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Organolanthanoids.
XII*. Reactions of Bis(cyclopentadienyl)ytterbium(II) with some Diorganomercurials

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Abstract

Reactions of $(C_5H_5)_2Yb(MeOCH_2)_2$ with R_2Hg ($R = C_6F_5$, C_6Cl_5, or $PhC{\equiv}C$) yield mercury metal and $(C_5H_5)_2YbR$, but diphenylmercury fails to react significantly. Bis(*trans*-2-chlorovinyl)mercury reacts with $(C_5H_5)_2Yb(MeOCH_2)_2$ to give $(C_5H_5)_2YbCl$. Ligand exchange occurs between $(C_5H_5)_2YbC_6F_5$ and phenylacetylene and with succinimide to give $(C_5H_5)_2YbCCPh$ and $(C_5H_5)_2Yb\overline{NC(O)CH_2CH_2C(O)}$, respectively.

Introduction

Bis(cyclopentadienyl)ytterbium(II) can be prepared easily in good yield by the redox transmetallation between ytterbium metal and thallium(I) cyclopentadienide in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) [1, 2], and hence is a convenient reagent for the synthesis of bis(cyclopentadienyl)ytterbium(III) compounds by redox reactions. We have recently given a preliminary account of the oxidation of $(C_5H_5)_2Yb(DME)$ by a variety of metal salts, particularly those of mercury(II) and thallium(I), to give $(C_5H_5)_2YbX$ (e.g. X = Cl, I, O_2CMe, $O_2CC_6F_5$) complexes [3]. An exploratory investigation of oxidation by mercurials, R_2Hg ($R = C_6F_5$ or PhCC), to give $(C_5H_5)_2YbR$ was briefly mentioned [3]. We now provide a detailed account of the reactions of bis(cyclopentadienyl)ytterbium(II) with these and other diorganomercurials, and two ligand exchange reactions of $(C_5H_5)_2YbC_6F_5$.

Results and Discussion

Preparations

Treatment of bis(cyclopentadienyl)(1,2-dimethoxyethane)ytterbium(II) with the organomercurials R_2Hg ($R = C_6F_5$, C_6Cl_5 or PhCC) in tetrahydrofuran results in precipitation of mercury and formation of corresponding bis(cyclopentadienyl)organoytterbium(III) complex (reaction (1)).

$$2(C_5H_5)_2Yb(DME) + R_2Hg \longrightarrow 2(C_5H_5)_2YbR + 2DME + Hg\downarrow \qquad (1)$$

Details of the reactions are in Table I. For both $R = C_6F_5$ or PhCC, oxidation occurs at room temperature, but in the latter case heating is needed to dissolve $(C_5H_5)_2Yb(CCPh)$ which is coprecipitated with mercury at room temperature. Heating is needed for $R = C_6Cl_5$ because of the low solubility of the mercurial [4]. Extended reaction times were used to ensure completion of reaction but may be unnecessary, since onset of precipitation of mercury is rapid in most cases. There was little reaction between $(C_5H_5)_2Yb(DME)$ and diphenylmercury even with prolonged heating (Table I), hence electron with-

TABLE I. Reactions of Bis(cyclopentadienyl)ytterbium(II) with some Diorganomercurials

$(C_5H_5)_2Yb(DME)$ (mmol)	R_2Hg (R)	(mmol)	THF (ml)	Temperature (°C)	Time (h)	Product	Yield (%)
1.51	C_6F_5	0.71	30	25	48	$(C_5H_5)_2YbC_6F_5$ (THF)	93
1.96	C_6Cl_5	0.98	30	65	168	$(C_5H_5)_2YbC_6Cl_5$	60
1.89	Ph	0.91	10	65	720	[a]	
1.75	PhCC	0.85	60.	25–65	9	$(C_5H_5)_2YbC{\equiv}CPh$	65
1.92	ClCH=CH[b]	0.97	30	25	16	$(C_5H_5)_2YbCl(THF)_{0.5}$	83

[a] Little reaction observed. [b] *Trans* isomer.

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*Part XI: G. B. Deacon, B. M. Gatehouse, S. N. Platts and D. L. Wilkinson, *Aust. J. Chem., 40,* 907 (1987).

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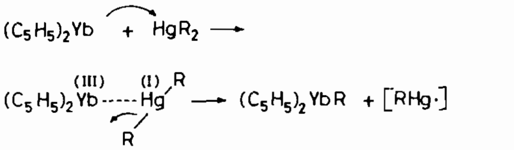
drawing groups on the mercurial clearly favour reaction (1). This may be correlated with $E_{1/2}$ values for the mercurials determined by polarography [5, 6], which show diphenylmercury is reduced considerably less readily than R_2Hg ($R = C_6F_5$, C_6Cl_5, or PhCC). Reaction (1) can be envisaged as involving one electron transfer from ytterbium to mercury and carbanion transfer between the resulting organomercury(I) and organoytterbium(III) species.



(2)

The organomercury radical would rapidly disproportionate into the diorganomercurial and mercury metal [reaction (3)], as observed for electrochemically generated [RHg$^\bullet$] species [7]. Moreover,

$$2[RHg^\bullet] \longrightarrow R_2Hg + Hg\downarrow \qquad (3)^*$$

treatment of mercurous chloride with pentafluorophenyllithium at −80 to −100 °C yields bis(pentafluorophenyl)mercury and mercury [8].

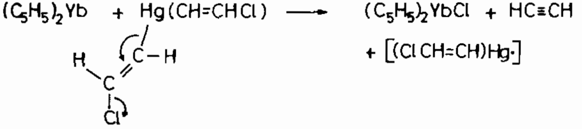
No polychloroaryllanthanoid nor any fluorocarbon organolanthanoid(III) complex has been isolated prior to this study [9–14]. The species $C_6F_5SmF_2$ has been detected in solution [15], whilst divalent ytterbium complexes $R_2Yb(THF)_4$ ($R = C_6F_5$ or p-HC_6F_4) have been prepared [16]. Bis(cyclopentadienyl)phenylethynylytterbium(III) has previously been prepared from $(C_5H_5)_2YbCl$ and lithium phenylacetylide [17, 18] and by ligand exchange between $(C_5H_5)_3Yb$ and phenylacetylene [19]. The present method (reaction (1)) is probably more convenient than either.

By contrast with reaction (1), bis(cyclopentadienyl)ytterbium(II) reacts with bis(*trans*-2-chlorovinyl)mercury to give chlorobis(cyclopentadienyl)ytterbium(III) (reaction (4)).

$$2(C_5H_5)_2Yb(DME) + trans\text{-}(ClCH{=}CH)_2Hg \longrightarrow$$

$$2(C_5H_5)_2YbCl + Hg\downarrow + 2HC{\equiv}CH + 2DME \qquad (4)$$

In this case the carbanion released on electron transfer to mercury undergoes acetylene elimination.



Facile acetylene release from *trans*-2-chlorovinylmercuric chloride is known when this compound is treated with sodium iodide or phenylmagnesium chloride [20].

Bis(cyclopentadienyl)pentafluorophenylytterbium(III) undergoes ligand exchange with phenylacetylene and with succinimide (reactions (5) and (6); suc = $\overline{NC(O)CH_2CH_2C(O)}$).

$$(C_5H_5)_2YbC_6F_5 + PhCCH \longrightarrow$$

$$(C_5H_5)_2YbCCPh + C_6F_5H \qquad (5)$$

$$(C_5H_5)_2YbC_6F_5 + H(suc) \longrightarrow$$

$$(C_5H_5)_2Yb(suc) + C_6F_5H \qquad (6)$$

Reactions (5) and (6) are favoured by the relative acidities of the C-acids (pK 23.2 [21] and 25.8 [22] for PhCCH and C_6F_5H respectively in cyclohexylamine) and succinimide (pK 10.5 in water [23] and the gas phase [24]). Group exchange analogous to (5) is observed between bis(pentafluorophenyl)ytterbium(II) and phenylacetylene [25]. Alkynyl for methyl [26], and t-butyl [26] exchange reactions are also known for organolanthanoids, and are favoured by very marked *C*-acidity differences. However, the synthesis of $(C_5H_5)_2YbCCPh$ from $(C_5H_5)_3Yb$ and phenylacetylene occurs even though the acidity of cyclopentadiene is greater than that of phenylacetylene [19].

Characterization and Structures

The organoytterbium compounds formed in reactions (1) and (4) showed near infrared absorption near 1000 nm (Experimental section) typical [27, 28] of f ← f transitions of cyclopentadienylytterbium(III) species. Infrared absorptions of $(C_5H_5)_2YbC_6F_5(THF)$ at 1048 and 865 cm^{-1} are attributable [29] to ring stretching modes of coordinated tetrahydrofuran. Bands at 1065 and 960 cm^{-1}, which can be assigned to modes involving carbon–fluorine stretching [30], are in the normal position for heavy metal pentafluorophenyl derivatives [31] by contrast with the corresponding absorptions (1036 and 920 cm^{-1}) of $(C_6F_5)_2Yb(THF)_4$ [16]. No distinct band could be clearly assigned to the 'X-sensitive' mode involving some X–C_6F_5 stretching (ν_6, a_1, [30]), normally observed at 900–750 cm^{-1} [32] and tentatively assigned to 837 cm^{-1} for $(C_6F_5)_2Yb(THF)_4$ [16]. This mode may be obscured by intense cyclopentadienyl absorption [33] at 775 cm^{-1}, may be coincident with THF absorption at

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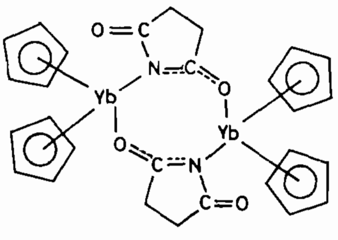
*It is conceivable but less likely that the radical reacts by electron transfer, $(C_5H_5)_2Yb + [RHg^\bullet] \rightarrow (C_5H_5)_2YbR + Hg$.

865 cm^{-1}, or possibly give rise to the weak band at 892 cm^{-1}. The complex is likely to have pseudotetrahedral stereochemistry with eight coordination for ytterbium, analogous to structures established by X-ray crystallography for $(C_5Me_5)_2SmPh(THF)$ [34] and $(C_5H_5)_2Lu(p\text{-}MeC_6H_4)(THF)$ [35]. Ions containing two ytterbium atoms, e.g. $(C_5H_5)_2Yb_2(C_6F_5)^+$ are observed in the mass spectrum (see Experimental), suggesting loss of THF and dimerization (reaction (7)) on being heated to induce volatization.

$$2(C_5H_5)_2YbC_6F_5(THF) \longrightarrow [(C_5H_5)_2YbC_6F_5]_2 + 2THF \qquad (7)$$

For $(C_5H_5)_2YbC_6Cl_5$, features characteristic of the C_6Cl_5 group [36, 37] were observed at 1328, 1300, and 685 cm^{-1}. It has been suggested that the strong band of $(C_6Cl_5)_2Hg$ at 854 cm^{-1} may be due to an 'X-sensitive' mode involving C_6Cl_5–Hg stretching [36] (*cf.* C_6F_5–X modes above), and $(C_5H_5)_2YbC_6Cl_5$ has a corresponding band at 850 cm^{-1}. However, the absence of intense absorption for either C_6Cl_5Br [38] or C_6Cl_5I [39] at 1000–750 cm^{-1} makes it unlikely that a vibration involving significant C_6Cl_5–X stretching is in this region. No ytterbium-containing ions were observed in the mass spectrum of $(C_5H_5)_2YbC_6Cl_5$, but features characteristic of the ligands were present. The compound is probably dimeric with bridging C_6Cl_5 groups and eight coordinate ytterbium. Analogous structures with bridging alkyl or alkynyl groups are well-established [9–13], and $(C_5H_5)_2YbC_6F_5(THF)$ gives a dimeric species in the gas phase (reaction (7)).

An associated structure with bridging phenylethynyl groups has been suggested for $(C_5H_5)_2YbCCPh$ [19], and a dimer is likely on the basis of crystal structures of $[(C_5H_5)_2ErCCBu^t]_2$ [40] and $[(MeC_5H_4)_2SmCCBu^t]_2$ [41]. The mass spectrum of $(C_5H_5)_2YbCCPh$ (Experimental section) reveals ions containing two ytterbium atoms, consistent with a dimeric structure. An ion with two ytterbium atoms is also observed in the mass spectrum of $(C_5H_5)_2Yb(suc)$. The infrared spectrum shows a free $\nu(C{=}O)$ band at 1700 cm^{-1} and an intense band at 1600 cm^{-1}, which can be assigned to a $\nu(N\text{⋯}C\text{⋯}O)$ absorption of the dimeric structure **I**. Succinimide has free $\nu(C{=}O)$ bands at 1776 and 1695 cm^{-1} [42], and $Hg[\overline{NC(O)CH_2CH_2C}(O)]_2$, which has digonal characteristic N–Hg–N coordination [43] and presumably additional weak O---Hg bonds has $\nu(C{=}O)$ at 1645 cm^{-1}. Analysis indicates the composition $[(C_5H_5)_2Yb(suc)]_2(THF)$, and the presence of THF is confirmed by mass spectrometry. However, the stoichiometry and the absence of significant infrared absorption due [29] to coordinated THF suggest it may be solvent of crystallization.



I

This study illustrates the value of oxidation reactions of bis(cyclopentadienyl)ytterbium(II) as a source of bis(cyclopentadienyl)ytterbium(III) compounds, which can themselves be useful synthetic reagents. However, oxidation at a useful rate by organomercurials appears to require electron-withdrawing organic groups.

Experimental

Methods, Instrumentation and Reagents

Details of analytical and spectroscopic methods, solvent purification, and handlng of air-sensitive compounds have been given [1, 15, 16, 44, 45]. Infrared spectra (4000–650 cm^{-1}) are of mulls in dried Nujol and Fluorolube. Each listed *m/z* value for an ytterbium-containing ion is the most intense peak [^{174}Yb; ^{346}(Yb$_2$)] of a cluster with the expected isotope pattern. A similar situation applies for chlorine-containing ions. All compounds showed *m/z* 66 [100%, $C_5H_6^+$] and 65[60–80, $C_5H_5^+$] in addition to listed features. Near IR λ_{max} values are for THF solutions in the range 800–1200 nm.

Phenylacetylene (BDH) was distilled and stored under nitrogen. Succinimide was from Tokyo Kasei, Ph_2Hg from Aldrich, and $Hg[\overline{NC(O)CH_2CH_2C}(O)]_2$ from BDH. $(C_6F_5)_2Hg$ [46], $(PhCC)_2Hg$ [47], *trans*-$(ClCH{=}CH)_2Hg$ [48], and $(C_5H_5)_2Yb(DME)$ [1] were prepared by the indicated reported methods. The preparation of $(C_6Cl_5)_2Hg$ has been given [39].

All organolanthanoids were extremely oxygen- and water-sensitive, and solid compounds were handled in nitrogen-filled recirculating dry boxes [1, 45]. All reactions, additions of solvent, and manipulations of solutions or reaction mixtures were carried out under purified (BASF R3/11 oxygen removal catalyst and molecular sieves) nitrogen.

Reaction of Bis(cyclopentadienyl)(1,2-dimethoxyethane)ytterbium(II) with Organomercury(II) Compounds

Amounts of reagents, conditions, and yields of products are given in Table I. The solvent was added by syringe to a mixture of the solid reagents in a greaseless Schlenk assembly. After reaction, precipitated mercury was filtered off, giving a solution of the organolanthanoid product, which was isolated as described below.

Bis(cyclopentadienyl)pentafluorophenyl(tetrahydrofuran)ytterbium(III)

Evaporation under vacuum, initially at room temperature, and then with gentle warming gave the yellow-orange compound. *Anal.* Found: C, 44.5; H, 3.1. Calc. for $C_{20}H_{18}F_5OYb$: C, 44.3; H, 3.3%. IR absorption (Nujol only): 3080w, 2720w, 1632sh, 1590m, 1530w, 1508sh, 1300w, 1250w, 1180w, 1110w, 1065m, 1048sh, 1010s, 960m, 892w, 865w, 775s, 728sh, 665w cm^{-1}. $\lambda_{max}(\epsilon)$: 920sh(5), 945(6), 984(21) nm. Mass spectrum: *m/z* 643[0.4%, $(C_5H_5)_2Yb_2C_6F_5^+$]; 578[2, $C_5H_5Yb_2C_6F_5^+$]; 513[0.4, $C_6F_5Yb_2^+$; 449[0,4 $(C_5H_5)Yb_2F_2^+$; 323[0.4; $(C_5H_5)_2YbF^+$]; 304[4, $(C_5H_5)_2Yb^+$]; 239[7, $(C_5H_5)Yb^+$]; 213 [30]; 187 [10]; 168 [3, $C_6HF_5^+$]; 167[3, $C_6F_5^+$]; 72[14, THF^+]; 71[14, $C_4H_7O^+$].

Bis(cyclopentadienyl)pentachlorophenylytterbium(III)

The unfiltered reaction mixture was evaporated to dryness under vacuum, and benzene (30 ml) was added. The resulting solution was stirred and heated (80 °C) for 24 h, filtered twice, and evaporated to dryness under vacuum with gentle warming giving an orange solid. *Anal.* Found: C, 33.7; 33.5; H, 2.7, 2.2; Yb, 31.4. Calc. for $C_{16}H_{10}Cl_5Yb$: C, 34.8; H, 1.8; Yb, 31.3%. IR absorption: 3080w, 2920w, 2840w, 1460w, 1370w, 1328m, 1300w, 1170w, 1120w, 1062w, 1015s, 850w, 785s, 725w, 685w cm^{-1}. $\lambda_{max}(\epsilon)$: 930(3), 946(8), 983sh(8); 989(20) nm. Mass spectrum: *m/z* 249[20%, $C_6Cl_5^+$]; 215[24, $C_6HCl_4^+$]; 178[7, $C_6HCl_3^+$]; 143[5, $C_6HCl_2^+$]; 108[9, C_6HCl^+].

Bis(cyclopentadienyl)phenylethynylytterbium(III)

The reaction mixture was filtered hot and the Schlenk filter was washed with THF. Evaporation of the filtrate and washings under vacuum gave the yellow compound. *Anal.* Found; Yb, 42.7. Calc. for $C_{18}H_{15}Yb$: Yb, 42.8%. IR absorption: 3080w, 3000w, 2040s[ν(CC)], 1650w, 1482m, 1440s, 1335w, 1310w, 1200w, 1162w, 1070w, 1015s, 925w, 780s, 760sh, 700 m cm^{-1}. (A similar spectrum has been reported for $(C_5H_5)_2GdCCPh$ [18]). $\lambda_{max}(\epsilon)$: 914(6), 924(7), 941(13), 984(50) nm. Mass spectrum: *m/z* 743[2, $(C_5H_5)_3Yb_2(CCPh)_2^+$]; 675[0.9, $C_{26}H_{15}Yb_2^+$]; 642[0.2, $(C_5H_5)_3Yb_2CCPh^+$]; 606[0.5, $(C_5H_5)_4Yb_2^+$]; 577[0.5, $(C_5H_5)_2Yb_2CCPh^+$]; 512[0.2, $(C_5H_5)Yb_2CCPh^+$]; 369[0.5, $(C_5H_5)_3Yb^+$]; 339 (1, $(C_5H_5)YbCCC_6H_4^+$]; 304[2, $(C_5H_5)_2Yb^+$]; 275[0.5, $YbCCPh^+$]; 239[3, $(C_5H_5)Yb^+$]; 202[7, $C_{16}H_{10}^+$]; 174[2, Yb^+]; 102[100, $PhCCH^+$]; 76[28, $C_6H_4^+$].

The Reaction of $(C_5H_5)_2Yb(DME)$ with Diphenylmercury

Only a small amount of mercury was deposited during prolonged heating. The mass spectrum of the solid obtained by evaporation of the filtered solution showed diphenylmercury to be present. Addition of DME to the solid gave the characteristic emerald–green colour [1] of $(C_5H_5)_2Yb(DME)$.

The Reaction of $(C_5H_5)_2Yb(DME)$ with trans-$(ClCH{=}CH)_2Hg$

Evaporation of the filtered solution under vacuum gave $[(C_5H_5)_2YbCl]_2(THF)$. *Anal.* Found: C, 38.8; H, 4.6; Yb, 47.5. Calc. for $C_{24}H_{28}Cl_2OYb_2$: C, 38.5; H, 3.8; Yb, 46.2%. The IR, near IR, and mass spectra were identical with those of an authentic analytically pure sample prepared by oxidation of $(C_5H_5)_2Yb(DME)$ with $HgCl_2$ [3]. The solution from hydrolysis of the product with dilute nitric acid gave a positive chloride test with Ag^+.

Ligand Exchange Reactions of Bis(cyclopentadienyl)pentafluorophenylytterbium(III)

Reaction with phenylacetylene

Phenylacetylene (1.0 ml, 9.1 mmol) was added under nitrogen to $(C_5H_5)_2YbC_6F_5(THF)$ (1.84 g, 3.39 mmol) dissolved in THF (20 ml), and the reaction mixture was stirred. After 15 min, precipitation of a yellow solid commenced. Stirring was continued for 5 d at room temperature, and then the precipitated $(C_5H_5)_2YbCCPh$ was filtered off and washed with THF (yield, 0.45 g, 33%). (IR, near IR, and mass spectral identification). The filtrate was evaporated to dryness, the residue redissolved in THF, and hexane was added precipitating further $(C_5H_5)_2YbCCPh$, which was similarly collected and identified (0.61 g, 44%).

Reaction with succinimide

A THF solution (20 ml) of $(C_5H_5)_2YbC_6F_5$, prepared *in situ* from $(C_5H_5)_2Yb(DME)$ (0.79 g, 2.02 mmol) and $(C_6F_5)_2Hg$ (0.54 g, 1.00 mmol) by the conditions of Table I, was filtered onto succinimide (0.21 g, 2.09 mmol) and the filter was washed with THF (20 ml). Rapid precipitation of a yellow solid occurred and the reaction mixture was stirred for 16 h at room temperature, when $[(C_5H_5)_2Yb(suc)]_2(THF)$ was filtered off (0.69 g, 79%). *Anal.* Found: Yb, 39.9. Calc. for $C_{32}H_{36}N_2O_5Yb_2$; Yb, 39.6%. IR absorption: 3080w, 2910w, 2840w, 1730sh, 1700s, 1600s(br), 1430m, 1405w, 1375s, 1318s, 1264m, 1238m, 1122w, 1064w, 1018s, 920w, 830sh, 810m, 785s, 710m, 680w cm^{-1} Mass spectrum: *m/e* 737 [0.3%, $(C_5H_5)_3Yb_2(suc)_2^+$] 402[4, $(C_5H_5)_2Yb(suc)^+$]; 385[1, $C_{14}H_{13}NOYb^+$]; 337[7, $(C_5H_5)Yb(suc)^+$] 320[1, $C_9H_8NOYb^+$]; 304[3, $(C_5H_5)_2Yb^+$]; 272[11, $Yb(suc)^+$]; 239[3, $(C_5H_5)Yb^+$]; 216[3, Yb-

$(CNO)^+$]; 174[1, Yb^+]; 99[54, $H(suc)^+$] 72[10, THF^+]; 71[10, $C_4H_7O^+$]. The complex was not sufficiently soluble for observation of the near infrared spectrum.

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