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ON THE FORMATION OF (TRIPHENYLPHOSPHINE)(ETHYLENE)-PENTAMETHYLCYCLOPENTADIENYLRHODIUM(I) IN THE REACTION OF DIIODO(TRIPHENYLPHOSPHINE)PENTAMETHYLCYCLOPENTA-DIENYLRHODIUM(III) WITH BUTANE-1,4-BIS(MAGNESIUM BROMIDE). AN EXAMPLE OF FACILE C—O CLEAVAGE OF DIETHYL ETHER BY AN ORGANOMAGNESIUM COMPOUND

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Summary

A study is described of the reaction between $[RhI_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ (I) and the alkylating reagents, $BrMg(CH_2)_4MgBr$ (II) or $Mg(CH_2)_4$, in diethyl ether, which gives a mixture of the ethylene—rhodium complex of formula $[Rh(C_2H_4)(PPh_3)(\eta^5\text{-}C_5Me_5)]$ (III) and the rhodacyclopentane derivative, $[Rh(CH_2)_4(PPh_3)(\eta^5\text{-}C_5Me_5)]$ (IV). In tetrahydrofuran these reactions give only IV. Pure IV is also obtained by treating $[RhCl_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ or I with 1,4-dilithiobutane. By use of deuterium-labelled alkylating reagents it has been shown that the formation of the ethylene—rhodium complex IV is due to a facile diethyl ether C—O cleavage by organomagnesium compounds.

The mechanism of the formation of III is briefly discussed.

Introduction

During studies of the synthesis of Group VIII transition metal metallocycles [1—3] we found that in the reaction of diiodo(triphenylphosphine)pentamethylcyclopentadienyrhodium(III) (I), with butane-1,4-bis(magnesium bromide) (II) in diethyl ether, the rhodium(I)—ethylene complex III is formed as the major product along with minor amounts of the expected rhodacyclopentane derivative IV. The method of preparation of III and the evolution of ethylene during the reaction as well as the observation that metallacyclopentane derivatives can

undergo reductive decoupling reaction [4—7], suggested that the rhodacycle IV could be the precursor of III which undergoes carbon—carbon σ-bond cleavage [1].

We have now carried out a study aimed at deciding: (i) how the experimental conditions influence the course of the reaction and (ii) whether III is formed from IV and if so, how. The results show that an unusually easy diethyl ether C—O bond rupture rather than a carbon—carbon σ-bond cleavage of the tetramethylene moiety of IV is responsible for ethylene formation.

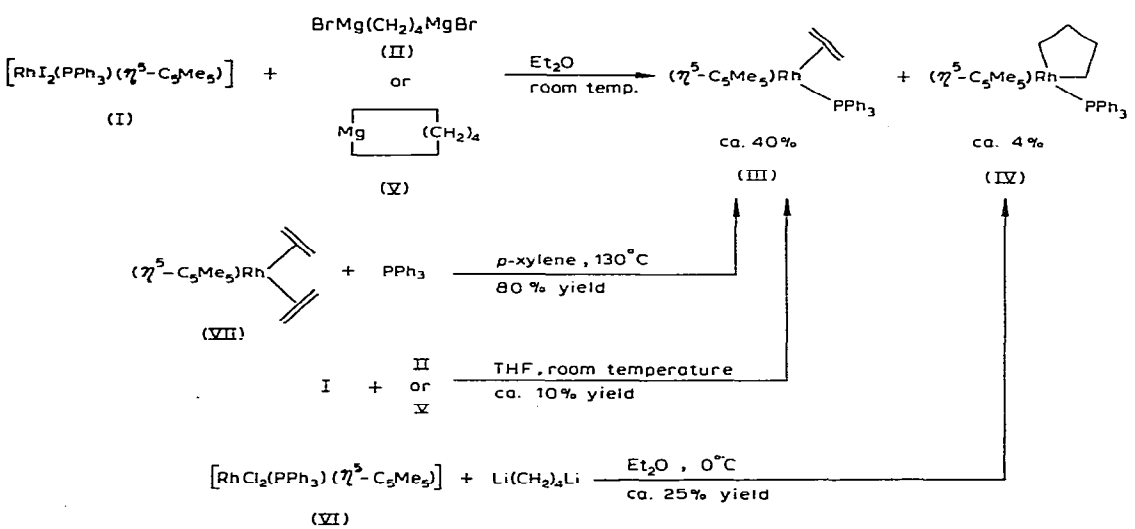
Results and discussion

Treatment of a suspension of $[RhI_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ (I) in diethyl ether at room temperature with a tetrahydrofuran solution of butane-1,4-bis(magnesium bromide) (II) (II/I molar ratio 3) eventually gives a mixture of III and IV (Scheme 1). Ethylene, detected by GLC, is formed during the reaction. A mixture of III and IV was obtained from the oily crude products by column chromatography. The same mixture, but in lower yields, was obtained when magnesiacyclopentane (V) was used as the alkylating reagent under the same conditions (Scheme 1).

Both the reaction temperature and the molar ratio of alkylating agent to diiodo compound strongly influence the total amount of III and IV. Thus, when the reaction is carried out below —20°C or when molar ratios of alkylating agent to I of less than 3 are employed, only traces of III and IV are obtained, along with large amounts of unidentified halogenated rhodium compounds.

Pure samples of III were obtained from the mixture of III and IV either by slow crystallization from pentane at —25°C, or by treating $[Rh(C_2H_4)_2(\eta^5\text{-}C_5Me_5)]$ (VII) with triphenylphosphine (Scheme 1). Several attempts to isolate IV from

SCHEME 1



the mixture invariably gave samples still contaminated by III.

Rather surprisingly, a simple change in the reaction medium, from diethyl

ether to tetrahydrofuran in the reaction of I with II or V, allowed the isolation of pure IV in ca. 10% yield. The reaction between I or $[RhCl_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ (VI) and 1,4-dilithiobutane in diethyl ether also leads to pure IV (Scheme 1).

Preliminary indication of the composition of the mixtures of III and IV was obtained from their reactions with dry HCl, which lead quantitatively to VI and mixtures of C_2 and n-C_4 hydrocarbons (Scheme 2). The C_2/C_4 molar ratio values

SCHEME 2

$$\text{III} + \text{IV} \xrightarrow[\text{benzene}]{\text{HCl}} \text{VI} + \begin{matrix}\text{ethylene, 40\%; ethane, 50\%} \\ \text{n-butenes, 4\%; n-butane, 6\%}\end{matrix}$$

$$\text{III} \xrightarrow[\text{benzene}]{\text{HCl}} \text{VI} + \text{ethylene, 45\%; ethane, 55\%}$$

$$\text{IV} \xrightarrow[\text{benzene}]{\text{HCl}} \text{VI} + \text{n-butenes, 40\%; n-butane, 60\%}$$

provided an estimate of the ratio of III and IV, since pure samples of these compounds on treatment with dry HCl gave, in addition to VI, only C_2 and n-C_4 hydrocarbons, respectively (Scheme 2). These results were confirmed by mass spectrometry. The mass spectra of pure III and IV are given in the Fig. 1. The mass spectrum of IV shows that the main fragmentation process is the loss of 56 mass units (C_4H_8) to give the base peak at *m/e* 500. Since there is no peak at *m/e* 528, which might have come by loss of 28 mass units (C_2H_4), it is possible to detect even the smallest traces of III.

Finally, the molecular structures of III [8] and IV [9] have been unambiguously established by single-crystal X-ray analysis.

Our first experiment aimed at throwing light on the above findings was the alkylation of the diiodo complex I with 2,3-butane-d_2-1,4-bis(magnesium bromide) (VIII), which was prepared by the reactions outlined in Scheme 3. The

SCHEME 3

$$\underset{\textit{trans}}{H_3COOCHC{=}CHCOOCH_3} \xrightarrow[D_2,\ \text{benzene}]{RhCl(PPh_3)_3} H_3COOCCHDCHDCOOCH_3$$

$$H_3COOCCHDCHDCOOCH_3 \xrightarrow{LiAlH_4} HOCH_2CHDCHDCH_2OH$$

$$HOCH_2CHDCHDCH_2OH \xrightarrow{PBr_3} BrCH_2CHDCHDCH_2Br$$

$$BrCH_2CHDCHDCH_2Br \xrightarrow{Mg/THF} \underset{\text{(VIII)}}{BrMgCH_2CH_2CHDCHDCH_2MgBr}$$

results should answer two questions, since the formation of deuterated ethylene—rhodium compounds would mean that ethylene is formed by fragmentation of the tetramethylene moiety, while moreover the deuterium content should give information about which carbon—carbon σ-bonds are cleaved.

The isotopic purity of all the products was tested by mass spectrometry and shown to be not less than 99%.

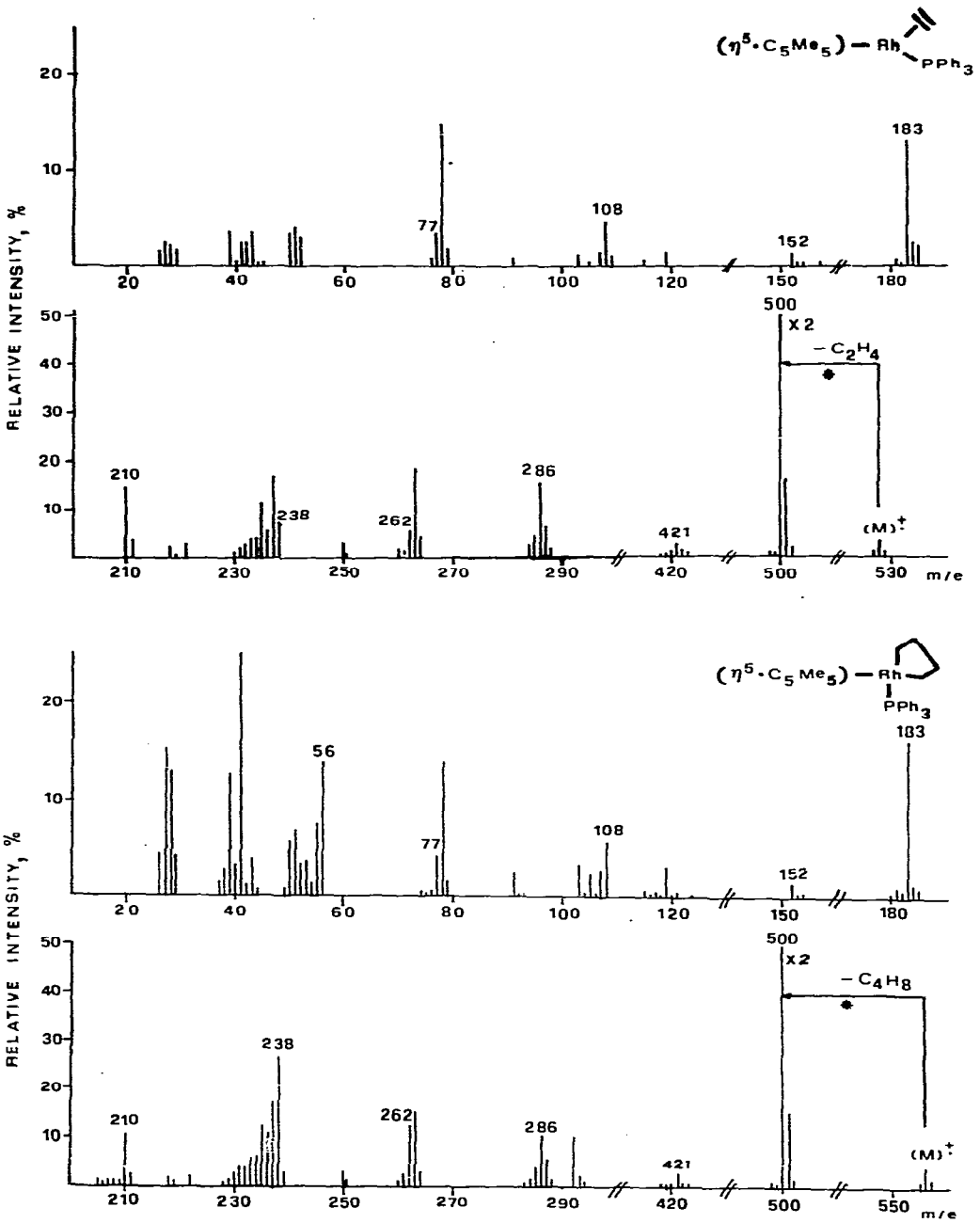
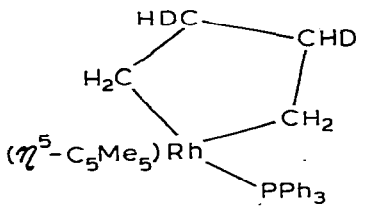


Fig. 1. Mass spectra of (triphenylphosphine)(ethylene)(pentamethylcyclopentadienyl)rhodium (III) (top), and of (triphenylphosphine)(butane-1,4-diyl)(pentamethylcyclopentadienyl)rhodium (IV) (bottom).

In this connection, we should point out that several attempts to prepare isotopically pure 2,3-d_2-succinic acids by the catalytic deuteration of fumaric or maleic acids in the presence of [$RhCl(PPh_3)_3$] in a benzene/ethanol mixture, as described in ref. 10 were unsuccessful and led to mixtures of d_1-, d_2-, and d_0-

succinic acids in a ratio of approximately 2/2/1. Similar results were obtained starting from the dimethyl esters of fumaric or maleic acids, contrary to expectation [11]. Only with benzene alone as solvent were the di-deuterated succinic esters of high isotopic purity obtained by deuteration of dimethyl fumarate or dimethyl maleate.

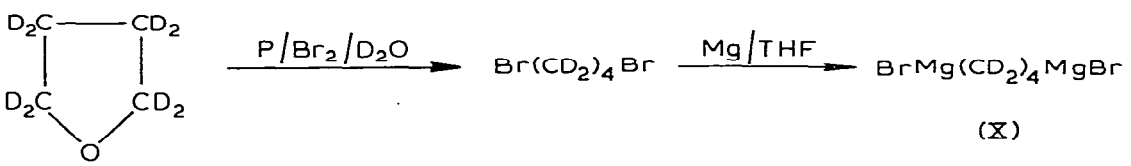
Alkylation of I with VIII led to a mixture whose mass spectrum revealed the presence of the non-deuterated ethylene—rhodium complex III and the di-deuterated rhodacyclopentane derivative IX.



(IX)

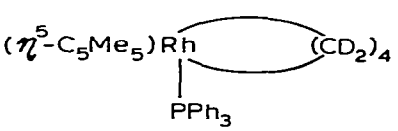
In order to prove that the ethylene is derived from the tetramethylene moiety of the alkylating reagent, I was alkylated with butane-d_8-1,4-bis(magnesium bromide) (X), which was prepared from tetrahydrofuran-d_8 (Scheme 4). Again, in

SCHEME 4



(X)

addition to the expected rhodacyclopentane derivative XI, the non-deuterated complex III was obtained. This finding, while unequivocally showing that III is not formed via the rhodacyclopentane compound, opened new questions on the origin of ethylene.



(XI)

The fact that the reaction between the di-iodo compound I and the di-Grignard II when carried out in tetrahydrofuran gives only the rhodacyclopentane derivative suggested that ethylebe could be formed by C—O rupture of diethyl ether. This proved to be the case, since treatment of diethyl ether with a tetrahydrofuran solution of II or a dioxane solution of V at room temperature for 4 h gave ethylene in ca. 0.2—0.3% yields. Under the same conditions, neither pentane-1,5-bis(magnesium bromide) nor hexane-1,6-bis(magnesium bromide) reacts in this way with diethyl ether.

These results explain why no trace of the ethylene—rhodium complex III was

detected in the preparation of the rhodacyclohexane and rhodacycloheptane derivatives by alkylation of I with the above di-Grignard reagents in diethyl ether [1].

The C—O bonds of ether are known to be cleaved by Grignard reagents [12], and this reaction has been successfully employed for the preparation of aromatic olefins [13]. However, the reaction proceeds with satisfactory conversions only in the case of phenyl or allyl ethers, and at temperatures above 100°C. Our results contribute the sole example of facile cleavage of aliphatic ether C—O bonds by a Grignard reagent.

We cannot at present fully account for the very different behaviour of the 1,4-di-Grignard II compared with its higher homologues in the diethyl ether cleavage, but the points are relevant: (i) magnesiacyclopentane (V) reacts with the diiodo compound I in the same way as II and (ii) V reacts with diethyl ether to give ethylene.

Additional relevant information is available in the literature: (i) the Schlenk equilibrium (eq. 1) is probably established in diethyl ether to some extent [14];

$$BrMg(CH_2)_4MgBr \rightleftharpoons Mg(CH_2)_4 + MgBr_2 \quad (1)$$

(ii) equilibrium 2 is not established, or lies completely over to the left, in diethyl ether [15], and consequently it is reasonable that equilibrium 3, if it is established, should also lie completely over to the left. In the light of all the evidence

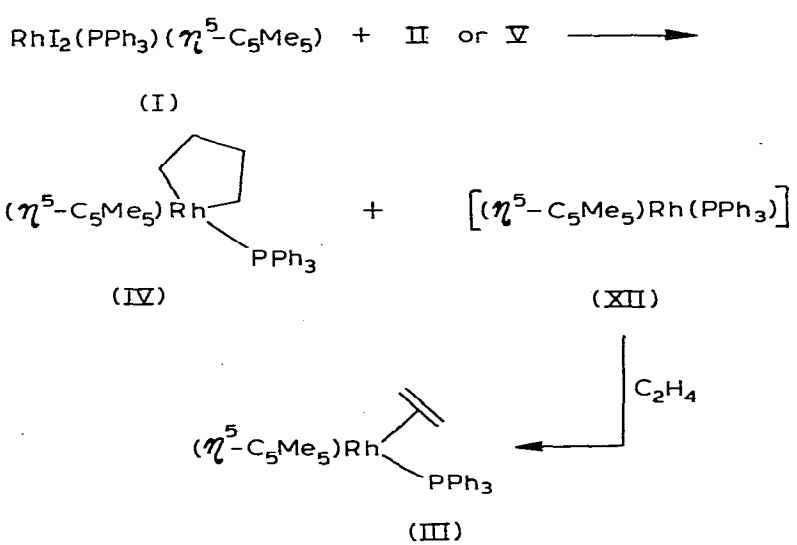
$$BrMg(CH_2)_5MgBr \rightleftharpoons Mg(CH_2)_5 + MgBr_2 \quad (2)$$

$$BrMg(CH_2)_6MgBr \rightleftharpoons Mg(CH_2)_6 + MgBr_2 \quad (3)$$

we are inclined to regard magnesiacyclopentane as a uniquely reactive reagent for diethyl ether cleavage.

For the formation of the ethylene—rhodium complex III the reactions outlined in Scheme 5 are suggested.

SCHEME 5



It is assumed that, in addition to the cyclodialkylation of I to IV, the organomagnesium derivatives II or V cause the reduction of I to XII which eventually traps ethylene derived from diethyl ether. Formation of III from IV by the action of ethylene can be rejected, since independent experiments showed that pure IV does not react with ethylene at room temperature and atmospheric pressure.

Experimental

All reactions involving organometallic compounds were carried out under dinitrogen or argon using standard techniques for air-sensitive compounds.

Diethyl ether and tetrahydrofuran were refluxed and distilled from sodium and then from lithium aluminum hydride. Pentane and benzene were washed free of olefins or thiophene with concentrated sulfuric acid, dried over calcium chloride, and distilled from lithium aluminum hydride. All distillations were carried out under dinitrogen. Unless otherwise noted other solvents were reagent grade, and were degassed under vacuum and dried over molecular sieves.

The compounds $[RhCl_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ [16], $[RhI_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ [16], $BrMg(CH_2)_nMgBr$ (n = 4, 5, 6) [17], $Li(CH_2)_4Li$ [4], $Mg(CH_2)_4$ [14], $[RhCl(PPh_3)_3]$ [10], $[Rh(C_2H_4)_2(\eta^5\text{-}C_5Me_5)]$ [18] were prepared as described in the references cited.

Deuterium was purchased from Merck and was 99.5% pure; tetrahydrofuran-d_8 was purchased from Aldrich and was 98% isotopically pure; neutral alumina for column chromatography was a Merck product, activity grade II—III.

Melting or decomposition points were determined on a Kofler hot-stage apparatus and are uncorrected. Molecular weights were determined at 37°C with a Mechrolab vapor-pressure osmometer Mod. 3019.

Microanalyses were performed by the Laboratorio di Microanalisi of Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa.

GLC analyses were performed on a Perkin—Elmer F30 instrument equipped with flame ionization detectors; products were identified by comparison of retention times with those of authentic samples.

Mass spectra were determined with a Varian Mat-CH7 mass spectrometer at 70 eV; the accelerating voltage was 3 kV and the emission current 100 μA. Samples were introduced into the ion source with a direct insertion probe at the minimum temperature which gave an adequate vapor pressure; the chamber temperature was approximately 100—120°C.

^{1}H NMR spectra were recorded with a Varian T60 or a Jeol PS-100 instrument.

Reaction of $[RhI_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ (I) with butane-1,4-bis(magnesium bromide) (II) or magnesiacyclopentane (V): preparation of III and IV mixture

To a stirred suspension of I (300 mg, 0.38 mmol) in diethyl ether (60 ml) 7.6 ml of a 0.15 *M* tetrahydrofuran solution of II (1.14 mmol) were added dropwise, at room temperature. The mixture was stirred for a further 2 h, then filtered. The solvent was evaporated off under vacuum and the red residue extracted with pentane (80 ml). The orange solution was evaporated to dryness and the red-oily crude product dissolved in benzene (2 ml). This solution was transferred to a dry 15 cm column of alumina and elution with n-pentane gave an orange

band, ca. 89 mg of a mixture of III and IV. Cooling of dilute pentane solutions of this mixture at —30°C gave orange crystals of pure III. M.p. 150—155°C (dec.). (Found: C, 67.89; H, 6.41. Mol. wt., 528 (mass spectrum). $C_{30}H_{34}PRh$ calcd.: C, 68.18; H, 6.48%. Mol. wt., 528.48).

Analogous results were obtained using a 0.14 *M* dioxane solution of magnesiacyclopentane (V) as the alkylating reagent.

Preparation of (triphenylphosphine)(ethylene)pentamethylcyclopentadienylrhodium(I) (III)

A mixture of $[Rh(C_2H_4)_2(\eta^5\text{-}C_5Me_5)]$ (VII) (160 mg, 0.54 mmol) and PPh_3 (140 mg, 0.53 mmol) in *p*-xylene (10 ml) was kept at 130°C for 3 h. The solvent was evaporated in vacuo to give an orange-red oil, which was dissolved in benzene (1 ml) and transferred to a dry 15 cm column of alumina. The column was eluted with pentane and an orange band was collected. Cooling of the resulting solution at —30°C gave orange-red needles of III (yield, 80%). M.p. 150—155°C (dec.).

Preparation of (pentamethylcyclopentadienyl)(triphenylphosphine)(butane-1,4-diyl)rhodium(III) (IV)

Method A. To a stirred suspension of $[RhI_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ (I) (300 mg, 0.38 mmol) in tetrahydrofuran (60 ml), 7.6 ml of a 0.15 *M* tetrahydrofuran solution of butane-1,4-bis(magnesium bromide) (II) (1.14 mmol) were added dropwise at room temperature. The mixture was stirred for further 1.4 h. The solvent was then evaporated off under vacuum and the red oily residue dissolved in benzene (2 ml). This solution was transferred to a dry 15 cm column of alumina. The column was eluted with pentane and a yellow band collected. Cooling of the resulting solution at —30°C gave yellow needles of IV (yield, 10%). M.p. 115°C (dec.). (Found: C, 69.13; H, 6.90. Mol. wt., 552 (benzene), 556 (mass spectrum). $C_{32}H_{38}PRh$ calcd.: C, 69.06; H, 6.88%. Mol. wt., 556.53).

Method B. The procedure was as in method A but with magnesiacyclopentane instead of II as the alkylating reagent. Starting from 200 mg of I (0.27 mmol) and using 6 ml of a 0.14 *M* dioxane solution of magnesiacyclopentane (0.804 mmol), 14.7 mg of IV were obtained (yield 10%).

Method C. To a stirred suspension of $[RhCl_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ (VI) (200 mg, 0.35 mmol) in diethyl ether (60 ml), 4 ml of a 0.23 *M* diethyl ether solution of 1,4-dilithiobutane (0.92 mmol) were added dropwise at 0°C. The mixture was stirred at this temperature for further 1.4 h then filtered. The resulting orange solution was taken to dryness by evaporation of diethyl ether under vacuum. The oily residue was extracted with pentane (40 ml) and the extract was concentrated to 5 ml and chromatographed on alumina, as above. The first yellow band eluted with pentane gave 58 mg of pure IV (yield, 30%). A second orange-red band, eluted with benzene, gave a microcrystalline orange product (16 mg) of formula $C_{32}H_{37}ClPRh$ (M^+, 579).

Method D. This preparation was carried out exactly as described for method C, using $[RhI_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ (I) instead of the dichloride VI. Starting from 300 mg of I (0.38 mmol) and using 7.34 ml of a 0.23 *M* diethyl ether solution of 1,4-dilithiobutane (1.14 mmol), pure IV was obtained in ca. 15% yield.

Reactions of III, IV, and their mixtures with HCl

In a typical experiment 50 mg of starting material were dissolved in 5 ml of benzene at room temperature. Pure dry HCl was then bubbled through the solution for 15 min, during which $[RhCl_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ (VI) was precipitated in almost quantitative yields; it was identified by elemental analysis and by comparison of its ^1H NMR spectrum with that previously reported [16]. The evolved gases were trapped at —190°C and then analyzed by GLC.

Preparation of threo-2,3-d_2-dimethylsuccinate

To a benzene (80 ml) solution of $[RhCl(PPh_3)_3]$ (0.49 mmol) was added dimethylfumarate (3.1 g, 0.021 mmol). Deuterium (600 ml) was introduced at room temperature, and after complete absorption (ca. 56 h) the solution was concentrated in vacuo and the residue distilled to give 5.25 g of pure *threo-2,3-d_2*-dimethylsuccinate (yield 60%). B.p. 43—44°C 0.2 mmHg. Mass spectrum (the ten most intense peaks): *m/e* 117, 116, 89, 59, 57, 56, 46, 43, 30, 15.

Preparation of threo-2,3-d_2-butane-1,4-diol

To a suspension of $LiAlH_4$ (3.9 g) in diethyl ether (90 ml) a solution of *threo*-2,3-d_2-dimethylsuccinate (12.3 g) in diethyl ether (90 ml) was added at 0°C. The mixture was refluxed for 1 h then stirred for 24 h at room temperature. It was then treated with moist diethyl ether and acidified with 10% H_2SO_4, at 0°C. The ethereal layer was separated and the aqueous layer was continuously extracted with diethyl ether for 48 h. The combined ethereal extracts were dried over Na_2SO_4 and distilled to give *threo*-2,3-d_2-butane-1,4-diol (6.12 g; yield, 79%), b.p. 132—133°C 15 mmHg.

Preparation of threo-2,3-d_2-1,4-dibromobutane

This was prepared by the procedure reported for the unlabelled compound [19]. From 5.5 g of *threo*-2,3-d_2-butane-1,4-diol, 7.7 g of the dibromide (yield 60%) were obtained. B.p. 84—85°C 14 mmHg. Mass spectrum (the ten most intense peaks): *m/e* 139, 137, 57, 56, 43, 40, 31, 30, 29, 27.

Preparation of threo-2,3-d_2-butane-1,4-bis(magnesium bromide) (VIII)

To a suspension of magnesium turnings (1.7 g) in tetrahydrofuran (5 ml) a solution of 1.6 ml of *threo*-2,3-d_2-1,4-dibromobutane in tetrahydrofuran (45 ml) was added dropwise during 40 min. The mixture was filtered to remove the excess of magnesium. Titration [17] showed the solution to be 0.16 *M* in VIII.

Reaction of $[RhI_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$ (I) with 2,3-d_2-butane-1,4-bis(magnesium bromide) (VIII)

This reaction was carried out as described for alkylation of I with the unlabelled di-Grignard reagent in diethyl ether. From 400 mg of I (0.53 mmol) and 10 ml of a 0.16 *M* tetrahydrofuran solution of VIII, 118 mg of a mixture of III and IX were obtained.

Preparation of 1,4-dibromobutane-d_8

The procedure for the preparation of the unlabelled compound [19] was used. In a 20 ml flask equipped with a refrigerant and a dropping funnel were

placed tetrahydrofuran-d_8 (3 g, 0.0375 mol), purified red phosphorus (0.58 g, 0.0187 mol), and D_2O (0.75 g, 0.0375 mol). The stirred mixture was kept at 40°C and 5.5 g of bromine (0.0375 mol) were added at such a rate that there was little bromine vapor above the surface of the mixture. The mixture was subsequently kept at 110—130°C for 1 h then cooled to room temperature. Water (10 ml) and diethyl ether (20 ml) were added and the excess of phosphorus was removed by filtration. The ethereal solution was washed with a 10% $Na_2S_2O_3$ solution then with water, and dried over Na_2CO_3. After removal of ether, the residue was distilled to give 6.16 g of 1,4-dibromobutane-d_8 (yield 73%). B.p. 83—84°C 14 mmHg. Mass spectrum (the ten most intense peaks): *m/e* 145, 143, 113, 111, 62, 46, 42, 34, 32, 30.

Preparation of butane-d_8-1,4-bis(magnesium bromide) (X)

To a suspension of magnesium turnings (1.7 g) in tetrahydrofuran (3 ml) a solution of 1.5 ml of 1,4-dibromobutane-d_8 in tetrahydrofuran (47 ml) was added dropwise during 40 min. The mixture was filtered to remove the excess of magnesium, titration [17] showed it to be 0.15 *M* in X.

Reaction of [$RhI_2(PPh_3)(\eta^5$-$C_5Me_5)$] (I) with butane-d_8-1,4-bis(magnesium bromide) (X)

This reaction was carried out exactly as described for alkylation of I with unlabelled di-Grignard reagent in diethyl ether. From 200 mg of I (0.265 mmol) and 5.3 ml of a 0.15 *M* tetrahydrofuran solution of X, 55 mg of a mixture of III and XI were obtained.

Reactions of butane-1,4-bis(magnesium bromide) (II) or magnesiacyclopentane (V) with diethyl ether

To dry diethyl ether (50 ml) contained in a flask equipped with a serum cap, 8 ml of a 0.17 *M* tetrahydrofuran solution of II were added at room temperature under dinitrogen. The mixture was stirred for 4 h. Small aliquots were withdrawn by a syringe and analyzed by GLC, which revealed the presence of ethylene (0.2—0.3%). Similar results were obtained when diethyl ether was treated with a dioxane solution of V.

Acknowledgements

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