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Synthesis and characterization of novel covalent biphenyldiyl Sm^{II} and Yb^{II} complexes

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Abstract

Biphenylene reacts with activated Sm and Yb powders in ethers giving 2,2′-biphenyldiyl-Sm^{II} and -Yb^{II} complexes by opening of the C_4 ring. They have been characterized by reactions with electrophiles such as the proton and dimethyldichlorosilane, and by ^1H, ^{13}C and ^{171}Yb NMR measurements. The Yb complex can be obtained by reaction of 2,2′-dilithiobiphenyl with YbI_2. Octamethylbiphenylene, the reduction potential of which is much more negative than that of biphenylene, does not react with Yb powder. In contrast, tricarbonyloctamethylbiphenylenechromium reacts with metal powder due to the presence of the electron-withdrawing $Cr(CO)_3$ group. This suggests that an electron transfer from the metal precedes the opening of the cyclobutane ring.

1. Introduction

Interest in the synthesis of organometallic compounds of the rare-earth metals is due in part to their activity in various catalytic reactions [1]. This chemistry has been dominated by bis(pentamethylcyclopentadienyl) derivatives owing to their high catalytic activity for olefin hydrogenation and ethylene polymerization [2]. Organolanthanides are generally prepared by reaction of an organoalkalimetal compound with an anhydrous halide, LnX_n, [3] and sometimes by redox transmetallation between mercury(II) or thallium(I) organometallics and lanthanide metals [4].

Certain rare-earth metallic powders (Yb, Sm, Ce, and Nd) have been reported recently to react in ether media with unsaturated hydrocarbons possessing high electronic affinities, such as anthracene, 1,4-diphenylbutadiene, and bifluorenylidene, to form a new class of organolanthanides [5]. These hydrocarbon-insoluble compounds, probably charge-transfer complexes, exhibit a low catalytic activity for ethylene polymerization and olefin hydrogenation.

To obtain more soluble organometallic compounds with covalent metal carbon σ-bonds, we exposed biphenylene directly to ytterbium and samarium powders. It is well known that biphenylene reacts with lithium to give biphenylenedilithium which is then converted at room temperature to 2,2′-dilithiobiphenyl by the opening of the four-membered ring [6]. Thus formation of 2,2′-biphenyldiyl-ytterbium or -samarium might be expected for these very electropositive metals.

2. Results and discussion

Reaction at room temperature of biphenylene with 4 equiv. of a suspension of activated samarium or ytterbium powder in dimethoxyethane (DME) with overnight stirring results in the formation of intense brown (Yb) or brown red (Sm) solutions.

These solutions are stable at room temperature but are very air-sensitive, and attempts to isolate the product by crystallization failed. However, analysis of the solutions shows that they contain 1 equiv. of metal per mole of hydrocarbon. Quenching these solutions with dry dioxygen does not regenerate biphenylene, but leads to oxygenated products derived from biphenyl, mainly 1,1′-biphenyl-2,2′-diol. This reactivity with dioxygen differs from that of ytterbium or samarium anthracene charge-transfer complexes which regenerate anthracene [5a].

Deuterolysis of these filtered solutions with MeOD leads to quantitative conversion to a mixture of biphenyl (45%) and dideuterobiphenyl (55%) (GC-MS analysis).

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TABLE 1. Reactions with dichlorodimethylsilane [a]

Addition of Me_2SiCl_2	Metal	Products (mol%)		
		Dimethyl-dibenzo silole	Biphenyl	Biphen-ylene
At the end of the reaction	Sm	68	31	
	Yb	54	42	
At the beginning of the reaction	Sm	98	1	
	Yb	83		12

[a] Standard conditions: metal (2 mmol); 1,2-diodoethane (0.1 mmol); biphenylene (0.5 mmol); DME (5 ml); 20°C, 24 h. Yields were determined by GC analysis using dodecane as internal standard.

This suggests the formation of 2-2′-biphenyldiylsamarium and -ytterbium. Clearly, the presence of undeuterated biphenyl results from the reaction of the organometallic compound, or of an intermediate species, with the solvent.

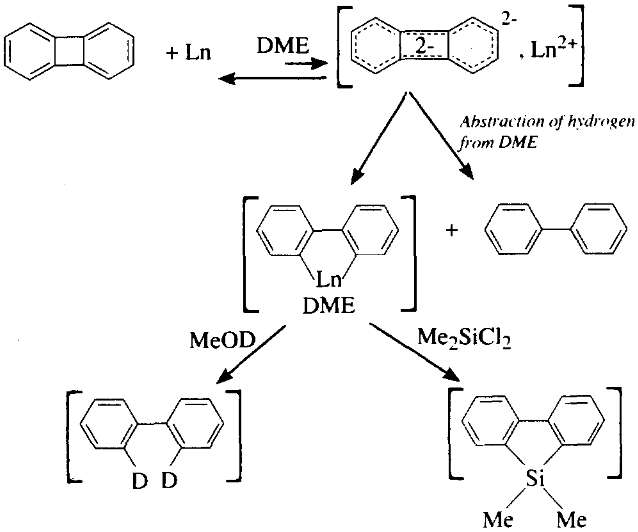
This solvolytic side-reaction is confirmed by the reaction with other electrophiles. Thus, addition of an excess of dichlorodimethylsilane at the end of the reaction gives a mixture of dimethyldibenzosilole and biphenyl (Table 1). These results confirm the structure of these cyclic lanthanoid compounds.

Chlorosilanes are commonly used to trap organometallic species formed by reaction of alkali metals with unsaturated hydrocarbons in ether solvents. In a similar way, the addition of dichlorodimethylsilane at the beginning of the reaction of biphenylene with the metal powder, leads to high yields of dimethyldibenzosilole (Table 1). Thus, dichlorodimethylsilane does not inhibit the reaction of Sm^0 or Yb^0 with biphenylene and no solvolysis product (*i.e.* biphenyl) is formed, which suggests that the intermediate species react with this electrophile rather than with the solvent.

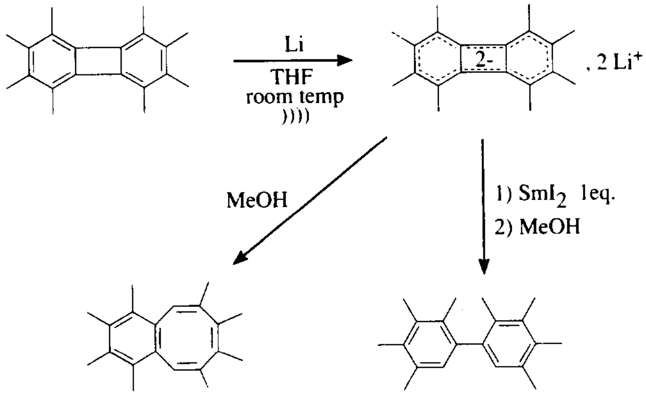
The NMR spectra of a THF-d_8 solution of the ytterbium-biphenylene complex obtained after removal of free hydrocarbons prove that the solution does not contain any paramagnetic species. They show that 1 mole of DME is coordinated to the metal of the biphenyldiyl dianion complex. ^{171}Yb NMR spectroscopy has been used recently to characterize Yb^{II} organometallic species [7]. When recording the ^{171}Yb NMR spectrum in THF-d_8, a single resonance at −300 ppm was observed, referenced to $[(C_5Me_5)Yb(THF)_2]$ at 0 ppm. The ^{13}C NMR spectrum displays four resonances at 127.6, 127.9, 129.4 and 142.0 ppm. The same NMR spectra (^1H, ^{171}Yb, ^{13}C) are observed after reaction of a solution of 2-2′-dilithiobiphenyl (which was prepared by reaction of lithium with biphenylene at room temperature) with YbI_2, thus confirming the cyclic lanthanoid structure.

All these results are summarized in Scheme 1. The first step could be an electronic transfer from Ln^0 to biphenylene. We have previously shown that Yb^0 or Sm^0 react readily only with hydrocarbons, the reduction potential of which is less negative than −2 V *vs.* SCE [5b]. Thus, the conversion of biphenylene (−2.36 V *vs.* SCE) should be limited, as observed for 1,1-diphenylethylene (−2.30 V *vs.* SCE) [5b]. The observed quantitative transformation of biphenylene can be ascribed to the fact that, as for lithium, the opening of the four-membered ring is a non-equilibrated reaction and shifts the electron-transfer equilibrium to the right (Scheme 1).

To confirm the suggested reaction scheme (first, electron-transfer, then opening of the four-membered ring), we turned to octamethylbiphenylene whose reduction potential is obviously more negative than that of biphenylene. Octamethylbiphenylene does not react at all with activated Yb or Sm powders in DME, even after several days of stirring (no coloration, no conversion). To overcome this lack of reactivity, we synthesized the tricarbonyl(octamethylbiphenylene)chromium by a classical method [8]. The tricarbonylchromium moiety is a strong electron-withdrawing group and the reduction potentials of (η^6-arene)tricarbonylchromium complexes are generally considerably less negative than those of the corresponding arenes [9]. Tricarbonyl(octamethylbiphenylene)chromium, which is expected to be more easily reduced, reacts with Yb^0 yielding an olive-coloured precipitate. Protolysis by methanol and removal of chromium with iodine results in octamethylbiphenyl (15%) and recovery of octamethylbiphenylene



Scheme 1.



Scheme 2.

(85%). These results confirm electron-transfer as the first step in the formation of the lanthanoid derivatives.

The opening of the four-membered ring by lanthanoids as a reaction subsequent to the electron transfer was demonstrated as follows. We prepared a THF solution of octamethylbiphenylenedilithium as previously described [10]; it is known that this compound is stable at room temperature for several days (no opening of the four-membered ring). This solution was then allowed to react with SmI_2. Protolysis of the reaction mixture gave only octamethylbiphenyl. The protolysis of octamethylbiphenylenedilithium under the same conditions leads to 1,2,3,4,6,7,8,9-octamethylbenzocyclooctene, which is formed by rearrangement of the dihydrobiphenylene moiety [11]. Only trace amounts of octamethylbiphenyl are formed (Scheme 2).

Catalytic activity toward polymerization of ethylene has been observed in toluene at room temperature only for the 2,2′-biphenyldiyl samarium compound [12 *]. This reactivity is almost 10 times higher than that observed with the anthracene samarium adduct under the same conditions [5a].

3. Conclusion

In a similar way to lithium, ytterbium and samarium powders react with biphenylene in ether with opening of the four-membered ring. However, due to their lower reduction potentials, electron-transfer from lanthanoids (the first step) is considerably reduced, to such an extent that the octamethylbiphenylene derivatives do not react at all, in the absence of a strong electron-withdrawing group. The second step (opening of the-four membered ring) is a very easy reaction with lanthanoids. This can be ascribed to the unusual stability of the lanthalol ring. The samarium complex exhibits some catalytic activity toward ethylene polymerization.

4. Experimental details

All the reactions were performed under argon in dry, dioxygen-free solvents. The products obtained after protolysis or reaction with electrophiles were analysed by GC: capillary column CP SIL5 (poly-dimethylsiloxane) $L = 25$ m, int. diam. = 0.22 mm, film thickness = 0.12 mm; 120–300°C at 3° per min, and by GC-MS using a Kratos MS 80. IR spectra were recorded on a Perkin–Elmer model 1430 spectrometer. NMR spectra were obtained using a Bruker AC 200 F or a Bruker MSL 400 spectrometer. Biphenylene [13] and octamethylbiphenylene [14] were prepared as described.

4.1. Reaction of Ln^0 with biphenylene

Metal powder (Aldrich, 40 mesh) (2 mmol), 1,2-diiodoethane 28 mg (0.1 mmol) and biphenylene 76 mg (0.5 mmol) were transferred in a glove box into a Schlenk flask containing a magnetic stirring bar. Dodecane (30–40 mg) was used as an internal standard. The flask was then filled with 5 ml of DME and stirred for 24 h after which the brown solution was filtered.

4.2. Deuterolysis

MeOD (0.2 mL) was added at room temperature to the filtered solutions of the Yb or Sm species. After addition of 0.2 N H_2SO_4 (5 ml) the mixture was extracted with ether (10 ml). The ether solution was washed with water, then dried with Na_2SO_4. After evaporation of the solvent, the white solid, 72 mg (Yb), m.p. = 70–71°C, was analysed by GC-MS: m/e 156 (M^+ dideuterated biphenyl) and 154 (M^+ biphenyl); no peak at 155 (monodeuterated biphenyl).

4.3. Reaction with dimethyldichlorosilane

The dibenzolanthalol solutions (Yb or Sm) were allowed to react at 20°C for 1 h with 194 mg (1.5 mmol) of Me_2SiCl_2. Degassed 0.2 N H_2SO_4 (10 mL) was added, and after extraction with ether (10 ml) the aqueous phase was separated and the amount of Sm or Yb was determined by titration with disodium ethylenediaminetetracetate using xylenol orange as indicator. 5,5-Dimethyldibenzosilol was isolated by thin-layer chromatography (silica, hexane/dichloromethane) 71 mg, 68% yield (Sm), m.p. = 56–57°C. Mass spectrum: m/e 210 (M^+), 195 ($M^+ - CH_3$; 100%). ^1H NMR (CD_2Cl_2, 200 MHz): δ 0.4 (s, 6H, $SiMe_2$); 7.3 (t, broad, $J = 7.3$ Hz, 2H); 7.4 (ddd, $J = 7.3$ Hz, $J = 1.2$ Hz, 2H);

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

7.7 (d, broad, $J = 7.3$ Hz, 2H); 7.8 (d, $J = 7.3$ Hz, 2H) ppm.

4.4. Reaction of octamethylbiphenylenedilithium with SmI_2

A solution of SmI_2 in THF [15] 5 ml (0.5 mmol) was added to a solution of octamethylbiphenylenedilithium prepared by sonication of octamethylbiphenylene 132 mg (0.5 mmol) with an excess of lithium metal in THF (25 ml) at room temperature for 3 h. After 24 h the brown solution was solvolysed with MeOH (0.3 ml), then 5 ml of 0.2 N H_2SO_4 was added. Next, the reaction mixture was extracted with dichloromethane (15 ml) and the organic layer was washed with water and dried over Na_2SO_4. A white solid (124 mg) was obtained by evaporation. The GC analysis reveals the presence of only one octamethylbiphenyl [14b] with traces of octamethylbiphenylene, m.p. 140°C. Mass spectrum: m/e 266 (73.5, M^+); 251 (100); 236 (77.1); 221 (24.3); 205 (14.2); 191 (10); 179 (11.4); 165 (17.1). ^1H NMR (CD_2Cl_2, 200 MHz): δ 1.9 (s, 6H); 2.26 (s, 12H); 2.28 (s, 6H); 6.7 (s, 2H) ppm. ^{13}C NMR (CD_2Cl_2, 50 MHz): δ 16.1; 16.4; 17.2; 20.8 (methyl carbons); 128.8; 132.1; 133.3; 133.6; 135.2; 140.3 (aromatic carbon atoms) ppm.

4.5. Protolysis of a THF solution of octamethylbiphenylenedilithium

Octamethylbiphenylenedithium was prepared by sonication (1 h) of a mixture of 26 mg of octamethylbiphenylene (0.1 mmol) and an excess of lithium (32 mg, 4.5 mmol) in THF. After separating the excess of lithium, the solution was solvolysed with MeOH (0.2 ml). Water (5 ml) was then added and the mixture was extracted with dichloromethane (5 ml). Evaporation to dryness yielded 25 mg of a white solid. GC-MS reveals the presence of octamethylbiphenylene 20% (m/e 264 (M^+), octamethylbiphenyl 7% m/e 266 (M^+) and 1,2,3,4,6,7,8,9-octamethylbenzocyclooctene 73% which was identified by its MS and NMR spectra: m/e 266 (100, M^+); 251 (97.4); 236 (67.8); 221 (47.1); 206 (14.3); 191 (8.6); 179 (7.4); 165 (10.3). ^1H NMR (CD_2Cl_2, 200 MHz): δ 1.6 (s, 6H); 1.89 (s, 3H); 1.90 (s, 3H); 2.12 (s, 6H); 2.19 (s, 6H); 6.1 (s, 2H) ppm.

4.6. Tricarbonyl(octamethylbiphenylene)chromium

This compound was prepared from $[Cr(CO)_3(NH_3)_3]$ and octamethylbiphenylene [16] by the method described for the synthesis of (biphenylene)tricarbonylchromium [8]. An orange solid was isolated with a yield of 25% after purification by chromatography on silica gel under argon, m.p. 244°C dec. Anal. Found: C, 68.4; H, 5.9. $C_{23}H_{24}CrO_3$ calc.: C, 69.0; H, 6.0%. IR (KBr): ν(CO) 1940, 1875, 1862 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.3 (s, 6H); 2.25 (s, 6H); 2.2 (s, 6H); 2.1 (s, 6H) ppm.

4.7. Reaction of ytterbium with tricarbonyl(octamethylbiphenylene)chromium

Tricarbonyl(octamethylbiphenylene)chromium (200 mg, 0.5 mmol) was treated with activated ytterbium powder according to the procedure outlined for Ln^0 and biphenylene. After 16 h of stirring, an olive precipitate formed, the solution remaining orange. Addition of DME (15 ml) after 2 days did not improve solubilization. The mixture was solvolysed with 0.2 ml of MeOH, filtered and evaporated to dryness. The crude product was then treated with iodine in THF solution to cleave the $Cr(CO)_3$ group [16]. After extraction, a white solid (68 mg) was obtained by evaporation to dryness. The GC analysis reveals the presence of octamethylbiphenylene (main product) and octamethylbiphenyl. ^1H NMR (CD_2Cl_2, 200MHz). δ 2.0 (s, 12H); 2.15 (s, 12H), (octamethylbiphenylene 85%) and 1.9 (s, 6H); 2.26 (s, 12H); 2.28 (s, 6H) 6.7 (s, 2H), (octamethylbiphenyl, 15%) ppm.

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