Journal of Organometallic Chemistry, 135 (1977) 103—114

ORGANOLANTHANIDES

I. BIS(POLYFLUOROPHENYL)YTTERBIUM COMPOUNDS*

G. B. Deacon, W. D. Raverty,** and D. G. Vince***

Chemistry Department, Monash University, Clayton, Victoria 3168 (Australia)

(Received May 5th, 1977)

Summary

Bis(pentafluorophenyl)ytterbium, prepared from reaction of bis(pentafluorophenyl)mercury with ytterbium metal in tetrahydrofuran (THF), has been isolated as the highly air-sensitive, thermally unstable complex $(C_6F_5)_2Yb(THF)_4$, which yielded pentafluorobenzene on acidolysis. The ^{19}F NMR, IR, and UV/Vis spectra of the complex are discussed. A tetrahydrofuran complex of bis(2,3,5,6-tetrafluorophenyl)ytterbium has been prepared in a similar manner and was identified spectroscopically, thermal instability preventing satisfactory analytical characterization. Reaction was observed between ytterbium and bis(2,3,4,5-tetrafluorophenyl)mercury, but the product decomposed too rapidly for isolation. Ytterbium metal failed to react with diphenylmercury or bis(pentachlorophenyl)mercury.

---

* Preliminary Communication, Ref. [1]

** Present address: Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600 (Australia).

*** Present address: Central Research Laboratories, ICI (Australia) Ltd., Ascot Vale, Victoria 3032 (Australia).

Introduction

Despite considerable recent activity in lanthanide and actinide organometallic chemistry [2-6], knowledge of σ-bonded derivatives is still quite limited. Thus, no preparations of fluorocarbon lanthanides have been reported except in the preliminary account of this study [1], and only one fluorocarbon actinide is known [7], viz. $(\eta\text{-}C_5H_5)_3UC_6F_5$. There are few σ-bonded derivatives that are not stabilised by attachment of $\eta\text{-}C_5H_5$ or related ligands [2-6], and species of the type $(\eta\text{-}C_5H_5)_3MR$ (M = U or Th) [7] and $(\eta\text{-}C_5H_5)_2MR$ (M = Lanthanide) [4,5,12] are predominant. Exceptions include the anionic complexes $Li[R_4Ln]$ (Ln = La, Pr, Lu, or Yb) [13,14] and $Li_2U(CH_2SiMe_3)_6(tmed)_7$ (tmed = N,N,N',N'-tetramethylethylenediamine) [15], and solution species of the type RLnI (e.g. Ln = Sm or Yb) [16]. Synthetic routes to σ-bonded lanthanide and actinide organometallics are largely restricted to use of Grignard and organo-alkali metal reagents [2-6], apart from direct syntheses of RLnI species from the elements and the organic iodides [16]. We now report syntheses of polyfluorophenylytterbium compounds, and the first use of the transmetallation reaction as a route to organolanthanides.

Results and Discussion

Preparation, Isolation, and Properties of Bis(pentafluorophenyl)tetrakis(tetrahydrofuran)ytterbium(II)

On stirring ytterbium metal and bis(pentafluorophenyl)mercury in tetrahydrofuran (THF) at room temperature with rigorous exclusion of moisture and oxygen, an exothermic reaction occurred giving an orange solution of bis(pentafluorophenyl)ytterbium and a precipitate of mercury metal [reaction (1), $R = C_6F_5$].

$$R_2Hg + Yb \xrightarrow{THF} R_2Yb + Hg \qquad (1)$$

Analytically pure crystals of bis(pentafluorophenyl)tetrakis(tetrahydrofuran)-ytterbium(II) were obtained on addition of petroleum ether and cooling. The compound is exceptionally sensitive to oxygen and moisture, and is thermally unstable, decomposing on mild heating or more slowly under nitrogen at room temperature (see Experimental). Acidolysis of the compound in tetrahydrofuran under nitrogen gave pentafluorobenzene as the sole major organic product [reaction (2); $R = C_6F_5$].

$$R_2Yb + 2H_3O^+ \xrightarrow{THF} 2RH + 2H_2O + Yb^{2+} \qquad (2)$$

The amount of pentafluorobenzene differed slightly from that expected for (2) owing to the presence of traces of an unidentified fluorocarbon which was detected by ^{19}F NMR spectroscopy. Since the ^{19}F NMR spectrum of analytically pure bis(pentafluorophenyl)ytterbium in tetrahydrofuran (below) showed no resonances attributable to impurities, the unidentified fluorocarbon may be formed by slight thermal decomposition of the organolanthanide because of local heating on acidolysis. Addition of acid directly to crystals of bis(polyfluorophenyl)lanthanides induced thermal decomposition in competition with acidolysis. The presence of 2H-nonafluorobiphenyl, which might have been formed if thermal decomposition and subsequent acidolysis paralleled that of pentafluorophenyllithium [17], was definitely ruled out. Acidolysis of an impure sample of $(C_6F_5)_2Yb(THF)_4$ gave not only pentafluorobenzene, but also a low yield (ca. 5%) of 1,2,4,5-tetrafluorobenzene, which was probably derived from an impurity of a 2,3,5,6-tetrafluorophenylytterbium species. Evidence for such an impurity was obtained from the ^{19}F NMR spectrum of impure $(C_6F_5)_2Yb(THF)_4$ (see Experimental). The origin of this species is not clear, but probably involves hydrogen abstraction from tetrahydrofuran, a phenomenon previously observed in reactions of polyfluoroarenes with η-$C_5H_5Fe(CO)_2^-$ [18]. Samples of bis(pentafluorophenyl)-mercury used in reaction (1) contained negligible impurities of 2,3,5,6-tetrafluorophenyl-mercurials.

The ^{19}F NMR chemical shifts of $(C_6F_5)_2Yb(THF)_4$ in tetrahydrofuran are similar to those [17] of σ-bonded pentafluorophenylorganometallics, and in particular those of pentafluorophenylmagnesium bromide [19], some planar pentafluorophenylplatinum(II) complexes [20], and, more surprisingly, some transition metal carbonyl derivatives, e.g. $C_6F_5Fe(CO)_2(\eta$-$C_5H_5)$ [21], suggesting at least partial covalent character in the pentafluorophenyl-ytterbium bonds. Confirmation of the analytically established oxidation state of II was provided by the lack of broadening or shifts in the ^{19}F NMR spectrum, consistent with the expected diamagnetism of ytterbium(II) compounds (Yb^{2+}, $4f^{14}$). By contrast, ^{19}F chemical shifts for the paramagnetic $(\eta$-$C_5H_5)_3UC_6F_5$ are observed [7] at 152.4, 162.8, and 179.2 p.p.m. upfield from $CFCl_3$, substantially displaced from values for most pentafluorophenylorganometallics [17]. Detailed analysis of the ^{19}F NMR spectrum of $(C_6F_5)_2Yb(THF)_4$ was not possible because of overlap between the multiplets of the meta and para fluorines. The same difficulty has previously precluded analyses of the spectra of other pentafluorophenyl-organometallics [20,22].

However, using data from analysis [20] of the ^{19}F NMR spectrum of trans-$[(Et_3P)_2Pd(C_6F_5)Cl]$ as an initial basis, computer simulation of the general appearance of the ortho-fluorine multiplet was partly achieved. Some unexplained features in the experimentally observed multiplet could possibly be attributed to ^{171}Yb-^{19}F satellites (^{171}Yb, 14.31% abundance, has spin 1/2; other major isotopes have spin 0, except for ^{173}Yb, 16.13% abundance, spin 5/2 [23]) with J(Yb-o-F) ca. 120 Hz, though the assignment is very tentative.

Comparison of the infra-red spectrum of $(C_6F_5)_2Yb(THF)_4$ with those of tetrahydrofuran complexes [24], pentafluorophenylorganometallics [25] and $(C_6F_5)_3In(THF)_2$ [26] enabled most C_6F_5 and THF absorptions to be distinguished (Experimental Section). Intense fluorocarbon absorptions at 1036 and 920 cm^{-1}, which can be assigned [25] to modes $\nu_5(a_1)$ and $\nu_{25}(b_2)$ (involving carbon-fluorine stretching) of the C_6F_5Yb group, are at significantly lower frequencies than in previously reported pentafluorophenyl compounds (ca. 1080-1050 and 980-945 cm^{-1} respectively [7,25,27]), possibly arising from partial ionic character in the C_6F_5 - Yb bonds. Apart from $(C_6F_5)_2Yb(THF)_4$, the lowest reported values of $\nu_5(a_1)$ and $\nu_{25}(b_2)$ appear to be those (1050 and 945 cm^{-1}) of $(\eta\text{-}C_5H_5)_3UC_6F_5$, assigned straightforwardly (this work) by comparison of the spectrum [7] with those of other $(\eta\text{-}C_5H_5)_3UR$ complexes. An 'X-sensitive' mode of C_6F_5X derivatives, $\nu_6(a_1)$, involving C-X stretching, is normally observed at ca. 900-750 cm^{-1} [17,25,27], e.g. at 885 cm^{-1} for C_6F_5Cl and 806 cm^{-1} for $(C_6F_5)_2Hg$ [17]. For $(C_6F_5)_2Yb(THF)_4$, this mode may give rise to a prominent shoulder at 837 cm^{-1}. Ring stretching modes of tetrahydrofuran at 1070 and 912 cm^{-1} are shifted to lower frequencies (1013 and 876 cm^{-1}) in $(C_6F_5)_2Yb(THF)_4$, as expected [24] on coordination. Metal-oxygen stretching frequencies of tetrahydrofuran complexes of transition metals and alkylaluminium compounds have been reported in the range 500-350 cm^{-1} [28], though other authors have been unable to assign them owing to marked spectral differences between closely related complexes [29]. A medium intensity band of $(C_6F_5)_2Yb(THF)_4$ at 463 cm^{-1} is not readily assigned to a mode of the C_6F_5 group or the THF ligand, and could arise from ytterbium-oxygen stretching.

The colour of the complex derives from three bands in the region 350-500 nm, and the similarity of the spectra for the complex in the solid state (Nujol mull) and in tetrahydrofuran is consistent with negligible structural change on dissolution. No absorption could be detected near 1000 nm, where absorption characteristic of ytterbium(III), viz. $^2F_{7/2} \longrightarrow {}^2F_{5/2}$, is

expected [30]. In confirmation, admission of a trace of air to allow partial oxidation to ytterbium(III) gave rise to a weak peak at 978 nm. The absorption maxima of $(C_6F_5)_2Yb(THF)_4$ are unlikely to arise from intraligand transitions, since numerous colourless C_6F_5 and THF complexes are known, and the mixed species $(C_6F_5)_3In(THF)_2$ is colourless [26]. In addition, f→f transitions are impossible. At least part of the absorption is attributable to 4f→5d transitions, since these give a broad diffuse band at 352 nm (log ε, 2.71) for aqueous ytterbium(II) chloride [31]. All the possible 4f→5d bands of $(C_6F_5)_2Yb(THF)_4$ are at lower energy than that of $YbCl_2$, reflecting the readier oxidation of the organometallic compound. Some correlation has previously been observed between ease of oxidation of divalent lanthanide ions and the energy of their 4f→5d transitions [31]. It is also likely that part of the visible absorption of $(C_6F_5)_2Yb(THF)_4$ derives from ligand → metal charge transfer, since such transitions have been observed for both σ- and π-bonded organolanthanides [12a, 32] with intensities similar to those observed for $(C_6F_5)_2Yb(THF)_4$.

Although a detailed discussion of the structure of the complex or of the C_6F_5 - Yb bonding would be premature, a brief comment on the bonding is possible. The successful isolation of $(C_6F_5)_2Yb(THF)_4$ and its moderate stability in tetrahydrofuran at room temperature compared with the failure to isolate pentafluorophenyllithium and its ready decomposition in diethyl ether above -10° [17] * can be attributed to greater covalent character in the C_6F_5 - Yb bonds. Significant covalent character is also suggested by ^{19}F NMR data (above). Crystals suitable for X-ray crystallography have not yet been obtained, and in any case actue handling problems could well preclude use of this technique.

Attempted Preparation and Isolation of Other Diorganoytterbium Compounds

Bis(2,3,5,6-tetrafluorophenyl)ytterbium has also been prepared by trans-metallation [reaction (1); R = p-HC_6F_4] and was isolated as orange air-sensitive crystals. However, the compound was too thermally unstable for satisfactory analytical characterization, and decomposition products were

---

* There is no reason to believe C_6F_5Li is significantly more stable in THF than in diethyl ether. Polyfluorophenyllithium compounds are more nucleophilic in THF than in ether [33], hence self-decomposition by nucleophilic displacement is more likely in the former. Pentafluorophenylmagnesium chloride appears less stable in THF than in ether [34].

visible in the crystals. 1,2,4,5-Tetrafluorobenzene was formed on acidolysis [reaction (2); R = p-HC_6F_4], and the ratio moles RH/moles Yb^{2+} determined after this reaction was ca. 1.8, consistent with formulation of the product as $(p\text{-}HC_6F_4)_2Yb$. The infra-red spectrum showed features indicative of coordinated tetrahydrofuran and of a 2,3,5,6-tetrafluorophenyl group (see Experimental). Intense fluorocarbon bands at 1200–850 cm^{-1} are lowered from their positions for reported 2,3,5,6-tetrafluorophenylorganometallics [35,36], as observed for corresponding bands of $(C_6F_5)_2Yb(THF)_4$. The similarity between the ultraviolet/visible spectrum of a mull of the tetrafluorophenyl compound and that of $(C_6F_5)_2Yb(THF)_4$ (Experimental Section) suggests that the compounds have similar compositions and structures. A ^{19}F NMR spectrum could not be obtained owing to the presence of paramagnetic impurities.

A transmetallation reaction was also observed between bis(2,3,4,5-tetrafluorophenyl)mercury and ytterbium, but the initially formed orange solution, presumably of bis(2,3,4,5-tetrafluorophenyl)ytterbium, rapidly turned brown owing to thermal decomposition, and no complex could be isolated. No reaction could be induced between ytterbium and either bis(pentachlorophenyl)mercury or diphenylmercury in tetrahydrofuran.

General and Mechanistic Comments on Transmetallation

Transmetallation reactions have not previously been used to give σ-bonded organolanthanides, but unsuccessful attempts to obtain phenyllanthanides by this method have been reported [37,38]. Conceptually related reactions are known, viz. conversion of $ClHgCr(CO)_3(\eta\text{-}C_5H_5)$ by ytterbium metal into $ClYb[Cr(CO)_3(\eta\text{-}C_5H_5)]_y$ (y = 1 or 2) [37], and the reduction of mercuric iodide by samarium metal giving SmI_2 [39]. Transmetallation reactions can be effected either at elevated temperatures with a hydrocarbon or no solvent, or in polar solvents under less severe conditions, e.g. as in (1). Recent studies [40] suggest that the latter class proceed via metal-metal bonded intermediates. Accordingly, a possible path for (1) is:

$$R_2Hg + Yb \longrightarrow \overset{+}{Yb} - \overline{H}gR_2 \xrightarrow{(4)} RYbHgR \longrightarrow R_2Yb + Hg$$

Reaction is accelerated by electron withdrawing substituents (C_6F_5 >>> Ph), hence the transition state for the rate determining step, presumably (4) (see [40]), has considerable carbanionic character. The failure of bis(pentachlorophenyl)mercury to react is probably due to insolubility of the mercurial in tetrahydrofuran and is not mechanistically significant.

Experimental

Reagents and Manipulative Techniques: Ytterbium powder was obtained from Koch-Light. Bis(polyfluorophenyl)mercurials were prepared and purified by reported methods [35,41,42]. Authentic samples of pentafluorobenzene and 1,2,4,5-tetrafluorobenzene were from Bristol Organics. Authentic 2H-nonafluorobiphenyl was provided by Dr. A. G. Massey. Nitrogen was purified by passage through columns of oxygen removing catalyst (BASF R3/11) and molecular sieves (Union Carbide 13X). Tetrahydrofuran was refluxed over and distilled from calcium hydride then lithium aluminium hydride under nitrogen. Light petroleum (b.p. 60-80°) and diethyl ether were refluxed over and distilled from sodium then lithium aluminium hydride under nitrogen. Solvents were stored under purified nitrogen. Reactions were carried out in Schlenk glassware, which had been heated at 120° and purged of air by at least three successive evacuation (10^{-2} mm)/nitrogen cycles. Solvents were added by syringe techniques and it was important to replace punctured rubber tubing immediately after removal of syringe needles. Solid complexes were manipulated in recirculating atmosphere dry boxes (Vacuum Atmospheres HE43-2/HE93B or a specially constructed box of the Division of Applied Organic Chemistry, CSIRO, Melbourne).

Analyses: Microanalyses were by the Australian Microanalytical Laboratory, Melbourne, the air-sensitive compound being submitted as weighed samples in sealed aluminium capsules. Ytterbium was determined after acidolysis of the complexes by titration with sodium ethylenediaminetetraacetate using xylenol orange indicator, the solution being buffered at pH 4.5 by sodium acetate [43]. Pentafluorobenzene and 1,2,4,5-tetrafluorobenzene were determined quantitatively by ultraviolet spectroscopy.

Instrumentation: ^{19}F NMR spectra were obtained with Varian A56/60A or Bruker WH-90 instruments. Chemical shifts are in p.p.m. upfield from external $CFCl_3$. Spectra of the ytterbium compounds were recorded immediately on dissolution. Infra-red spectra compounds as Nujol mulls were recorded with Perkin-Elmer 521, 577, or 257 spectrophotometers. Hexachlorobutadiene could not be used, since it reacted immediately with the compounds. Ultra-violet/visible spectra of compounds as Nujol mulls or dissolved in tetrahydrofuran were obtained with Cary 17, or Unicam SP800A spectrophotometers. Quantitative fluorocarbon determinations were carried out with Varian Techtron 335 or Unicam SP800A instruments.

Preparation of Bis(pentafluorophenyl)tetrakis(tetrahydrofuran)ytterbium(II) (nc).

Ytterbium powder (0.581 g, 3.36 mmol) and bis(pentafluorophenyl)mercury (1.61 g, 3.00 mmol) in tetrahydrofuran (10 ml) were stirred under nitrogen at room temperature. After an induction period (1-2 min.), the mixture became yellow-green, an exothermic reaction commenced, and mercury was deposited. The reaction mixture was cooled (10°) and stirring was continued for 4 hr. giving a deep orange-red solution, which was then filtered through a celite pad to remove precipitated mercury. The filtrate was concentrated to 5-8 ml by evaporation under vacuum. Petroleum ether was then added until turbidity appeared, and the solution was cooled overnight at -20° giving bright orange-red crystals of the required compound. These were collected either by filtration or by removal of the mother liquor by syringe, were washed with petrol (2 ml) and ether (2 ml), and were dried under vacuum for 2-3 min at room temperature (yield, 0.70 g, 29%), dec. temp. under nitrogen, 78° (with explosion; darkens at 75°) (Found: C, 41.9; H, 3.9; Yb, 21.6. C_6F_5 (by acidolysis, below), 44.4, 43.9%. $C_{28}H_{32}F_{10}O_4Yb$ calcd.: C, 42.3; H, 4.1; Yb, 21.8; C_6F_5, 42.0%). ^{19}F NMR spectrum (tetrahydrofuran): 108.3 (m, 2F, F 2,6) and 161.4 (complex m, 3F, F 3,4,5) p.p.m. An impure sample (Found: C, 40.0; H, 3.8; Yb, 21.1%) showed weak multiplets centred at 114.5 (F ortho to Yb) and 139.1 (F ortho to H [35,42]) in addition to the foregoing intense multiplets. Infra-red absorption (1700-400 cm^{-1}): 1626s, 1595m, 1513m, ca. 1460s (coincident with Nujol, but detectable), 1410s, 1360sh, 1295s, 1244w, 1219s, 1179m, 1139w, 1067m-s, 1036 and 1013vs (br), 985w, 950sh, 920vs (br), 876vs (br), 837sh, 709m, 668m (br), 570m, and 463m cm^{-1}. Frequencies underlined are attributable [24] to tetrahydrofuran and the others to the pentafluorophenyl group [25,27]. Ultraviolet/visible absorption (300-1000 nm):
(i) in tetrahydrofuran, 370 (log ε, 2.76), 399 (2.73), and 444 (2.74) nm.
(ii) as a Nujol mull, 373, 405sh, 455-480vbr. After a brief exposure to air, a weak absorption was observed at 978 nm. On being stored for 48 hr. under nitrogen at room temperature, the crystals turned black, attributable to thermal decomposition, as heating caused a similar colour change.
Acidolysis: A weighed sample (ca. 0.25 g; accurately weighed) was dissolved in pure tetrahydrofuran (8 ml) under nitrogen and was cooled to 0°. Degassed dilute sulphuric acid (ca. 5 ml, 0.2-0.3 M) precooled to 0° was added by syringe. The reaction mixture was distilled and pentafluorobenzene was collected quantitatively (a control experiment gave a recovery of 98.0%)

together with tetrahydrofuran in a cooled (0°) vessel. The distillation was terminated when the boiling point remained at 100° for 10 min. The distillate was diluted quantitatively with rectified white spirit before spectrophotometric determination of the fluorocarbon. The ultraviolet spectrum of the diluted distillate was identical with that of authentic pentafluorobenzene, whilst the ^{19}F NMR spectrum of a typical undiluted distillate showed the resonances expected for pentafluorobenzene together with additional very weak broad features at 133, 158, and 167 p.p.m. Addition of authentic 2H-nonafluorobiphenyl to the solution established that this compound was not the source of the additional fluorine resonances. The ^{19}F NMR spectrum of the fluorocarbon product from acidolysis of an analytically impure sample (see above) showed not only the resonances of pentafluorobenzene and the above impurity, but also a sharp triplet at 139.4 p.p.m. indicative (comparison with the spectrum of an authentic sample) of 1,2,4,5-tetrafluorobenzene. Addition of degassed sulphuric acid directly to crystals of $(C_6F_5)_2Yb(THF)_4$ resulted in a reaction of explosive violence, and a black product typical of thermal decomposition was obtained rather than the acidolysis product, white ytterbium(II) sulphate.

The Tetrahydrofuran Complex of Bis(2,3,5,6-tetrafluorophenyl)ytterbium.

Reaction of ytterbium powder (0.486 g, 2.81 mmol) with bis(2,3,5,6-tetrafluorophenyl)mercury (1.01 g, 2.02 mmol) in tetrahydrofuran (10 ml) was carried out using conditions similar to those for the preparation of bis(pentafluorophenyl)ytterbium. A similar isolation procedure or rapid precipitation of the product from tetrahydrofuran by petrol gave orange-red crystals (containing specks of discoloured solid) of an impure tetrahydrofuran complex of bis(2,3,5,6-tetrafluorophenyl)ytterbium [yield, 0.52 g, 48%, calculated as $(\underline{p}\text{-}HC_6F_4)_2Yb(THF)_4$] [Found: $\underline{p}\text{-}HC_6F_4$/Yb ratio (determined following acidolysis), 1.8; absolute values for % Yb, % HC_6F_4 differed substantially from calculated values]. Infra-red absorption (4000-650 cm^{-1}): 3095w (ν(CH) of $\underline{p}\text{-}HC_6F_4$ [35], 1644w, 1585s, 1494s (br), ca. 1410vs, 1347w, 1292m, 1267m, 1217w, 1167sh, 1137vs (br), 1110w, 1062w, 1022vs, 960vw, 907s, 864 and 844vs (br), 815w, 742s, and 678 and 668vs cm^{-1}. Frequencies underlined are attributable [24] to tetrahydrofuran and the others are attributable [35, 36] to the 2,3,5,6-tetrafluorophenyl group. Ultraviolet/visible absorption (Nujol mull; 300-700 nm): 391 and 480 nm. Satisfactory ^{19}F NMR and PMR spectra could not be obtained, probably owing to paramagnetic impurities. The compound slowly turned brown (4-48 hr. depending on the

sample) on standing at room temperature, presumably owing to thermal instability.

Acidolysis: Cleavage of the complex with acid and determination of the fluorocarbon product, identified as 1,2,4,5-tetrafluorobenzene by ultraviolet and ^{19}F NMR spectroscopy, was carried out as for $(C_6F_5)_2Yb(THF)_4$ (above). Direct addition of acid to crystals of the complex resulted in violent decomposition into a black solid.

Other Reactions

(i) Reaction of bis(2,3,4,5-tetrafluorophenyl)mercury (3.00 mmol) with ytterbium (6.46 mmol) in tetrahydrofuran (10 ml) for 5 hrs. at 0-30° gave a precipitate of mercury and, initially, an orange-red solution, which rapidly turned brown indicative of thermal decomposition. No complex could be crystallized from solution.

(ii) Bis(pentachlorophenyl)mercury (1.73 mmol) and ytterbium (1.79 mmol) in tetrahydrofuran (13 ml) were stirred overnight at room temperature, and at 55-60° for 3 hrs, no reaction being observed.

(iii) Diphenylmercury (1.78 mmol) and ytterbium (1.90 mmol) in tetrahydrofuran (12 ml) were stirred overnight at room temperature then under reflux for 2 hrs, and no reaction was observed.

Acknowledgement

We are grateful to the Australian Research Grants Committee for support, Dr. N. Ham, CSIRO Division of Chemical Physics, for carrying out the simulation of the NMR spectrum, Dr. A. J. Koplick for experimental assistance, Dr. P. C. Wailes and Dr. H. Weigold, CSIRO Division of Applied Organic Chemistry, for assistance with dry box facilities, and Dr. A. G. Massey, University of Technology, Loughborough for a sample of 2H-nonafluorobiphenyl.

References

1. G. B. Deacon and D. G. Vince, J. Organometal. Chem., 112 (1976) C1.
2. B. Kanellakopulos and K. W. Bagnall, MTP Int. Rev. Sci., Inorg. Chem., Ser. One, 7 (1972) 299.
3. E. Cernia and A. Mazzei, Inorg. Chim. Acta, 10 (1974) 239.
4. M. Tsutsui, N. Ely, A. E. Gebala, and J. L. Atwood, Ann. N.Y. Acad. Sci., 239 (1974) 160.
5. M. Tsutsui, N. Ely, and R. Dubois, Acc. Chem. Research, 9 (1976) 217.
6. T. J. Marks, Acc. Chem. Research, 9 (1976) 223.

7. T. J. Marks, A. M. Seyam, and J. R. Kolb, J. Amer. Chem. Soc., 95 (1973) 5529.
8. T. J. Marks and W. A. Wachter, J. Amer. Chem. Soc., 98 (1976) 703.
9. A. E. Gebala and M. Tsutsui, J. Amer. Chem. Soc., 95 (1973) 91.
10. G. W. Halstead, E. C. Baker, and K. N. Raymond, J. Amer. Chem. Soc., 97 (1975) 3049.
11. G. Brandi, M. Brunelli, G. Lugli, and A. Mazzei, Inorg. Chim. Acta, 7 (1973) 319.
12. a N. M. Ely and M. Tsutsui, Inorg. Chem., 14 (1975) 2680;
b J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, Chem. Commun., (1976) 480.
13. F. A. Hart, A. G. Massey, and M. S. Saran, J. Organometal. Chem., 21 (1970) 147.
14. S. A. Cotton, F. A. Hart, M. B. Hursthouse, and A. J. Welch, Chem. Commun. (1972) 1225.
15. R. Andersen, E. Carmona-Guzman, K. Mertis, E. Sigurdson, and G. Wilkinson, J. Organometal. Chem., 99 (1975) C19.
16. D. F. Evans, G. V. Fazakerley, and R. F. Phillips, J. Chem. Soc. (A), (1971) 1931.
17. S. C. Cohen and A. G. Massey, Adv. Fluorine Chem., 6 (1970) 83.
18. M. I. Bruce and F. G. A. Stone, J. Chem. Soc. (1966) 1837.
19. D. F. Evans and M. S. Khan, Chem. Commun. (1966) 67; J. Chem. Soc. (A), (1967) 1643.
20. F. J. Hopton, A. J. Rest, D. T. Rosevear, and F. G. A. Stone, J. Chem. Soc. (A), (1966) 1326.
21. M. I. Bruce, J. Chem. Soc. (A), (1968) 1459.
22. R. L. Bennett, M. I. Bruce, and R. C. F. Gardner, J. Chem. Soc. Dalton (1973) 2653.
23. Handbook of Chemistry and Physics, 50th Edn. (CRC:Ohio 1969/1970), p. B 439.
24. J. Lewis, J. R. Miller, R. L. Richards, and A. Thompson, J. Chem. Soc. (1965) 5850; R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, J. Chem. Soc. (1963) 379.
25. e.g. G. B. Deacon and J. H. S. Green, Spectrochim. Acta (A), 24 (1968) 1125; G. B. Deacon and J. C. Parrott, Aust. J. Chem., 24 (1971) 1771.
26. G. B. Deacon and J. C. Parrott, Aust. J. Chem., 25 (1972) 1169.

27. I. J. Hyams, E. R. Lippincott, and R. T. Bailey, Spectrochim. Acta, 22 (1966) 695; D. A. Long and D. Steele, Spectrochim. Acta, 19 (1963) 1947, 1955.

28. S. Takeda and R. Tarao, Bull. Chem. Soc. Japan, 38 (1965) 1567; N. M. Karayannis, E. E. Bradshaw, J. Wysoczanski, L. L. Pytlewski, and M. M. Labes, Inorg. Chim. Acta, 4 (1970) 272; J. H. Morris and W. E. Smith, Chem. Commun. (1970) 245.

29. G. W. A. Fowles, D. A. Rice, and R. A. Walton, J. Inorg. Nuclear Chem., 31 (1969) 3119.

30. F. Calderazzo, R. Pappalardo, and S. Losi, J. Inorg. Nucl. Chem., 28 (1966) 987.

31. F. D. S. Butement, Trans. Farad. Soc., 44 (1948) 617; see also D. S. McClure and Z. Kiss, J. Chem. Phys., 39 (1963) 3251.

32. K. O. Hodgson, F. Mares, D. F. Starks, and A. Streitwieser, J. Amer. Chem. Soc., 95 (1973) 8650.

33. R. J. De Pasquale and C. Tamborski, J. Organometal. Chem., 13 (1968) 273.

34. A. E. Jukes and H. Gilman, J. Organometal. Chem., 17 (1969) 145.

35. H. B. Albrecht and G. B. Deacon, Aust. J. Chem., 25 (1972) 57.

36. G. B. Deacon and D. G. Vince, Aust. J. Chem., 28 (1975) 1931.

37. A. E. Crease and P. Legzdins, Chem. Commun., (1973) 775.

38. H. Gilman and R. G. Jones, J. Org. Chem., 10 (1945) 505.

39. C. Hirayama, P. M. Castle, R. W. Liebermann, R. J. Zollweg, and F. E. Camp, Inorg. Chem., 13 (1974) 2804.

40. O. A. Reutov and K. P. Butin, J. Organometal. Chem., 99 (1975) 171.

41. H. B. Albrecht, G. B. Deacon, and M. J. Tailby, J. Organometal. Chem., 70 (1974) 313.

42. H. B. Albrecht and G. B. Deacon, J. Organometal. Chem., 57 (1973) 77.

43. J. Korbl and R. Prebil, Chemist-Analyst, 45 (1956) 102.