Journal of Organometallic Chemistry, 277 (1984) C21—C24
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESES OF ORGANOYTTERBIUM(III) COMPOUNDS BY OXIDATION OF DICYCLOPENTADIENYLYTTERBIUM(II). CRYSTAL STRUCTURE OF $[(\eta\text{-}C_5H_5)_2Yb(O_2CC_6F_5)]_2$

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(Received September 12th, 1984)

Summary

Organoytterbium(III) complexes $[(\eta\text{-}C_5H_5)_2YbX]$ (X = O_2CMe, $O_2CC_6F_5$, $O_2CC_5H_4N$, Cl, Br, I, C≡CPh, C_6F_5, $(MeCO)_2CH$, $(PhCO)_2CH$) have been synthesized in high yield from $[(\eta\text{-}C_5H_5)_2Yb(MeOCH_2)_2]$ and the corresponding HgX_2, TlX, AgX_2 or CuX species. An X-ray diffraction study of the pentafluorobenzoate has shown it to be dimeric, with a somewhat unsymmetrical bridging carboxylate.

The reaction between lanthanoid elements and thallous cyclopentadienide is a simple route to cyclopentadienyllanthanoids and provides dicyclopentadienyl(1,2-dimethoxyethane)ytterbium(II) in good yield [1,2]. Thus, this compound is now a potential convenient source of $(\eta\text{-}C_5H_5)_2YbX$ (X = anionic ligand) by oxidation reactions, and we have shown it reacts with thallous cyclopentadienide to yield tricyclopentadienylytterbium(III) as a step in the transmetallation synthesis of this compound [2]. We now report preparations of a number of $(\eta\text{-}C_5H_5)_2YbX$ compounds by oxidation of $(\eta\text{-}C_5H_5)_2Yb$ with thallous, mercuric, argentic and cuprous salts, including the first synthesis of an isolable lanthanoid(III)fluorocarbon derivative.

The preparations (reactions 1 and 2) were carried out in tetrahydrofuran or 1,2-dimethoxyethane under an atmosphere of purified nitrogen.

$$(C_5H_5)_2Yb + MX \rightarrow (C_5H_5)_2YbX + M\downarrow \quad (M = Tl, Cu) \qquad (1)$$

$$2(C_5H_5)_2Yb + MX_2 \rightarrow 2(C_5H_5)_2YbX + M\downarrow \quad (M = Hg, Ag) \qquad (2)$$

(X = O_2CMe, $O_2CC_6F_5$, $O_2CC_5H_4N$, Cl, Br, I, C_6F_5, CCPh, $(MeCO)_2CH$ or $(PhCO)_2CH$)

0022-328X/84/$03.00

Deposited metal was removed by filtration through a celite pad, and the resulting $(\eta\text{-}C_5H_5)_2YbX$ complexes were obtained in 80—100% yield by evaporation of the filtrate to dryness or crystallization. The acetate [3], chloride [3,4], phenylacetylide [5] and acetylacetonate [6] are known compounds, but the other derivatives are new and were obtained as yellow to orange-red air-sensitive solids. All were characterized spectroscopically (generally MS, IR and UV/vis/near IR), and most by analysis. The mass spectrum of the dibenzoylmethanate shows a parent ion (monomer) and loss of one and two cyclopentadienyl groups, whereas the acetate, pentafluorobenzoate, halide, and acetylacetonate (acac) complexes show, in addition, ions which can be assigned to diytterbium species. For example, $(\eta\text{-}C_5H_5)_2Yb(acac)$ shows peaks attributable to $(C_5H_5)_3Yb_2(acac)_2{}^+$ and $(C_5H_5)_2Yb_2(acac)_2{}^+$. This evidence for dimeric structures is consistent with earlier observations that $(\eta\text{-}C_5R_5)_2YbX$ (R = H or Me) complexes are often dimeric in the solid state and in non-coordinating solvents [3,7,8]. The dimeric nature of the pentafluorobenzoate has been confirmed by a single-crystal X-ray study*.

Crystal data: $C_{34}H_{20}O_4F_{10}Yb_2$, M = 1028.6, triclinic, space group $P\bar{1}$ (No. 2) a 23.506(23), b 8.417(8), c 8.805(9) Å, α 91.01(18), β 109.71(22), γ 99.79(20)°, U 1610.8 Å^3, Z = 2 (dimers), D_c 2.12 g cm^{-3}, $F(000)$ = 971.8, $\mu(\text{Cu-}K_{\bar{\alpha}})$ 106.0 cm^{-1}, R = 0.0481 for 4048 absorption corrected reflections (283 K, $0 \leqslant \sin\theta/\lambda \leqslant 0.561$, $F \geqslant 6\sigma(F)$, Phillips PW1100 diffractometer, Cu-K_α X-radiation, $\bar{\lambda}$ 1.5418 Å).

The unit cell contains two similar dimer molecules A and B. Each dimer is centred about the inversion centres. Molecule A is represented in Fig. 1. Interestingly, the bonding of the bridging carboxylate groups is not symmetric. This is most easily seen by comparing the C—O—Yb angles, since there is not a significant variation in Yb—O bond lengths. This distortion is most pronounced in molecule A. The cyclopentadienyl ligands of both molecules are staggered. The *ortho*-fluorine atoms of the carboxylate groups are close to the oxygen atoms (2.74 Å, average) compared with the sum (2.75 Å) of the Van der Waals' radii of fluorine and oxygen. In addition, one *ortho*-fluorine of each carboxylate group shows close non-bonding contacts with two ring carbons of one cyclopentadienyl group (e.g. C(15)—F(1) 3.11, C(16)—F(1) 3.14 Å). It is surprising that these contacts are not minimized by an increased dihedral angle between the planes of the pentafluorophenyl groups and the plane formed by the ytterbium and oxygen atoms. Limited data has been reported for the structure of $[Yb(\eta\text{-}C_5H_5)_2O_2CC_6H_5]$ which crystallizes in space group $P2_1/c$ (Z = 8) [8]. The structure is dimeric but only the ytterbium atoms and the O_2C groups of the benzoate ligands could be satisfactorily located. Within these constraints, there are similarities with the structure of $[(\eta\text{-}C_5H_5)_2\text{-}YbO_2CC_6F_5]_2$. Thus, the dimer halves are related by the symmetry centres and the Yb. . . .Yb contacts 4.95 and 5.02 Å are similar to 5.01 and 5.06 Å respectively for the present structure.

Isolation of $(\eta\text{-}C_5H_5)_2YbO_2CC_6F_5$ from reaction 1 (X = $O_2CC_6F_5$) is of particular interest since both bis(pentafluorophenyl)- [9] and dicyclopenta-

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

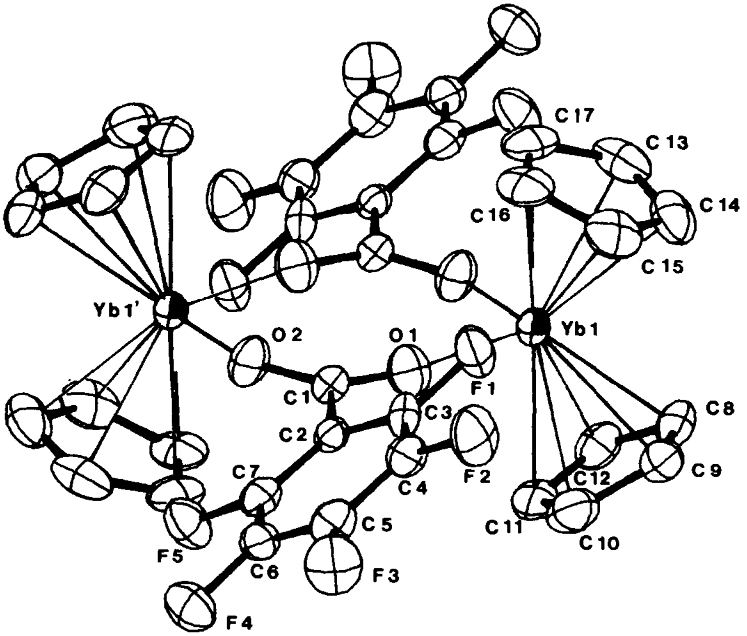

Fig. 1. Molecular structure of $[(\eta\text{-}C_5H_5)_2YbO_2CC_6F_5]_2$, Molecule A. Important parameters (values for molecule B in parentheses) include: internuclear separation Yb—cyclopentadienyl carbon (av.) 2.595(11) (2.590), Yb—ring centroid (av.) 2.298 (2.300), Yb(1)—O(1) 2.178(7), Yb(1)′—O(2) 2.201(8), [Yb(2)—O(3) 2.201(7), Yb(2)—O(4)′ 2.182(8)], O(1)—C(1) 1.246(11), O(2)—C(1) 1.258(11) [O(3)—C(18) 1.228(13), O(4)—C(18) 1.239(14)], benzenoid C—C (av.) 1.376(20) [1.380(14)], cyclopentadienyl C—C (av.), 1.398(15) [1.390(33)], Yb(1)- - -Yb(1)′ 5.06 [Yb(2)- - -Yb(2)′ 5.01], O(1)- - - -O(2)′ 3.29 [O(3)- - - -O(4)′ 3.31] Å; angles centroid—Yb(1)—centroid 131.9 (132.1), O(1)—Yb—O(2)′ 97.4(3) [O(3)—Yb(2)—O(4)′ 98.2(3)], C(1)—O(1)—Yb(1) 171(1) C(1)—O(2)—Yb(1)′ 145(1) [C(18)—O(4)—Yb(2)′ 164(1), C(18)—O(3)—Yb(2) 150(1)]°.

dienyl-ytterbium(II) [10] readily reduce pentafluorobenzoic acid at −78°C to give 2,3,4,5-tetrafluorobenzoic acid after hydrolytic work up. Evidently reduction of thallium(I) is even more facile than fluorine abstraction. Reaction with a similar substrate containing iodine substituents would be of interest, since aryl—iodine bonds are more readily reduced than aryl—fluorine bonds by organoytterbium(II) species [11]. The complex $(\eta\text{-}C_5H_5)_2YbC_6F_5(THF)$ is the first lanthanoid(III) fluorocarbon derivative to be isolated. Hitherto such species, e.g. $C_6F_5SmF_2$ have only been characterized in solution as part of complex reaction mixtures [12], though isolable ytterbium(II) fluorocarbons, e.g. $(C_6F_5)_2Yb(THF)_4$ are known [13].

This study suggests that the oxidation reactions 1 and 2 provide a simple general route to $(\eta\text{-}C_5H_5)_2YbX$ complexes and preliminary results using $(\eta\text{-}C_5H_5)_2Sm(THF)$ indicate the method can be extended to other lanthanoid elements with an accessible divalent oxidation state.

Acknowledgements. We are grateful for support from the Australian Research Grants Committee, and for an Australian Institute of Nuclear Science Engineering Scholarship (PIMcK), a Commonwealth Postgraduate Research Award (DLW) and a Monash Postdoctoral Fellowship (GNP).

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