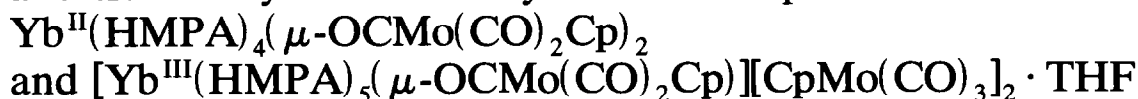


Synthesis and X-ray structure of the divalent and trivalent ytterbium-molybdenum complexes



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Abstract

Reaction of the ytterbium-benzophenone dianion complex $[\text{Yb}^{\text{II}}(\mu\text{-OCPh}_2)(\text{HMPA})_2]_2$ with two molar equivalents of $\text{CpMo}(\text{CO})_3\text{H}$ in THF/HMPA (THF = tetrahydrofuran, HMPA = hexamethylphosphoramide) gave a divalent ytterbium-molybdenum complex $\text{Yb}^{\text{II}}(\text{HMPA})_4(\mu\text{-OCMo}(\text{CO})_2\text{Cp})_2$ (1) in which the two molybdenumcarbonylate units are coordinated to Yb^{II} in *cisoid* orientation. When four equivalents of $\text{CpMo}(\text{CO})_3\text{H}$ were used, the trivalent ytterbium-molybdenum complex $[\text{Yb}^{\text{III}}(\text{HMPA})_5(\mu\text{-OCMo}(\text{CO})_2\text{Cp})][\text{CpMo}(\text{CO})_3]_2 \cdot \text{THF}$ (2) was formed. Both 1 and 2 were structurally characterized by X-ray crystallography.

Key words: Ytterbium; Molybdenum; Carbonyl; Ketone dianion; X-ray diffraction; Crystal structure

Stimulated by the potential use of d-f block mixed metal complexes as new catalysts or precursors for new materials, a variety of lanthanide/d-block transition metal carbonyl complexes has recently been synthesized and structurally characterized [1,2]. In most of these complexes the lanthanides and d-block transition metals have been crystallographically confirmed to be linked by isocarbonyl bridges (Ln-O-C-M ; Ln = lanthanide metal, M = d-block transition metal) due to the highly oxophilic nature of lanthanide ions [1a-g]. This shows that d-block transition metal carbonyl anions might function as new ligands in lanthanide coordination chemistry. Considering the novel reactivities of divalent lanthanide compounds [3], the mixed metal complexes that contain divalent lanthanide species are of particular interest. Although a few divalent lanthanide d-transition metalcarbonylate complexes have been reported [4], only one such complex has been structurally characterized [1f].

We have previously reported that the ytterbium-benzophenone dianion complex $[\text{Yb}^{\text{II}}(\mu\text{-OCPh}_2)(\text{HMPA})_2]_2$ reacted with four equivalents of an aryl alcohol (ArOH) to give a divalent ytterbium aryloxide $\text{Yb}(\text{OAr})_2(\text{HMPA})_2$ [5]. This reaction shows that this ytterbium-benzophenone complex may easily be transferred to other divalent ytterbium compounds if appropriate proton donors are given. If acidic d-block transition metal hydrides are chosen as the proton donors, the formation of mixed metal complexes that include divalent ytterbium may be possible. In this paper, we report on the reactions of $[\text{Yb}^{\text{II}}(\mu\text{-OCPh}_2)(\text{HMPA})_2]_2$ with $\text{CpMo}(\text{CO})_3\text{H}$, from which a novel divalent ytterbium-molybdenum complex $\text{Yb}^{\text{II}}(\text{HMPA})_4(\mu\text{-OCMo}(\text{CO})_2\text{Cp})_2$ (1) and a new trivalent ytterbium-molybdenum complex $[\text{Yb}^{\text{III}}(\text{HMPA})_5(\mu\text{-OCMo}(\text{CO})_2\text{Cp})][\text{CpMo}(\text{CO})_3]_2 \cdot \text{THF}$ (2) were selectively obtained simply by changing the reactant molar ratios.

Slow addition of two molar equivalents of $\text{CpMo}(\text{CO})_3\text{H}$ [6] to the *in situ* synthesized purple $[\text{Yb}^{\text{II}}(\mu\text{-OCPh}_2)(\text{HMPA})_2]_2$ in THF/HMPA gave a yellow solution in a few minutes. This mixture was stirred at room

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temperature for 2 h and was then put under vacuum. Removal of HMPA by washing the residue with diethyl ether gave a yellow solid which was then recrystallized from THF/ether to give orange blocky crystals of $\text{Yb}^{\text{II}}(\text{HMPA})_4(\mu\text{-OCMo}(\text{CO})_2\text{Cp})_2$ (**1**) in about 50% yield (based on Mo). Its IR spectrum in THF showed absorptions at both terminal and bridging carbonyl regions (ν_{CO} : 1922, 1895, 1831, 1776, 1674, 1625 cm^{-1}), indicating that isocarbonyl bridges might exist [1]. X-ray analysis [7*] revealed that the divalent Yb^{II} ion was six coordinated by four HMPA ligands and two $\text{CpMo}(\text{CO})_3^-$ anions in distorted octahedral form (Fig. 1 and Table 1). Interestingly the two molybdenum carbonylate anions are oriented in unusual *cis* positions, which might be due to the larger cone angle of the HMPA ligand as compared to that of the isocarbonyl bridged molybdenum moiety. *Transoid* orientation of the two molybdenum units would put four bulkier HMPA ligands in one square plane. Actually in complex **1** the bond angle between two isocarbonyls ($\angle\text{O}(5)\text{YbO}(6) = 81.7(6)^\circ$) is significantly smaller than that between two adjacent HMPA ligands (av. $90.6(5)^\circ$), indicating that even in the present state the two molybdenum units are pushed to some extent towards each other by the HMPA ligands. The average bond distance of $\text{Yb}-\text{O}(\text{HMPA})$ (2.33(1) Å) is comparable with that found in $[\text{Yb}^{\text{II}}(\mu\text{-OCPh}_2\text{X}(\text{HMPA})_2)_2]$ (2.28(3) Å) [5]. However, the average bond distance of $\text{Yb}-\text{O}(\text{bridging CO})$ (2.47(2) Å) in **1** is much longer than that in $\{[(\text{CH}_3\text{CN})_3\text{Yb}^{\text{II}}\text{Fe}(\text{CO})_4]_2 \cdot \text{CH}_3\text{CN}\}_n$ (2.374(7) Å) [1f], showing that the interaction between the Yb^{II} cation and the $\text{CpMo}(\text{CO})_3^-$ anions in complex **1** is very weak. This could be due to the steric effect and the decrease of Lewis acidity of the Yb^{II} cation, which are caused by strong coordination of four polar and bulky HMPA ligands to the central Yb^{II} atom [8]. Unlike what happened in other lanthanide metacarbonylate complexes [1a–e], lengthening of C–O(bridge) bond and shortening of Mo–C(bridging CO) bond are not observed in complex **1** although these distances could not be determined with high accuracy in the present case. The average bond distances of C–O(bridge) (1.17(4) Å) and C–O(terminal) (1.20(3) Å) are almost same within the standard deviations, and so are those of Mo–C(bridging CO) (1.93(3) Å) and Mo–C(terminal CO) (1.89(3) Å). The average bond distance of Mo–C(Cp) is 2.40(3) Å. All these data for $\text{CpMo}(\text{CO})_3^-$ moieties in **1** are comparable to those reported for $[\text{Bu}_4\text{N}][\text{CpMo}(\text{CO})_3]$ (Mo–C(Cp): 2.371(8), Mo–C(CO): 1.909(9), C–O: 1.176(8) Å) [9].

When four molar equiv of $\text{CpMo}(\text{CO})_3\text{H}$ were used

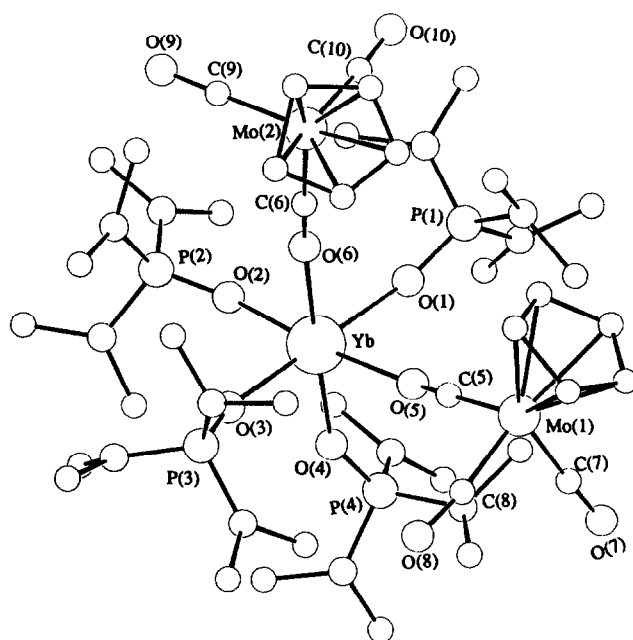


Fig. 1. ORTEP drawing of complex **1**.

in the reaction with $[\text{Yb}^{\text{II}}(\mu\text{-OCPh}_2\text{X}(\text{HMPA})_2)_2]$, yellow crystalline product **2** insoluble in THF was obtained. Although its IR spectrum in CH_2Cl_2 (ν_{CO} : 1922, 1896, 1826, 1776, 1672, 1622 cm^{-1}) was very similar to that of **1**, X-ray crystallographic study revealed that **2** was a trivalent ytterbium complex in which the central Yb^{III} was directly bonded by one molybdenumcarbonylate anion and five HMPA ligands, while the other two molybdenumcarbonylate anions were located in the outer sphere (Fig. 2 and Table 2). This complex represents the first example of a lanthanide/d-block transition metal complex with metacarbonylate moieties in both inner and outer spheres. The four HMPA ligands in the square plane in complex **2** are actually not cofacial due to their steric hindrance. Two of them are pushed towards the molybdenum unit, forming angle $\angle\text{O}(1)\text{YbO}(11)$ of $83.8(6)^\circ$ and angle $\angle\text{O}(3)\text{YbO}(11)$ of $82.8(6)^\circ$, which are significantly smaller than a right angle. The average bond distance of $\text{Yb}-\text{O}(\text{HMPA})$ (2.18(2) Å) is 0.15 Å shorter than that in **1** but comparable with that in $[\text{Yb}^{\text{III}}(\text{HMPA})_2(\text{H}_2\text{O})_5]\text{Cl}_3 \cdot \text{HMPA} \cdot \text{H}_2\text{O}$ (2.178(7) Å) [8]. The $\text{Yb}-\text{O}(11)$ (bridging CO) (2.29(1) Å) bond in complex **2** is 0.18 Å shorter than that in complex **1**. Such a difference between $\text{Yb}^{\text{II}}-\text{O}$ and $\text{Yb}^{\text{III}}-\text{O}$ is not unexpected, since Yb^{III} is *ca.* 0.16 Å smaller than Yb^{II} in radius when both have the same coordination number [10]. Due to the steric and electronic effects of the HMPA ligands as observed in complex **1**, the interaction between the Yb^{III} ion and the isocarbonyl of the inner sphere $\text{CpMo}(\text{CO})_3^-$ in **2** appears to be weaker

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

TABLE 1. Bond lengths (Å) and angles (°) for $\text{Yb}^{\text{II}}(\text{HMPA})_4(\mu\text{-OCMo}(\text{CO})_2\text{Cp})_2$ (1)

Yb–O(1)	2.33(1)	Mo(2)–C(6)	1.89(3)
Yb–O(2)	2.34(2)	Mo(2)–C(9)	1.84(3)
Yb–O(3)	2.33(1)	Mo(2)–C(10)	1.91(2)
Yb–O(4)	2.33(2)	Mo(2)–C(Cp)	av. 2.39(3)
Yb–O(5)	2.47(2)	C(5)–O(5)	1.14(4)
Yb–O(6)	2.47(2)	C(6)–O(6)	1.20(3)
Mo(1)–C(5)	1.97(4)	C(7)–O(7)	1.18(4)
Mo(1)–C(7)	1.92(3)	C(8)–O(8)	1.22(4)
Mo(1)–C(8)	1.84(3)	C(9)–O(9)	1.23(3)
Mo(1)–C(Cp)	av. 2.40(3)	C(10)–O(10)	1.19(3)
O(1)–Yb–O(2)	90.7(5)	O(5)–Yb–O(6)	81.7(6)
O(1)–Yb–O(3)	176.3(5)	C(5)–O(5)–Yb	166(2)
O(1)–Yb–O(4)	92.3(5)	C(6)–O(6)–Yb	172(2)
O(1)–Yb–O(5)	85.8(7)	O(5)–C(5)–Mo(1)	174(3)
O(1)–Yb–O(6)	90.2(6)	O(6)–C(6)–Mo(2)	174(2)

TABLE 2. Bond lengths (Å) and angles (°) for $[\text{Yb}^{\text{III}}(\text{HMPA})_5(\mu\text{-OCMo}(\text{CO})_2\text{Cp})[\text{CpMo}(\text{CO})_3]_2$ (2)

Yb–O(1)	2.18(2)	Mo(1)–C(Cp)	av. 2.39(3)
Yb–O(2)	2.18(1)	Mo(2)–C(O21)	1.75(3)
Yb–O(3)	2.16(2)	Mo(2)–C(O22)	1.93(3)
Yb–O(4)	2.16(2)	Mo(2)–C(O23)	1.90(3)
Yb–O(5)	2.21(1)	Mo(2)–C(Cp)	av. 2.38(4)
Yb–O(11)	2.29(1)	Mo(3)–C(O31)	1.80(3)
Mo(1)–C(O11)	1.92(2)	Mo(3)–C(O32)	1.87(3)
Mo(1)–C(O12)	1.91(4)	Mo(3)–C(O33)	1.86(3)
Mo(1)–C(O13)	1.87(4)	Mo(3)–C(Cp)	av. 2.37(4)
O(1)–Yb–O(2)	86.9(5)	O(2)–Yb–O(8)	90.4(5)
O(1)–Yb–O(3)	166.6(5)	O(2)–Yb–O(11)	89.5(5)
O(1)–Yb–O(4)	88.9(6)	O(3)–Yb–O(4)	90.7(6)
O(1)–Yb–O(5)	99.5(5)	O(3)–Yb–O(5)	94.0(5)
O(1)–Yb–O(11)	83.8(5)	O(3)–Yb–O(11)	82.8(6)
O(2)–Yb–O(3)	93.3(6)	O(4)–Yb–O(5)	90.6(5)
O(2)–Yb–O(4)	175.8(5)	O(4)–Yb–O(11)	89.8(5)

than that in other trivalent ytterbium metalcarbonylate complexes such as $[\text{Cp}_2^*\text{Yb}^{\text{III}}]_2[\text{Fe}(\text{CO})_{11}]$ (Yb–O(bridging CO): 2.243(3) Å) [1b] and $[\text{Cp}_2^*\text{Yb}^{\text{III}}]_2(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Co}_3(\mu_3\text{-CO})_4$ (Yb–O(bridging CO): 2.230(4) Å) [1d]. Reflecting this, the bond distances for $\text{CpMo}(\text{CO})_3^-$ moieties in both inner and outer spheres do not differ significantly. The average bond distance of Mo(1)–C(Cp) (2.39(3) Å) is almost the same as that found in outer sphere $\text{CpMo}(\text{CO})_3^-$ moieties (av. Mo–C(Cp): 2.38(4) Å). The average bond distances of Mo(1)–C(terminal CO) (1.89(4) Å) and C–O(terminal) (1.19(4) Å) in inner sphere $\text{CpMo}(\text{CO})_3^-$ are comparable to those in outer sphere $\text{CpMo}(\text{CO})_3^-$ moieties (Mo–C(CO): 1.85(3), C–O: 1.20(4) Å). These data are also comparable to those of $[\text{Bu}_4\text{N}][\text{CpMo}(\text{CO})_3]$ [9]. The bond distances of Mo–C(bridging CO)

(1.92(3) Å) and C–O(bridge) (1.15(3) Å) in complex 2 are similar to those found in complex 1 and are not significantly different from those for terminal carbonyls.

The easy formation of complexes 1 and 2 in the present reactions shows that reactions of acidic d-block transition metal hydrides with lanthanide compounds which have lanthanide–carbon or heteroatom σ -bonds could be a convenient method for the synthesis of the corresponding mixed metal complexes. Studies in this direction are under progress.

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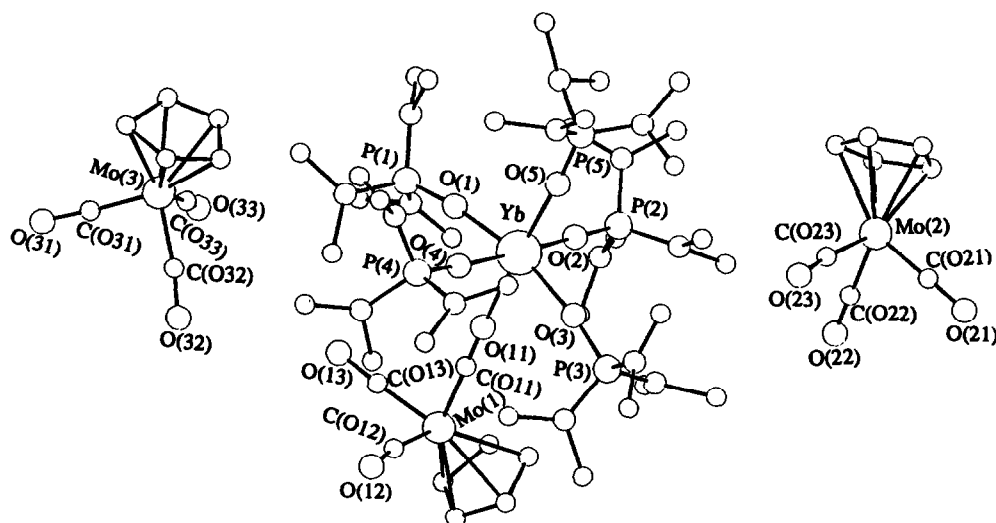


Fig. 2. ORTEP drawing of complex 2. Lattice solvent THF is omitted.

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