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Preliminary communication

STEREOCHEMICAL INVESTIGATION OF THE REACTION OF CYCLOPENTADIENYL(DIPHOSPHINE)METHOXYCARBENE-RUTHENIUM(II) COMPLEXES WITH $LiAlH_4$

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Summary

$[(\eta\text{-}C_5H_5)Ru\{Ph_2PCHRCHR'PPh_2\}\{C(OCH_3)CH_2C_6H_5\}]PF_6$ (where R, R' = H or CH_3) reacts with $LiAlH_4$ in THF at —80°C to give the corresponding 2-phenylethyl complexes, which have an antiperiplanar conformation around the $H_2C—CH_2$ bond in solution; the reaction takes place with retention of configuration at the ruthenium atom.

Nucleophilic attack on alkoxycarbene complexes normally takes place at the carbene atom [1] and the reaction of various hydrides with $[CpFeLL'C(OR)(R')]^+$ provides a standard route to η^1-α-alkoxyalkyl complexes $[M]—CH(OR)R'$ [2]. In contrast, when $[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH(CH_3)PPh_2\}\{C(OCH_3)CH_2C_6H_5\}]PF_6$ * (1) is treated with $LiAlH_4$ in tetrahydrofuran at —80°C, the product obtained after hydrolysis with water and extraction into benzene is shown by ^1H and ^{31}P NMR spectroscopy to be almost exclusively (>95%) $(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH(CH_3)PPh_2\}CH_2CH_2C_6H_5$ (2) (Scheme 1 and Table 1). The only similar reaction of a hydride with an alkoxycarbene complex that we are aware of is that of $[(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)\{C(CO_2H_5)CH_3\}]BF_4$ with $NaBH_4$, which yields ca. 50% of the corresponding ethyl complex in addition to the normal η^1-α-ethoxyethyl complex [6].

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*Complex 1 was prepared [3] from $(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH(CH_3)PPh_2\}Cl$ [4], phenylacetylene, and KPF_6 in boiling methanol [5].

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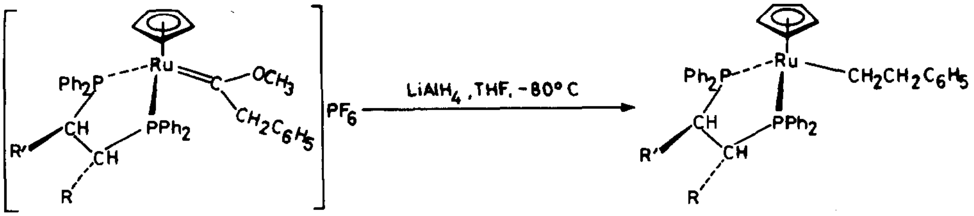

1 R=R'=CH3 2

3 R=CH3,R'=H 4

3' R=H, R'=CH3 4'

SCHEME 1

TABLE 1

NMR PARAMETERS OF 2 [a]

P	97.0 and 83.1: J(P—P) 42.0
η-C_5H_5	4.62 84.0
CH_3	0.71 [b]; J(H—H) 6.7; J(P—H) 10.4 13.8; J(C—P) 4.6 and 18.4
CH_3	0.78 [b]; J(H—H) 7.1: J(P—H) 10.4 15.8; J(C—P) 4.6 and 16.9
CH	1.52; J(H—H) 6.7 and 10.5; J(P—H) 4.8 and 9.5 36.0; J(C—P) 17.6 and 29.3
CH	2.25 [b]; J(H—H) 6.7 and 9.6; J(P—H) n.d. 42.8; J(C—P) 21.9 and 28.1
CH_2^{α}	0.60 [b]; J(H—H) 11.0, 13.3 and 4.4; J(P—H) 3.0 and 8.8 0.84 [b]; J(H—H) 11.4, 13.2 and 4.8; J(P—H) 4.4 and 7.6 5.1; J(C—P) 11.0
CH_2^{β}	1.91; J(H—H) 14.0, 14.0 and 4.1 2.26 [b]; J(H—H) 14.0, 14.0 and 3.8 44.1
C_6H_5	6.8—7.8 150—126

[a] The spectra were recorded with benzene solutions on a Bruker AM 300 WB; frequencies are in ppm (relative to external TMS or H_3PO_4) and coupling constants in Hz. [b] Partially or completely overlapping signals.

The ruthenium product 2 can be isolated pure (~70% yield) by crystallization from benzene/pentane (yellow crystals), and the elemental analysis is consistent with the formula given. Use of $LiAl^2H_4$ as the reducing agent followed by hydrolysis with water gives (η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}-$C^2H_2CH_2Ph$ (2-$^2H_2$). Complete deuteriation at the α-position of the 2-phenylethyl substituent is revealed not only by integration of the ^1H NMR spectrum, but also by the fact that the two benzylic hydrogen atoms appear as an AB quartet (J ~ 14 Hz). Similar results were reported for the aforementioned iron complex [6].

The structure of 2 was confirmed by multinuclear NMR spectroscopy (Table 1) and by a DEPT experiment [7]. Furthermore, a two-dimensional J-resolved procedure [7] allowed separation of H—H and P—H coupling constants (reported in Table 1). The vicinal J(H—H) coupling constants (~4 and

14 Hz) found for the hydrogen atoms on the two methylene groups indicate, on the basis of the Karplus relationship [8], that the most abundant conformer for (2) in solution is that for which the largest substituents on the C—C bond are antiperiplanar. The similarity of the two J(P—H) for the two protons on the α-methylene group may again imply an antiperiplanar situation for the η-C_5H_5 ligand on the ruthenium atom and for the benzylic substituent on the carbon atom [9]. Reaction of (η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}Cl [4] with $C_6H_5CH_2CH_2MgBr$ also gives 2 together with ~60% of the corresponding hydrido complex (η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}H. Hydrido complex formation strongly competes with alkylation when halide complexes are treated with alkylating reagents which have available β-hydrogens.

We have synthesized $(S)_{Ru'}(R)_C$-3 and $(R)_{Ru'}(R)_C$-[(η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}{$C(OCH_3)CH_2C_6H_5$}]PF_6 (3′) stereospecifically starting from $(S)_{Ru'}(R)_C$-5 and $(R)_{Ru'}(R)_C$-(η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}Cl (5′), respectively [3]. The analogous reaction of either of the diastereomers 3 and 3′ with $LiAlH_4$ in THF at −80°C gives the corresponding $(S)_{Ru'}(R)_C$-4 and $(R)_{Ru'}(R)_C$-(η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}$CH_2CH_2C_6H_5$ (4′) complexes. According to the ^1H and ^{31}P NMR spectra (Table 2) of the crude reaction products recovered as previously described, the reaction is stereospecific within the limits of the NMR detection (±2%). The structure of 4 and 4′ is again confirmed by correct elemental analysis, by DEPT experiments and by comparison of their ^{31}P and ^1H NMR spectra with those of the products from reactions of either 5 or 5′ with $C_6H_5CH_2CH_2MgBr$; in these latter reactions a mixture of the hydrido complexes [11] $(S)_{Ru'}(R)_C$-6 and $(R)_{Ru'}(R)_C$-(η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}H (6′) is again formed, together with the corresponding alkyl complexes 4 and 4′. We have previously determined the stereochemical course of the alkylation of 5 and 5′ [11], and observed retention of configuration at the ruthenium atom. The reaction of diastereomerically pure 5 or 5′ with $C_6H_5CH_2CH_2MgBr$ gives diastereomerically pure 4 or 4′, with NMR parameters identical to those of 4 and 4′ obtained from 3 and 3′, respectively. Thus the transformation of the methoxybenzylcarbene complexes

TABLE 2

NMR-PARAMETERS OF COMPLEXES 4 AND 4′ [a]

Group	4		4′	
	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$
CH	1.30 [b]	31.3	2.08—2.37 [c]	38.7
CH_2	2.40 [b,c]	37.1		37.2
CH_3	0.81 [c]	16.7	0.90 [c]	16.0
α-CH_2	0.75—0.95 [c]	6.2	0.77—1.02 [c]	4.8
β-CH_2	2.31 [c]; 1.80	44.3	2.08—2.37 [c]	45.6
η-C_5H_5	4.77	82.9	4.66	83.5
C_6H_5	6.74—7.70	124—150	6.82—7.76	125—150
P	100.4; 74.3; J(P—P) 35.7		89.6; 82.4; J(P—P) 36.3	

[a] Same conditions as in Table 1. [b] Signals may be interchanged. [c] Partially or completely overlapping signals.

3 and 3′ into the 2-phenylethyl complexes 4 and 4′ must take place stereospecifically, with retention of the configuration at the ruthenium atom. The stereochemical and labelling results show that the reaction in Scheme 1 can be defined as a nucleophilic displacement of the methoxy group accompanied by a nucleophilic addition involving only the carbene ligand, but the available data do not reveal the chronological order of these two processes or provide the basis for more detailed mechanistic proposals.

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