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Metalloligands containing samarium(III). Access to binuclear *f*-metal (samarium)–*d*-metal (rhodium) complexes

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Abstract

The synthesis of the new dimethylphosphinotetramethylcyclopentadiene $HC_5Me_4PMe_2$ and of its potassium salt $KC_5Me_4PMe_2$ are reported. Reactions of this potassium salt (as well as of the known $LiC_5H_4PPh_2$ and $KC_5Me_4PPh_2$) with $[(COT)SmCl(THF)_2]_2$ gave a series of metalloligands $(COT)Sm(C_5R_4PR'_2)(THF)_n$ (R = H or Me; R′ = Me or Ph; $n = 0$ or 2; COT = η^8-cyclooctatetraenyl; THF = tetrahydrofuran). The X-ray crystal structure of $(COT)Sm(C_5H_4PPh_2)(THF)_2$ is described. These metallophosphines reacted quantitatively with $(C_5H_5)Rh(CO)_2$ to give phosphido-bridged bimetallic samarium(III)-rhodium(I) complexes $(COT)Sm(\mu\text{-}C_5R_4PR'_2)Rh(C_5H_5)(CO)$ (R = H or Me; R′ = Me or Ph). Crystal data: $C_{33}H_{38}O_2PSm$, triclinic, $P\bar{1}$, $a = 8.606(2)$, $b = 11.458(3)$, $c = 14.632(2)$ Å, $\alpha = 87.09(2)$, $\beta = 86.93(2)$, $\gamma = 87.18(2)°$, $V = 1437.3$ Å^3, $Z = 2$, $D_x = 1.497$ g cm^{-3}, $m = 21.305$ cm^{-1}, λ (Mo-K_α) = 0.71073 Å, $R = 0.036$.

Introduction

The synthesis and characterization of heterobinuclear compounds containing both an *f*-element and a late *d*-transition metal in close proximity represent an area that has been recently developed [1–3]. Heterodifunctional phosphinocyclopentadienyl ligands have been used largely for the synthesis of bimetallic derivatives of *d*-transition metals [4,5], but similar complexes with an *f*-element are still limited to the compounds containing ytterbium(II) or uranium(IV): $Yb(THF)_2(\mu\text{-}C_5H_4PPh_2)_2PtMe_2$ [2], $(NEt_2)_2U(\mu\text{-}C_5H_4PPh_2)_2M(CO)_4$, and

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$(C_5H_4PPh_2)_2U(\mu\text{-}C_5H_4PPh_2)_2M(CO)_4$ (M = Cr, Mo) [3] in which the metal centres are bridged by two $C_5H_4PPh_2$ groups.

Here we present the synthesis of the first metallocyclopentadienylphosphines of samarium(III) $(COT)Sm(C_5R_4PR'_2)(THF)_n$ from the precursor $\{(COT)SmCl(THF)_2\}_2$ and of the corresponding phosphinocyclopentadienide anion (**including the new $KC_5Me_4PMe_2$**). Then we describe the reactions of these metallophosphines of samarium(III) with $(C_5H_5)Rh(CO)_2$ which provides a route to heterobimetallic complexes of samarium and rhodium.

Results

Synthesis of $HC_5Me_4PMe_2$ (1) and $KC_5Me_4PMe_2$ (2)

1 was synthesized as described [6] for $HC_5Me_4PPh_2$. The chlorodimethylphosphine reacted in Et_2O at −78°C with a stoichiometric amount of lithium tetramethylcyclopentadienide [7*] to give, after 4 h, the cyclopentadienyldimethylphosphine **1**, which was converted directly by 48 h stirring with KH at room temperature into its white potassium salt **2**. Not surprisingly, **2** is soluble only in coordinating solvents; its ^1H NMR spectrum in THF-d_8 showed three signals: $\delta = 1.80$ and 2.05 ppm (s, C_5Me_4), $\delta = 1.07$ ppm (d, $^2J(PH) = 4$ Hz, PMe_2); the ^{31}P NMR spectrum exhibited a resonance at −72.9 ppm. Hydrolysis with D_2O regenerated deuterated **1**, characterized by its ^1H NMR spectrum which exhibited a doublet at 0.85 ppm with a coupling constant characteristic of a methyl group bonded to a phosphorus atom ($^2J(PH) = 4$ Hz), and two singlets at 1.73 and 1.94 ppm of relative intensities 1:1 assigned to the tetramethylcyclopentadienyl ring. The ^{31}P NMR spectrum showed a single resonance at −36 ppm. Like its homologue $C_5H_5PMe_2$ [8], **1** is extremely air-sensitive and should be prepared just before use.

The mass spectrum could not be obtained from the potassium salt **2**, but was recorded very easily from that of the thallium derivative, which is not moisture sensitive. This thallium compound was found to be dimeric and this may be the reason why the first attempts to synthesize organometallic compounds with it failed.

Synthesis of $(COT)Sm(C_5H_4PPh_2)(THF)_2$ (3), $(COT)Sm(C_5Me_4PPh_2)$ (4), and $(COT)Sm(C_5Me_4PMe_2)$ (5)

The (cyclooctatetraenyl)(diphenylphosphinocyclopentadienyl) samarium(III) complexes $(COT)Sm(C_5R_4PR'_2)(THF)_n$ (COT = η^8-cyclooctatetraenyl; THF = tetrahydrofuran; R = H, R′ = C_6H_5, $n = 2$, **3**; R = Me, R′ = C_6H_5, $n = 0$, **4**; R = R′ = Me, $n = 0$, **5**) were easily synthesized in THF according to eq. 1.

$$\tfrac{1}{2}[(COT)SmCl(THF)_2]_2 \xrightarrow[MC_5R_4PR'_2]{THF} (COT)Sm(C_5R_4PR'_2)(THF)_n \qquad (1)$$

(**3**: M = Li, R = H, R′ = C_6H_5, $n = 2$; blue;

4: M = K, R = CH_3, R′ = C_6H_5, $n = 0$; red brown;

5: M = K, R = R′ = CH_3, $n = 0$; dark green crystals, deep red in solution)

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* Reference number with asterisk indicates a note in the list of references.

These compounds are thermally stable but extremely air-sensitive [9*] and satisfactory elemental analyses could not be obtained for **3** and **5**. Nevertheless, they were well characterized by their ^1H and ^{31}P NMR spectra, and the X-ray crystal structure of **3** was determined.

Storing the blue crystals of **3** in a saturated THF atmosphere led reversibly to the formation of a stable pink crystalline species **3′**, which was identified by ^1H NMR spectroscopy in C_6D_6 as $(COT)Sm(C_5H_4PPh_2)(THF)_4$. It is noteworthy that **3′** is soluble in benzene whereas the blue **3** is soluble only in THF, or in C_6D_6 after addition of two equivalents of THF (to give a pink solution having the same NMR spectrum as **3′**). Only two signals were assigned to the four THF molecules, and the α protons signal was shifted by 0.6 ppm from the diamagnetic position (see Table 1). Nevertheless, it is reasonable to think that, in the solid state of **3′**, only two of the four THF molecules are directly coordinated to the metal atom.

4 was obtained as a mixture of purple and red-brown crystals. The purple crystals were found (^1H NMR solution) to contain one molecule of coordinated THF. The red-brown ones were free of solvent and gave a satisfactory elemental analysis.

Synthesis of $(COT)Sm(\mu\text{-}C_5H_4PPh_2)Rh(C_5H_5)(CO)$ (6), $(COT)Sm(\mu\text{-}C_5Me_4PPh_2)Rh(C_5H_5)(CO)$ (7), and $(COT)Sm(\mu\text{-}C_5Me_4PMe_2)Rh(C_5H_5)(CO)$ (8)

The reaction of **3**, **4** or **5**, with $(C_5H_5)Rh(CO)_2$ gave the heterobimetallic species $(COT)Sm(\mu\text{-}C_5R_4PR'_2)Rh(C_5H_5)(CO)$ **6**, **7** and **8** respectively (eq. 2).

$$\mathbf{3,\ 4}\text{ or }\mathbf{5}\ \xrightarrow[\text{refluxing THF (3) or toluene (4, 5)}]{(C_5H_5)Rh(CO)_2}\ (COT)Sm(\mu\text{-}C_5R_4PR'_2)Rh(C_5H_5)(CO) \qquad (2)$$

$$(\mathbf{6}\text{: } R = H;\ R' = C_6H_5;$$
$$\mathbf{7}\text{: } R = CH_3;\ R' = C_6H_5;$$
$$\mathbf{8}\text{: } R = R' = CH_3)$$

Table 1

^1H NMR data recorded at 25°C for the complexes **1** to **8**; multiplicities in parentheses

Compound	^1H NMR (δ/TMS)					
	R = H	R = Me	R′ = C_6H_5	R′ = Me	COT	Cp_{Rh}
1 [d]		1.94; 1.73		0.85; $^2J(PH) = 4$ Hz		
2 [a]		2.05; 1.80		1.07; $^2J(PH) = 4$ Hz		
–						
3 [a]	9.35 [f]		7.00 (*m*, *p*); 6.80 (*o*)		11.23	
3′ [b,e]	9.98; 9.26		7.30 (*m*, *p*); 6.70 (*o*)		11.52	
4 [b]		3.52; 0.30	7.20 (*m*, *p*); 6.05 (*o*)		10.28	
5 [b]		2.43; 0.76		−0.04	9.37	
6 [a]	9.81; 7.66		7.39 (*o*, *m*, *p*)		11.63	4.52
6 [b]	16.79; 4.01		6.70 (*o*, *m*, *p*)		11.85	6.70
7 [b]		4.84; −1.24	7.10 (*o*); 6.70 (*m*, *p*)		11.39	7.10
8 [b]		4.65; −1.07		0.03; $^2J(PH) = 12$ Hz	11.27	6.90

[a] TDF. [b] C_7D_8. [c] C_6D_6. [d] $C_6D_6 + D_2O$. [e] THF signals at 4.1 and 1.76 ppm (each of intensity corresponding to 8 H). [f] Cp is masked by phenyl protons. It appears at higher fields at higher temperatures. Half-width = *ca.* 6–10 Hz:(Sm)COT.

Table 2

^{31}P NMR data, recorded at 25°C

Compound	^{31}P NMR (δ/H_3PO_4)
$HC_5Me_4PMe_2$, **1** [c]	−36
$KC_5Me_4PMe_2$, **2** [a]	−72.9
$(COT)Sm(C_5H_4PPh_2)(THF)_2$, **3** [a]	−10.5
$(COT)Sm(C_5Me_4PPh_2)$, **4** [b]	−31.6
$(COT)Sm(C_5Me_4PMe_2)$, **5** [b]	−76.8
$(COT)Sm(C_5H_4PPh_2)Rh(C_5H_5)(CO)$, **6** [b]	37.2; $^1J(PRh) = 180$ Hz
$(COT)Sm(C_5Me_4PPh_2)Rh(C_5H_5)(CO)$, **7** [b]	47.3; $^1J(PRh) = 180$ Hz
$(COT)Sm(C_5Me_4PMe_2)Rh(C_5H_5)(CO)$, **8** [b]	44; $^1J(PRh) = 195$ Hz

[a] TDF. [b] C_7D_8. [c] $C_6D_6 + D_2O$.

The way the metallophosphine reacts depends on the ability of phosphorus atoms to coordinate to the rhodium. Indeed, by heating an equimolar mixture of **3** (which is very poorly soluble in aromatic solvents) and $(C_5H_5)Rh(CO)_2$ [10] in refluxing THF for 40 h, the heterobimetallic compound **6** was formed in almost quantitative yield, and easily isolated. Under similar conditions, **4** did not lead to the expected bimetallic complex, but a ligand redistribution was observed and both $(COT)Sm(C_5H_5)$ [11] and "$(C_5Me_4PMe_2)Rh$" moieties were characterized, among other products. In refluxing toluene (60 h) this redistribution did not occur and the bimetallic **7** was obtained. For the analogous reaction of the precursor **5**, which bears a more basic phosphido-group, only two hours reflux in toluene with an equimolar amount of $(C_5H_5)Rh(CO)_2$ were necessary for quantitative formation of **8**.

6, **7** and **8** were characterized by ^1H (Table 1) and ^{31}P NMR (Table 2) and IR spectroscopy. Satisfactory elemental analyses were obtained for **7**.

X-ray crystal structure of $(COT)Sm(C_5H_4PPh_2)(THF)_2$ *(3)*

The X-ray crystal structure determination of **3** (Fig. 1, Tables 3 and 4) revealed the formally ten-coordinate [12*] samarium compound with *octahapto*-C_8H_8, *pentahapto*-$C_5H_4PPh_2$, and two THF molecules bonded to the central samarium atom. The geometry of **3** is best described as a very distorted *pseudo*-tetrahedron. Both cyclooctatetraenyl and cyclopentadienyl rings are planar. The plane defined by the Sm atom and the centroids of the two rings roughly bisects the O1–Sm–O2 angle. The geometry of **3** is similar to those of Sm^{II} and Sm^{III} permethylated biscyclopentadienides containing two molecules of THF: $[(C_5Me_5)_2Sm(THF)_2]^{0 \text{ or } +}$ [13,14]. The Cp–Sm–COT angle of 137.1° in **3** is the same as in the neutral Sm^{II} complex (137°) but greater than in the cationic Sm^{III} (134.2°). Whereas the O1–Sm–O2 angle, 71.7(2)°, is much smaller than the values observed in neutral Sm^{II} (82.6(4)°) and cationic Sm^{III} (92.9(4)°) complexes, the average Sm–C (C1–C5) distance of 2.80(2) Å is intermediate between the corresponding distances in the neutral (2.86(3) Å) and cationic (2.69(2) Å) derivatives.

The geometry of **3** is more like that of the Sm^{II} complex than that of the Sm^{III}, and so the ionic radius of ten-coordinate Sm^{III} should be close to that of eight-coordinate Sm^{II} (the values of the ionic radii of Sm^{II} and Sm^{III} in halides and chalcogenides with different coordination numbers (CN) reported by Shannon

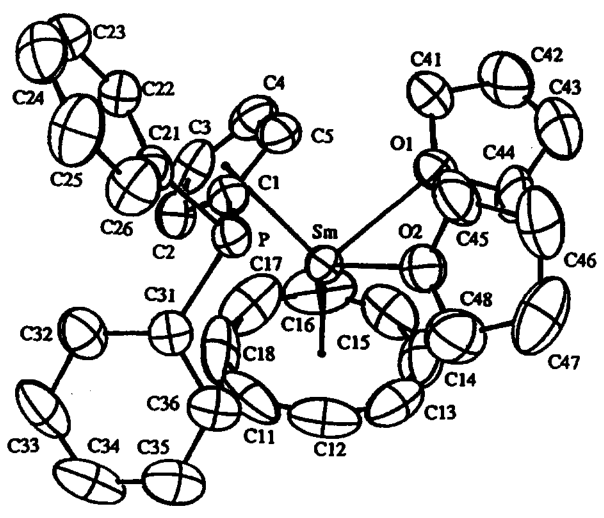


Fig. 1. ORTEP drawing of (COT)Sm($C_5H_4PPh_2$)(THF)$_2$, **3**. Thermal ellipsoids scaled at 50% probability.

are: Sm^{II} (CN 8) 1.41 Å, Sm^{III} (CN 8) 1.219 Å, Sm^{III} (CN 9) 1.272 Å, Sm^{III} (CN 12) 1.38 Å [15]). Bond lengths and radii may be considered as good indicators for the determination of the formal oxidation level: Recknagel *et al.* [16] reported recently the structure of an 1-4 diazadiene adduct of a Sm^{II} compound and, according to Evans [17], the complex should be described as a Sm^{III} derivative containing a diazadiene radical anion, in view of the spectroscopic and structural data.

The geometry of **3** is also reminiscent of that of the thorium complex [(COT)(C_5Me_5)Th(μ-Cl)$_2$Mg(CH_2CMe_3)(THF)] · $0.5C_6H_5CH_3$; in this compound the (C_5Me_5 centroid)Th (COT centroid) and the Cl–Th–Cl angles are 138.0 and 74.4° [18], respectively.

Discussion

Metalloligands 3, 4 and 5

3, **4**, and **5** are the first (phosphinocyclopentadienyl)samarium(III) complexes isolated. A series of mixed-sandwich lanthanide complexes (COT)Ln(C_5R_5)(THF)$_n$ has been already prepared [19,20] and two of them were characterized crystallographically: (COT)Lu(C_5R_5) (with R = Me [19] and R = CH_2Ph [20]). In these compounds, it is assumed that the bulky cyclopentadienyl ligands preclude the coordination of solvent molecules [2]. The behaviour of complexes **4** and **5** suggests that the coordination around the samarium atom is controlled by electronic rather than by steric factors. The sterically less hindered dimethylphosphino-complex **5** is isolated free of solvent, whereas the more hindered diphenylphosphino-complex **4** is able to coordinate reversibly one molecule of THF or one of phosphide oxide: evaporation of a toluene solution of the solvated purple form led to solvent-free red-brown crystals. Complex **3**, which contains a less electron-releasing diphenylphosphido-group, is soluble in a non-coordinating solvent only in the presence of at least four molecules of THF (**3'**).

Table 3

Summary of crystallographic data for $[Sm(C_5H_4PPh_2)(C_8H_8)] \cdot 2THF$

Molecular formula	$C_{33}H_{38}O_2PSm$
Formula weight, g	647.99
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
Cell dimensions:	
a, Å	8.606(2)
b, Å	11.458(3)
c, Å	14.632(2)
α, deg	87.09(2)
β, deg	86.93(2)
γ, deg	87.18(2)
V, Å^3	1437.3
Z	2
ρ_{calc}, g cm^{-3}	1.497
$F(000)$	658
Radiation, Å	λ (Mo-K_α) 0.71073
Scan type	$\omega - 2\theta$
Scan speed, deg min^{-1}	1.0–8.3
Scan width, deg	$\Delta\omega = 0.9 + 0.347 \tan\theta$
Reflections measured	h −10+10, k −13+13, l −2+16
θ range, deg	2–23
Linear absorption, μ, cm^{-1}	21.305
No. of reflections measured	5451
Decay, %	−12.5, corrected
Cut off for observed data	$I \geqslant 2.5\sigma(I)$
No. of unique observed data (NO)	2880
No. of variables (NV)	334
Absorption correction, DIFABS absmin-absmax	0.7337–1.2290
$R(F)$	0.036
$R_w(F)$	0.039
Weighting scheme	$w^{-1} = [\sigma^2(I) + (0.05I)^2]^{1/2}$
G.O.F.	1.365
ρ, residual, e Å^{-3}	1.05, two peaks close to Sm

Binuclear complexes

The binding of the phosphorus atom to the rhodium moiety is clearly established by the ^{31}P NMR coordination shift (*ca.* 70 ppm) and the $^1J(PRh)$ coupling constant [5] (*ca.* 180 Hz).

Table 4

Selected bond lengths (Å) and bond angles (deg) for $[Sm(C_5H_4PPh_2)(C_8H_8)] \cdot 2THF$

Sm–Cp [a]	2.527	Cp–Sm–COT	137.1
Sm–COT [a]	1.984	Cp–Sm–O1	98.2
Sm–O1	2.600(5)	Cp–Sm–O2	97.4
Sm–O2	2.652(5)	COT–Sm–O1	115.0
Sm–C(C1–C5)	2.797(20) [b]	COT–Sm–O2	117.8
Sm–C(C11–C18)	2.683(39) [b]	O1–Sm–O2	71.7(2)

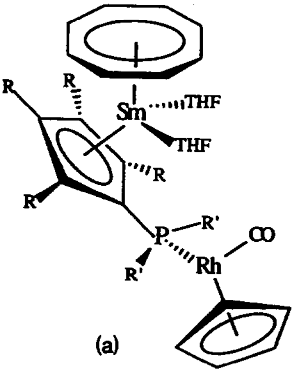
[a] Cp and COT are the gravity centres of the C_5(C1–C5) and C_8(C11–C18) rings, respectively. [b] Mean value.

In the IR spectrum, the single absorption near to 1945 cm^{-1} is characteristic of a CO ligand in a $(C_5H_5)Rh(CO)$ unit bonded to a phosphido-group [5] and indicates a lack of direct samarium–oxygen interaction.

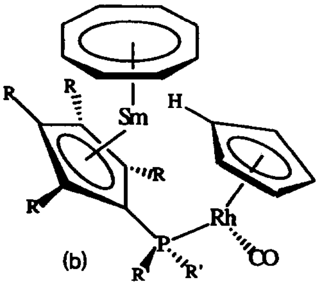
The ^1H shift difference between the (phosphinoCp)–H or –Me resonances increases upon the coordination of the rhodium moiety and is especially large in **6** (*ca.* 12 ppm). If it is assumed that isotropic ring proton shifts are dominated by dipolar interactions [21], these differences denote an enhanced polarization in the bimetallic species.

It is noteworthy that a strong deshielding (*ca.* 2 ppm) of the $(C_5H_5)Rh$ protons is observed in the toluene NMR spectra of **6**, **7** and **8**. This deshielding implies a short distance between the paramagnetic samarium atom and the cyclopentadienyl ring. Moreover, the complex **6**, synthesized in THF, was isolated free of solvent whereas 2 molecules of THF were strongly coordinated to the metal in the starting material **3**. In the same way, when the NMR spectrum of **6** was recorded in THF-d_8, some drastic changes occurred: the signal of the $(C_5H_5)Rh$ protons appeared near diamagnetic its diamagnetic position ($\delta = 4.52$); the signals of the phosphinocyclopentadienyl units were found at $\delta = 9.8$ and 7.6, respectively, instead of 16.8 and 6.7 in toluene-d_8. These values are very close to those found for **3** ($\delta = 9.35$ and 6.8).

These variations in the chemical paramagnetic shift should be related to a dramatic change in the geometry of the bimetallic complex, depending on the solvent. In THF solutions, molecules of solvent are coordinated to the samarium atom which adopts a pseudotetrahedral geometry with a large samarium–rhodium distance (Scheme 1(a)). In non-polar solvents (assuming that the dinuclear molecule is fluxional), there may be an important through-space or even localized pseudo-bonding interaction between the hydrogen atoms of the C_5H_5 ring bound to the rhodium and the electrophilic samarium atom. An extreme localized structure implying an interaction of Sm with Rh through the C_5H_5 sequence is depicted in Scheme 2(b). We checked the possibility of through-space Sm–Cp_{Rh} interaction by the calculations of hypothetical Sm $\cdots$ Rh, Sm $\cdots$ Cp_{Rh} and Sm $\cdots$ $H_{C_5H_5}$ distances taking as a basis the parameters in the structure of **3** (Sm–P, 3.985(2) Å; Sm–Cp_{Sm}, 2.527 Å; Cp_{Sm}–P, 3.02 Å; and Sm–P–Cp_{Sm}, 38.2°) and assuming that the atoms and the ring centroids of interest, *i.e.* Sm, CP_{Sm}, P, Rh, and Cp_{Rh} are



Scheme 1.



Scheme 2.

coplanar (Cp denotes the centroid of a cyclopentadienyl ring). The typical values of Cp–C (1.20 Å), C–H (1.08 Å), Rh–P (2.30 Å) [22], and Rh–Cp (1.90–1.94 Å) [22,23] distances were used. The C–P–Rh and P–Rh–Cp_{Rh} angles taken were 115–125° and 140–150°, respectively. These calculations show that the Sm ··· Rh distance may be 4.00–4.43 Å and that of Sm ··· Cp_{Rh} may fall in the range 3.80–4.71 Å. Notably, the Rh–Rh separation in $\{\mu\text{-}Ph_2PC_5H_4)Rh(CO)\}_2$ is 4.30 Å [23]. The Sm ··· Sm distance in the hydride-bridged dimer $\{(C_5Me_5)_2SmH\}_2$ is 3.90 Å [24].

Finally, by subtracting a Cp–H distance of 2.28 Å from that of Sm ··· Cp_{Rh}, we obtain a range of 1.52–2.43 Å for Sm ··· H contacts. This range indicates that even if an actual conformation in solution cannot be planar (a Sm ··· H contact of 1.52 Å would be too short), the possibility of Sm ··· Cp_{Rh} interaction remains strong. It is also worth noting that in $\{(C_5Me_4)_2Si\}NdC\mathit{H}(SiMe_3)_2$ [25], in which the hydrogen atom was found to be bent toward the neodymium ion, the resulting Nd ··· H distance is *ca.* 2.5 Å and the CH ··· Nd interaction has been described as agostic or semi-bridging. The Sm ··· Cp_{Rh} interaction suggested may reflect the high electrophilicity and electron deficiency at the Sm^{III} centre.

Conclusion

It is now established that $(COT)Sm(C_5R_4PR'_2)$ compounds are precursors of particular interest for building bimetallic complexes, in which the metal–metal distance is easy to control. Other similar complexes should be obtainable. The synthesis and properties of complexes $(COT)Nd(C_5R_4PR'_2)$ and the corresponding bimetallic species, obtained similarly, will be described in a forthcoming paper.

Experimental

General methods

All experiments were performed under argon in a drybox or using Schlenk techniques. Solvents were dried under argon and transferred directly into the reaction vessels by distillation under vacuum. $\{(COT)SmCl(THF)_2\}_2$ [26], $LiC_5H_4PPh_2$ [27], $KC_5Me_4PPh_2$ [6] and $(C_5H_5)Rh(CO)_2$ [10] were prepared according to the literature procedures. ^1H and ^{31}P NMR spectra were recorded on Bruker WP80 and AC200 spectrometers, respectively. Chemical shifts are reported in ppm, and referenced to external tetramethylsilane or H_3PO_4. IR spectra were recorded on a Perkin-Elmer 580B spectrophotometer. Mass spectra were recorded on a Kratos Concept 32S spectrometer.

Syntheses

$HC_5Me_4PMe_2$, 1; $KC_5Me_4PMe_2$, 2. PMe_2Cl (1.18 g, 10.35 mmol) in Et_2O (10 ml) was added dropwise at −78°C to a suspension of LiC_5Me_4H (1.66 g, 10.35 mmol) in Et_2O (20 ml). The mixture was allowed to warm to room temperature and was stirred for 4 h. The deep yellow solution of $HC_5Me_4PMe_2$ was filtered and slightly less than an equivalent amount of KH (0.33 g, 8.5 mmol) was added. After 48 h of stirring, the white precipitate was filtered off and dried to yield 1.8 g (79%) of **2**.

Thallium derivative. To a solution in Et_2O of $HC_5Me_4PMe_2$, freshly prepared as described above (based on 6.5 mmol, 0.84 g of LiC_5Me_4H), was added a near stoichiometric amount of TlOEt (1.6 g, 6.4 mmol). The mixture was stirred for 24 h. The solvent was evaporated off and the crude yellow product was washed with cold heptane (10 ml), dried, and sublimed (120°C, 5 torr) to yield 1.23 g (49% based on $TlC_5Me_4PMe_2$) of intense yellow needles. Mass spectrum (m/e with ^{205}Tl relative abundance): 591 ($Tl_2C_5Me_4PMe_2^+$, 4.5), 387 ($TlC_5Me_4PMe_2^+$, 66), 205 (Tl^+, 100), 181 ($C_5Me_4PMe_2^+$, 67).

$(COT)Sm(C_5H_4PPh_2)(THF)_2$, 3. $LiC_5H_4PPh_2$ (0.126 g, 0.49 mmol) was added at −78°C to $[\{(COT)SmCl(THF)_2\}_2]$ (0.197 g, 0.46 mmol) in THF (20 ml). The mixture was allowed to warm to room temperature and was stirred for 2 h. The deep blue solution was filtered and concentrated. Slow addition of pentane (5 ml) yielded, quantitatively, deep blue crystals of **3**. Storage of **3** in a THF atmosphere led to pink crystals of **3′** of general formula $(COT)Sm(C_5H_4PPh_2)(THF)_4$.

$(COT)Sm\{C_5(CH_3)_4PPh_2\}$, 4. $KC_5(CH_3)_4PPh_2$ (0.254 g, 0.738 mmol) was added at −78°C to $[\{(COT)SmCl(THF)_2\}_2]$ (0.306 g, 0.705 mmol) in 20 ml of THF. The mixture was allowed to warm to room temperature and was stirred for 2 h. After evaporation of the solvent, the brown red solid was extracted with toluene. The solution was filtered and concentrated. Slow addition of pentane (5 ml) yielded, quantitatively, a mixture of purple and red-brown crystals. The latter were identified as **4**, free of solvent. Anal. Found: C, 59.27; H, 5.20; P, 5.57. $C_{29}H_{30}PSm$ calcd.: C, 62.1; H, 5.40; P, 5.53%. The purple crystals were found to contain one molecule of THF: ^1H NMR (80 MHz, C_7D_8, 25°C) δ 10.37 (8 H, C_8H_8), 7.2 (6 H, m, p, C_6H_5), 6.09 (4 H, o, C_6H_5), 3.97 (4 H, THF), 3.33 (6 H, CH_3), 1.67 (4 H, THF), 0.53 (6 H, CH_3).

$(COT)Sm\{C_5(CH_3)_4PMe_2\}$, 5. $KC_5Me_4PPh_2$ (0.254 g, 0.738 mmol) was added at −78°C to $[\{(COT)SmCl(THF)_2\}_2]$ (0.306 g, 0.705 mmol) in 20 ml of THF. The mixture was allowed to warm to room temperature and was stirred for 2 h. After evaporation of the solvent, the deep red solid was extracted with toluene. This solution was filtered and concentrated. Slow addition of pentane (5 ml) yielded, quantitatively, deep red crystals of **5**.

$(COT)Sm(\mu\text{-}C_5H_4PPh_2)Rh(C_5H_5)(CO)$, 6. (0.150 g, 0.23 mmol) of **3** was heated under reflux with an excess of $Rh(C_5H_5)(CO)_2$ (0.070 g, 0.31 mmol) in THF for 40 h. The solvent was evaporated off and the crude product was washed with pentane. Recrystallization from THF/pentane gave 88% (0.142 g, 0.20 mmol) of pink-grey crystals of **6**. ν(CO)(Nujol): 1942 cm^{-1}.

$(COT)Sm[\mu\text{-}C_5Me_4PPh_2]Rh(C_5H_5)(CO)$, 7. (0.286 g, 0.51 mmol) of **4** was heated under reflux with an excess of $Rh(C_5H_5)(CO)_2$ (0.151 g, 0.67 mmol) in toluene for 60 h. After removal of the solvent, the crude product was washed with pentane. Recrystallization from toluene/pentane gave 90% (0.347 g, 0.46 mmol) of brown crystals of **7**. Anal. Found: C, 55.41; H, 4.60; P, 4.29. $C_{35}H_{35}OPRhSm$ calcd.: C, 55.59; H, 4.67; P, 4.10%. ν(CO)(toluene): 1949 cm^{-1}.

$(COT)Sm[\mu\text{-}C_5Me_4PMe_2]Rh(C_5H_5)(CO)$, 8. (0.355 g, 0.82 mmol) of **5** was heated under reflux with an equimolar amount of $Rh(C_5H_5)(CO)_2$ (0.182 g, 0.82 mmol) in toluene for 3 h. The solvent was removed and the crude product was washed with pentane. Recrystallization from toluene gave 45% (0.160 g, 0.37 mmol) of red crystals of **8**.

X-ray structure analysis of 3

A selected crystal (0.35 × 0.20 × 0.20 mm) was sealed in a thin-walled glass capillary under an inert atmosphere and mounted on an Enraf-Nonius CAD4 diffractometer. The unit cell was determined and refined from 25 randomly selected reflections (CAD4 routines). Intensities of 5451 reflections were measured with filtered Mo radiation, $\omega-2\theta$ scan, $2° < \theta < 23°$. A total of 2880 unique

Table 5

Atom position parameters with equivalent isotropic temperature factors for $[Sm(C_5H_4PPh_2)(C_8H_8)] \cdot 2THF$

Atom	x	y	z	B (Å^2)
Sm	0.47564(5)	0.27247(4)	0.18086(3)	3.366(7)
P	0.3602(2)	0.2166(2)	0.4463(1)	3.37(4)
O1	0.2374(6)	0.2574(5)	0.0809(4)	5.0(1)
O2	0.3276(6)	0.0825(5)	0.2379(4)	4.7(1)
C1	0.3596(8)	0.3301(6)	0.3558(5)	3.3(2)
C2	0.4718(9)	0.4144(6)	0.3326(5)	4.0(2)
C3	0.416(1)	0.4893(7)	0.2618(6)	5.2(2)
C4	0.271(1)	0.4532(7)	0.2400(6)	5.0(2)
C5	0.2345(9)	0.3542(7)	0.2963(5)	4.3(2)
C11	0.7700(9)	0.239(1)	0.2246(7)	7.0(3)
C12	0.729(1)	0.1316(9)	0.1975(7)	6.7(2)
C13	0.670(1)	0.0951(8)	0.1212(7)	6.5(2)
C14	0.614(1)	0.1465(9)	0.0416(7)	6.8(2)
C15	0.594(1)	0.261(1)	0.0044(6)	6.8(3)
C16	0.627(1)	0.369(1)	0.0341(7)	7.8(3)
C17	0.694(1)	0.4090(9)	0.1092(7)	8.1(3)
C18	0.757(1)	0.3537(9)	0.1879(7)	7.9(2)
C21	0.2734(7)	0.2918(6)	0.5455(5)	3.4(2)
C22	0.1997(8)	0.4030(6)	0.5395(6)	4.0(2)
C23	0.1228(9)	0.4477(8)	0.6165(6)	5.1(2)
C24	0.117(1)	0.3854(8)	0.6995(6)	5.4(2)
C25	0.190(1)	0.2759(8)	0.7055(6)	6.0(2)
C26	0.265(1)	0.2298(7)	0.6300(6)	5.1(2)
C31	0.5649(8)	0.2060(6)	0.4756(5)	3.5(2)
C32	0.6348(9)	0.2921(7)	0.5221(6)	4.8(2)
C33	0.793(1)	0.2788(8)	0.5371(7)	6.3(2)
C34	0.878(1)	0.1813(8)	0.5070(7)	6.3(2)
C35	0.810(1)	0.0951(8)	0.4654(7)	5.8(2)
C36	0.6535(9)	0.1083(7)	0.4491(6)	4.2(2)
C41	0.1254(9)	0.3486(8)	0.0550(6)	5.0(2)
C42	0.048(1)	0.304(1)	−0.0243(7)	7.4(3)
C43	0.071(1)	0.175(1)	−0.0139(8)	8.2(3)
C44	0.216(1)	0.1577(8)	0.0284(7)	8.7(3)
C45	0.1626(9)	0.0763(8)	0.2594(7)	6.2(2)
C46	0.120(1)	−0.0460(9)	0.2444(8)	7.9(3)
C47	0.272(1)	−0.1141(8)	0.2372(8)	8.4(3)
C48	0.387(1)	−0.0325(8)	0.2627(8)	7.2(3)
Cp	0.3506	0.4082	0.2973	
COT	0.6817	0.2505	0.1150	

Cp and COT are the centroids of the C_5 and C_8 rings, respectively. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

reflections with $I > 2.5\sigma(I)$ were used in structure determination and refinement. Crystal data and refinement residuals are given in Table 3. All calculations were carried out by using the Enraf–Nonius SDP library with neutral-atom scattering factors. The structure was solved and refined by conventional Patterson, Fourier and full-matrix least-squares methods. An empirical absorption correction (DIFABS) was applied after isotropic refinement of all atoms. All non-hydrogen atoms were finally refined with anisotropic thermal parameters. H atoms were placed in calculated positions (HYDRO program of SDP riding on the corresponding carbon atoms with weighting scheme $w^{-1} = [\sigma^2(F_o)^2 + (0.05\ I_o)^2]^{1/2}$. The final atomic coordinates of non-hydrogen atoms are given in Table 5. Tables of general displacement parameters, full bond distances and angles, least-squares planes, hydrogen atom positions and a listing of F_o/F_c may be obtained from the authors.

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