared data were also unhelpful.

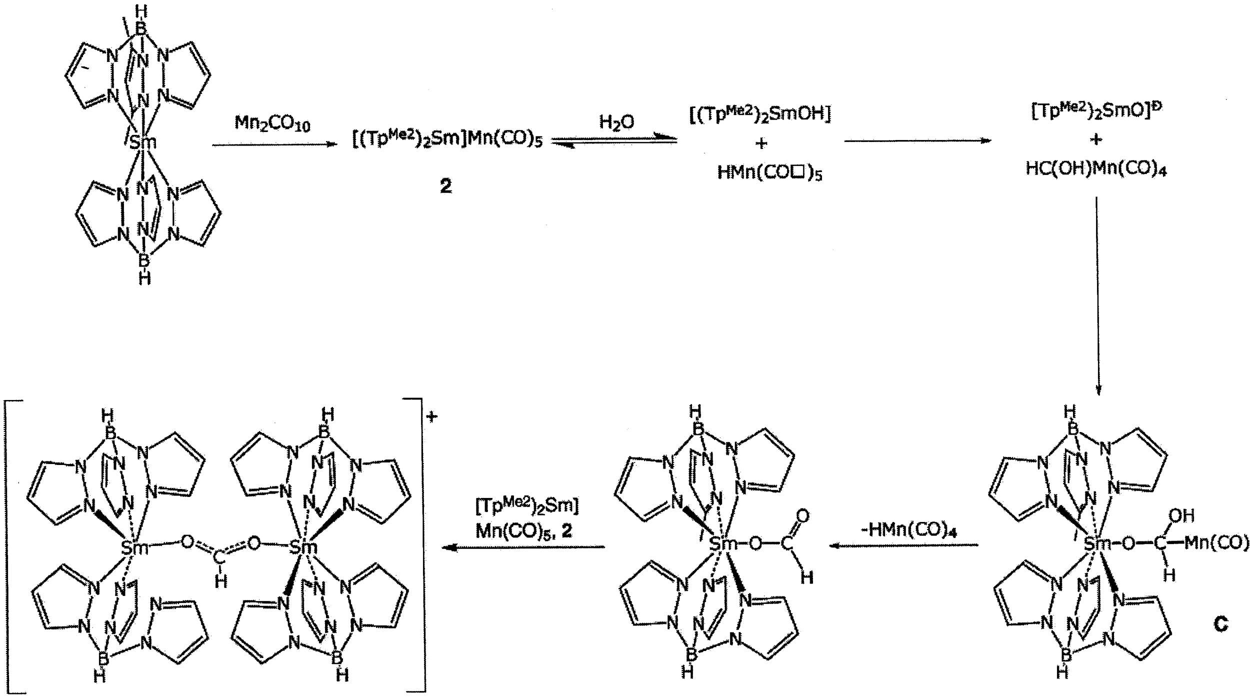
In the final step, the mononuclear samarium formate intermediate, **D**, reacts with a further equivalent of **2** to give the less soluble $[(SmTp_2^{Me2})_2(\mu\text{-}O_2CH)][Mn(CO)_5]$.

An alternative mechanism, mechanism β (Scheme 2), may also be envisaged. We have recently reported evidence that adventitious hydrolysis of a wide range of complexes of the type $[Sm(Tp^{Me2})_2X]$ results in the formation of the unpredented terminal hydroxo species $[Sm(Tp^{Me2})_2(OH)]$. Although this complex is rather unstable, decomposing to the highly insoluble borinate-bridged species $[Ln(Tp^{Me2})(\mu\text{-}BOp^{Me2})]_2$ $\{BOp^{Me2} = (HBO(dmpz)_2)^{2-}\}$ [61], Takats and Ference have successfully intercepted this species using a basic divalent hydride [62]. It is therefore possible that hydrolysis of $[Sm(Tp^{Me2})_2][Mn(CO)_5]$ results in the formation of $[Sm(Tp^{Me2})_2(OH)]$ and $[HMn(CO)_5]$. Given that the latter is in equilibrium with the corresponding formyl species, protonation of the formyl group by $[Sm(Tp^{Me2})_2(OH)]$ would lead to an anionic species $[Sm(Tp^{Me2})_2(O)]^-$ capable of attacking the protonated formyl to give **C**.

Attempts to test these mechanistic proposals have been stymied by our failure to reproduce the reaction, an observation which lends further credence to the involvement of adventitious water. Attempts to identify formate C–H stretching bands in the IR by carrying out the reaction in glassware pretreated with D_2O showed no evidence for appropriate shifted bands. A key problem in this system is the moisture sensitivity of the ancillary Tp^{Me2} ligands themselves which are prone to hydrolysis giving borinate-bridged dimers [61]. Attempts to prepare the formate complex by metathesis resulted in decomposition to the borinate-bridged dimer $[Sm(Tp^{Me2})((dmpz)_2BH(\mu\text{-}O))]_2$ [61] owing to the difficulty of obtaining rigorously anhydrous sodium formate. In view of the ease of formation of such dimers, the isolation of **3** is even more surprising.

6. Conclusions

We have shown that a samarium(II) pyrazolylborate complex reductively cleaves $Mn_2(CO)_{10}$ in the expected manner. In contrast to the corresponding metallocene systems, the major product appears to be the salt-like compound **2** rather than an isocarbonyl-bridged analogue. This is consistent with the relatively low negative charge delocalized onto the carbonyls (as has been observed for $Co(CO)_4^-$) and to the much greater steric hindrance associated with the Tp^{Me2} ligands. The isolation of a bridging formate complex is intriguing and suggests that the samarium centre can significantly alter the reactivity of the $Mn(CO)_5^-$ anion towards water. This observation suggests that the addition of Lewis acids to WGS systems may result in significant changes in product distribution.



Scheme 2. Mechanism β for the formation of **2** and **3** (methyl groups Tp^{Me_2} ligands omitted for clarity).

7. Experimental

7.1. General procedures

All operations were performed using standard Schlenk line and dry box techniques under an inert atmosphere of nitrogen. THF, toluene and *n*-hexane were dried by standard methods and degassed prior to use. Deuterated solvents, benzene-d_6 and toluene-d_8, were dried over Na or Na/K alloy and distilled. [$SmTp_2^{Me2}$] and [$Sm(Tp^{Me,Me\text{-}4\text{-}Et})_2$] were synthesized by published methods.[5,7,63] $Mn_2(CO)_{10}$ was purchased from Aldrich and was recrystallised from petrol (boiling range 30–40 °C). ^{1}H-NMR spectra were recorded on a Bruker AMX 400 spectrometer and referenced internally using the residual solvent resonances relative to tetramethylsilane. IR spectra were recorded in toluene solution or as KBr pellets on a Nicolet 205 FTIR spectrometer. Elemental analyses were determined by Alan Stones of the UCL Analytical Services using Perkin–Elmer automatic analysers.

*7.2. Preparation of [$Sm(Tp^{Me2})_2$][$Mn(CO)_5$] (**2**)*

[$Sm(Tp^{Me2})_2$] (103 mg, 0.138 mmol) and $Mn_2(CO)_{10}$ (26 mg, 0.067 mmol) were mixed in a Schlenk tube, cooled to −78 °C and toluene (50 ml) added with stirring. The purple mixture was stirred for 2 h at −78 °C, then slowly warmed to room temperature (r.t.), during which time it turned red, then orange and finally yellow. The solution was filtered and the volume of solvent reduced in vacuo to 15 ml. Slow cooling to −25 °C gave 42 mg (0.045 mmol, 32%) of orange/yellow crystals which readily desolvated on removal from the mother liquor.

Elemental Anal. Calc. for $Sm(Tp_2^{Me2})Mn(CO)_5 \cdot$toluene $C_{42}H_{50}N_{12}O_5B_2MnSm$: C, 48.89; H, 5.08; N, 16.29. Found: C, 48.96; H, 4.97; N, 17.06%. IR (toluene solution, cm^{-1}): 2563 (B–H); 1897, 1853 cm^{-1} (CO). IR (KBr pellet): 2564 (B–H); 1911, 1887 and 1854 cm^{-1} (CO).

*7.3. Preparation of [$Sm(Tp^{Me,Me\text{-}4\text{-}Et})_2$][$Mn(CO)_5$] (**2a**)*

This reaction was carried out in an analogous fashion to the preparation of **3**·**3**. The reaction of [$Sm(Tp^{Me,Me\text{-}4\text{-}Et})_2$] (100 mg, 0.11 mmol) and $Mn_2(CO)_{10}$ (21 mg, 0.055 mmol) afforded 50 mg (0.045 mmol, 41%) of yellow crystals which crumbled when removed from the mother liquor.

Elemental Anal. Calc. for $C_{47}H_{68}N_{12}O_5B_2SmMn$: C, 50.95; H, 6.18; N, 15.17. Found: C, 48.94; H, 6.14; N, 14.99%. IR (toluene solution, cm^{-1}): 2554 (BH); 1632, 1828, 1918 (CO). IR (KBr pellet, cm^{-1}): 2563 (BH); 1642–1653, 1814, 1910 (CO).

^{1}H-NMR (C_6D_6): −1.39 (s, 18H, 3Me), 0.81 (t, 18H, CH_3), 2.04 (q, 12H, CH_2), 3.17 (d, 18H, 5Me).

7.4. X-ray crystallography for $\mathbf{2}\cdot\mathbf{C_7H_8}$ and $\mathbf{3}\cdot\mathbf{4(C_7H_8)}$

Data were collected on a Bruker SMART 1K CCD diffractometer at 160 K using narrow frames and ω-rotation. The data were corrected for absorption semi-empirically.

7.5. Crystal data for $\mathbf{2}\cdot\mathbf{C_7H_8}$

$C_{35}H_{44}B_2MnN_{12}O_5Sm\cdot C_7H_8$, $M = 1031.87$, triclinic, space group $P\bar{1}$, $a = 10.6613(16)$, $b = 11.5186(17)$, $c = 20.715(3)$ Å, $\alpha = 97.437(4)$, $\beta = 98.612(3)$, $\gamma = 105.281(4)^\circ$, $U = 2387.9(6)$ Å^3, $Z = 2$, $\mu(\text{Mo–K}_\alpha) = 1.537$ mm^{-1}, 14347 data measured, of which 8309 unique with $R_{\text{int}} = 0.0623$, $R = 0.0881$ {for 5010 data with $I > 2\sigma(I)$}, $wR_2 = 0.2401$ {for all unique data}. The structure was solved by placing atom Sm(1) at 0.5 0.5 0.5 and refined on F^2 values. The structure comprises two half-cations, (each on a centre of symmetry, one being disordered), one anion and one toluene molecule of crystallisation.

7.6. Crystal data for $\mathbf{3}\cdot\mathbf{4(C_7H_8)}$

$C_{66}H_{89}B_4MnN_{24}O_7Sm_2\cdot 4C_7H_8$, $M = 2098.03$, orthorhombic, space group $Pna2_1$, $a = 21.1214(12)$, $b = 17.4688(9)$, $c = 27.3426(15)$ Å, $U = 10088.5(10)$ Å^3, $Z = 4$, $\mu(\text{Mo–K}_\alpha) = 1.336$ mm^{-1}, 61153 data measured, of which 20411 unique with $R_{\text{int}} = 0.0413$, $R = 0.0361$ {for 17043 data with $I > 2\sigma(I)$}, $wR_2 = 0.0781$ {for all unique data}. The structure was solved by Patterson synthesis and refined on F^2 values. The structure comprises one cation one anion and four toluene molecules of crystallisation.

8. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 192154 and 192155 for compounds $\mathbf{2}\cdot C_7H_8$ and $\mathbf{3}\cdot 4C_7H_8$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the EPSRC for a studentship to A.C.H. (GR/K11338). We would like to thank Prof. W. Clegg for use of the X-ray diffractometer and associated computer programs and facilities and the EPSRC for provision of the X-ray diffractometer at the University of Newcastle-upon-Tyne. We are grateful to Prof. Josef Takats, Dr Maurizio Volpe and Prof. A.J. Deeming for helpful discussions.

References

[1] F.T. Edelmann, Angew. Chem. Int. Ed. Engl. 34 (1995) 2466.
[2] F.T. Edelmann, in: M.F. Lappert (Ed.), Comprehensive Organometallic Chemistry, vol. 4, Pergamon, Oxford, 1995, p. 11.
[3] I. Santos, N. Marques, New J. Chem. 19 (1995) 551.
[4] N. Marques, A. Sella, J. Takats, Chem. Rev. 102 (2002) 2137.
[5] A.C. Hillier, X.W. Zhang, G.H. Maunder, S.Y. Liu, T.A. Eberspacher, M.V. Metz, R. McDonald, Â. Domingos, N. Marques, V.W. Day, A. Sella, J. Takats, Inorg. Chem. 40 (2001) 5106.
[6] Â. Domingos, J. Marcalo, N. Marques, A.P. de Matos, A. Galvao, P.C. Isolani, G. Vicentini, K. Zinner, Polyhedron 14 (1995) 3067.
[7] J. Takats, X.W. Zhang, V.W. Day, T.A. Eberspacher, Organometallics 12 (1993) 4286.
[8] G.H. Maunder, A. Sella, D.A. Tocher, J. Chem. Soc. Chem. Commun. (1994) 885.
[9] X.W. Zhang, G.R. Loppnow, R. McDonald, J. Takats, J. Am. Chem. Soc. 117 (1995) 7828.
[10] A.C. Hillier, S.Y. Liu, A. Sella, M.R.J. Elsegood, Inorg. Chem. 39 (2000) 2635.
[11] I. Lopes, A.C. Hillier, S.Y. Liu, A. Domingos, J. Ascenso, A. Galvao, A. Sella, N. Marques, Inorg. Chem. 40 (2001) 1116.
[12] I. Lopes, Â. Domingos, G.Y. Lin, X.W. Zhang, A.C. Hillier, A. Sella, N. Marques, J. Takats, 22nd Rare Earth Research Conference, Argonne, IL, 1999, p. PIII.
[13] G.Y. Lin, R. McDonald, J. Takats, Organometallics 19 (2000) 1814.
[14] A.C. Hillier, S.Y. Liu, A. Sella, O. Zekria, M.R.J. Elsegood, J. Organomet. Chem. 528 (1997) 209.
[15] A.C. Hillier, A. Sella, M.R.J. Elsegood, J. Organomet. Chem 588 (1999) 200.
[16] J.M. Boncella, R.A. Andersen, Inorg. Chem. 23 (1984) 432.
[17] M.Y. Darensbourg, D.J. Darensbourg, D. Burns, D.A. Drew, J. Am. Chem. Soc. 98 (1976) 3127.
[18] A.C. Hillier, S.Y. Liu, A. Sella, M.R.J. Elsegood, Angew. Chem. Int. Ed. Engl. 38 (1999) 2745.
[19] B.A. Frenz, J.A. Ibers, Inorg. Chem. 11 (1972) 1109.
[20] M. Herberhold, F. Wehrmann, D. Neugebauer, G. Huttner, J. Organomet. Chem. 152 (1978) 329.
[21] A.C. Hillier, A. Sella, M.R.J. Elsegood, J. Chem. Soc. Dalton Trans. (1998) 3871.
[22] L.A. Aslanov, V.M. Ionov, V.B. Ribakov, I.D. Kiekbaer, Koord. Khim. 4 (1978) 1598.
[23] D.L. Reger, S.J. Knox, J.A. Lindeman, L. Lebioda, Inorg. Chem. 29 (1990) 416.
[24] A. Lossin, G. Meyer, R. Fuchs, J. Strähle, Z. Naturforsch. Teil B 47 (1992) 179.
[25] J.W. Moore, M.D. Glick, W.A. Baker, Jr, J. Am. Chem. Soc. 94 (1972) 1858.
[26] A.C. Hillier, PhD Thesis, University of London, 1998.
[27] R.J.H. Clark, S.Y. Liu, G.H. Maunder, A. Sella, M.R.J. Elsegood, J. Chem. Soc. Dalton Trans. (1997) 2241.
[28] A.C. Hillier, S.Y. Liu, A. Sella, M.R.J. Elsegood, J. Alloys Compounds 303 (2000) 83.
[29] L.S. Pu, A. Yamamoto, S. Ikeda, J. Am. Chem. Soc. 90 (1968) 3896.
[30] M.K. Whittlesey, R.N. Perutz, M.H. Moore, Organometallics 15 (1996) 5166.

[31] F. Graf, W. Leitner, J. Chem. Soc. Chem. Commun. (1992) 623.

[32] F. Gassner, W. Leitner, J. Chem. Soc. Chem. Commun. (1993) 1465.

[33] T. Burgemeister, F. Kastner, W. Leitner, Angew. Chem. Int. Ed. Engl. 32 (1993) 739.

[34] W. Leitner, Angew. Chem. Int. Ed. Engl. 34 (1995) 2207.

[35] P.G. Jessop, T. Ikariya, R. Noyori, Chem. Rev. 95 (1995) 259.

[36] W.J. Evans, C.A. Seibel, J.W. Ziller, Inorg. Chem. 37 (1998) 770.

[37] W.-K. Wong, L.-L. Zhang, F. Xue, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (2000) 2245.

[38] W.C. Arsem, US, 1926 US patent 1606394.

[39] A. Aguillo, T. Horlenko, Hyrocarbon Process. 59 (1980) 120.

[40] W. Reutemann, H. Kieczka, Industrial Organic Chemicals: Starting Materials and Intermediates, vol. 5, VCH, Weinheim, 1999, p. 2711.

[41] P.C. Ford, Acc. Chem. Res. 14 (1981) 31.

[42] P.C. Ford, in: B.P. Sullivan, K. Krist, H.E. Guard (Eds.), Electrochemical and Electrocatalytic Reactions of CO_2, Elsevier, Amsterdam, 1993, p. 68.

[43] N. Grice, S.C. Rao, R. Pettit, J. Am. Chem. Soc. 101 (1979) 1627.

[44] S.W. Lee, D. Tucker, M.G. Richmond, Inorg. Chem. 26 (1990) 3053.

[45] P.A. Chaloner, M.A. Esteruelas, F. Joó, L.A. Oro, Homogeneous Hydrogenation, Kluwer, Dordrecht, 1994, p. 223.

[46] D.J. Darensbourg, B.J. Baldwin, J.A. Froelich, J. Am. Chem. Soc. 102 (1980) 4688.

[47] R.M. Laine, R.G. Pinker, P.C. Ford, J. Am. Chem. Soc. 99 (1977) 252.

[48] M. Angoletta, L. Malatesta, G. Caglio, J. Organomet. Chem. 94 (1975) 99.

[49] E.J. Moore, J.M. Sullivan, J.R. Norton, J. Am. Chem. Soc 108 (1986) 2257.

[50] F. Calderazzo, Angew. Chem. Int. Ed. Engl. 16 (1977) 299.

[51] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.

[52] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, 2nd ed., Wiley Interscience, New York, 1994.

[53] J.M. Manriquez, D.R. McAlister, R.D. Sanner, J.E. Bercaw, J. Am. Chem. Soc. 98 (1976) 6733.

[54] P.J. Fagan, K.G. Moloy, T.J. Marks, J. Am. Chem. Soc. 103 (1981) 6959.

[55] P.T. Wolczanski, R.S. Threlkel, J.E. Bercaw, J. Am. Chem. Soc. 101 (1979) 218.

[56] P.A. Belmonte, F.G.N. Cloke, R.R. Schrock, J. Am. Chem. Soc 105 (1983) 2643.

[57] B.B. Wayland, B.A. Woods, R. Pierce, J. Am. Chem. Soc 104 (1982) 302.

[58] S.B. Butts, E.M. Holt, S.H. Strauss, N.W. Alcock, R.E. Stimson, D.F. Shriver, J. Am. Chem. Soc. 101 (1979) 5864.

[59] B.F.G. Johnson, R.D. Johnston, J. Lewis, B.H. Robinson, J. Chem. Soc. Chem. Commun. (1966) 851.

[60] B.F.G. Johnson, R.D. Johnston, J. Lewis, B.H. Robinson, J. Organomet. Chem. 10 (1967) 105.

[61] Â. Domingos, M.R.J. Elsegood, A.C. Hillier, G. Lin, S.Y. Liu, I. Lopes, N. Marques, G.H. Maunder, R. McDonald, A. Sella, J.W. Steed, J. Takats, Inorg. Chem., in press.

[62] J. Ferrence, G.M. Takats, J. Organomet. Chem. 647 (2002) 84.

[63] M.A.J. Moss, R.A. Kresinski, C.J. Jones, W.J. Evans, Polyhedron 12 (1993) 1953.