

Preliminary communication

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

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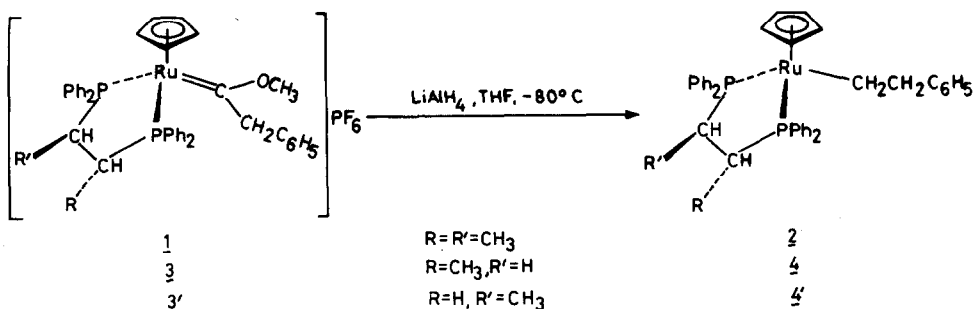
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Summary

$[(\eta\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCHRCHR}'\text{PPh}_2\}\{\text{C}(\text{OCH}_3)\text{CH}_2\text{C}_6\text{H}_5\}]\text{PF}_6$ (where $\text{R}, \text{R}' = \text{H}$ 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 $\text{H}_2\text{C}-\text{CH}_2$ bond in solution; the reaction takes place with retention of configuration at the ruthenium atom.

Nucleophilic attack on alkoxy-carbene complexes normally takes place at the carbene atom [1] and the reaction of various hydrides with $[\text{CpFeLL}'\text{C}(\text{OR})\text{-(R')}]^+$ provides a standard route to η^1 - α -alkoxyalkyl complexes $[\text{M}]-\text{CH}(\text{OR})\text{R}'$ [2]. In contrast, when $[(\eta\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{-PPh}_2\}\{\text{C}(\text{OCH}_3)\text{CH}_2\text{C}_6\text{H}_5\}]\text{PF}_6$ * (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 ($>95\%$) $(\eta\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2\}\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ (2) (Scheme 1 and Table 1). The only similar reaction of a hydride with an alkoxy-carbene complex that we are aware of is that of $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\{\text{C}(\text{CO}_2\text{H}_5)\text{CH}_3\}]\text{BF}_4$ with NaBH_4 , which yields ca. 50% of the corresponding ethyl complex in addition to the normal η^1 - α -ethoxyethyl complex [6].

*Complex 1 was prepared [3] from $(\eta\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2\}\text{Cl}$ [4], phenylacetylene, and KPF_6 in boiling methanol [5].



SCHEME 1

TABLE 1

NMR PARAMETERS OF 2^a

P	97.0 and 83.1: $J(\text{P}-\text{P})$ 42.0
$\eta\text{-C}_5\text{H}_5$	4.62 84.0
CH_3	0.71 ^b ; $J(\text{H}-\text{H})$ 6.7; $J(\text{P}-\text{H})$ 10.4 13.8; $J(\text{C}-\text{P})$ 4.6 and 18.4
CH_3	0.78 ^b ; $J(\text{H}-\text{H})$ 7.1; $J(\text{P}-\text{H})$ 10.4 15.8; $J(\text{C}-\text{P})$ 4.6 and 16.9
CH	1.52; $J(\text{H}-\text{H})$ 6.7 and 10.5; $J(\text{P}-\text{H})$ 4.8 and 9.5 36.0; $J(\text{C}-\text{P})$ 17.6 and 29.3
CH	2.25 ^b ; $J(\text{H}-\text{H})$ 6.7 and 9.6; $J(\text{P}-\text{H})$ n.d. 42.8; $J(\text{C}-\text{P})$ 21.9 and 28.1
CH_2^α	0.60 ^b ; $J(\text{H}-\text{H})$ 11.0, 13.3 and 4.4; $J(\text{P}-\text{H})$ 3.0 and 8.8 0.84 ^b ; $J(\text{H}-\text{H})$ 11.4, 13.2 and 4.8; $J(\text{P}-\text{H})$ 4.4 and 7.6 5.1; $J(\text{C}-\text{P})$ 11.0
CH_2^β	1.91; $J(\text{H}-\text{H})$ 14.0, 14.0 and 4.1 2.26 ^b ; $J(\text{H}-\text{H})$ 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 LiAlH_4 as the reducing agent followed by hydrolysis with water gives $(\eta\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2\}\text{-C}^2\text{H}_2\text{CH}_2\text{Ph}$ ($2\text{-}^2\text{H}_2$). Complete deuteration 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 ($J \sim 14$ 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 $J(\text{H}-\text{H})$ 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 $J(\text{P—H})$ for the two protons on the α -methylene group may again imply an antiperiplanar situation for the $\eta\text{-C}_5\text{H}_5$ ligand on the ruthenium atom and for the benzylic substituent on the carbon atom [9]. Reaction of $(\eta\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2\}\text{Cl}$ [4] with $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{MgBr}$ also gives 2 together with $\sim 60\%$ of the corresponding hydrido complex $(\eta\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2\}\text{H}$. Hydrido complex formation strongly competes with alkylation when halide complexes are treated with alkylating reagents which have available β -hydrogens.

We have synthesized $(S)_{\text{Ru}}(R)_{\text{C-3}}$ and $(R)_{\text{Ru}}(R)_{\text{C-}}[(\eta\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}_2\text{PPh}_2\}\{\text{C}(\text{OCH}_3)\text{CH}_2\text{C}_6\text{H}_5\}]\text{PF}_6$ (3') stereospecifically starting from $(S)_{\text{Ru}}(R)_{\text{C-5}}$ and $(R)_{\text{Ru}}(R)_{\text{C-}}(\eta\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}_2\text{PPh}_2\}\text{Cl}$ (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 $(S)_{\text{Ru}}(R)_{\text{C-4}}$ and $(R)_{\text{Ru}}(R)_{\text{C-}}(\eta\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}_2\text{PPh}_2\}\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ (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 ($\pm 2\%$). 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 $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{MgBr}$; in these latter reactions a mixture of the hydrido complexes [11] $(S)_{\text{Ru}}(R)_{\text{C-6}}$ and $(R)_{\text{Ru}}(R)_{\text{C-}}(\eta\text{-C}_5\text{H}_5)\text{Ru}\{\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}_2\text{PPh}_2\}\text{H}$ (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 $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{MgBr}$ 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'	
	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$
CH	1.30 ^b	31.3		38.7
CH ₂	2.40 ^{b,c}	37.1	2.08–2.37 ^c	37.2
CH ₃	0.81 ^c	16.7	0.90 ^c	16.0
$\alpha\text{-CH}_2$	0.75–0.95 ^c	6.2	0.77–1.02 ^c	4.8
$\beta\text{-CH}_2$	2.31 ^c ; 1.80	44.3	2.08–2.37 ^c	45.6
$\eta\text{-C}_5\text{H}_5$	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; $J(\text{P—P})$ 35.7		89.6; 82.4; $J(\text{P—P})$ 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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References

- 1 F.R. Kreissl in *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, 1983, p. 152; K.H. Dötz, *ibid.*, p. 192; N.M. Kostic and R.F. Fenske, *Organometallics*, 1 (1982) 528.
- 2 M.L.H. Green, L.C. Mitchard, and M.G. Swanwick, *J. Chem. Soc. A*, (1971) 794; T. Bodnar, S.J. La Croce, and A.R. Cutler, *J. Am. Chem. Soc.*, 102 (1982) 3292; T. Bodnar and A.R. Cutler, *J. Organomet. Chem.*, 213 (1981) C31.
- 3 G. Consiglio, F. Morandini, G. Ciani and A. Sironi, in preparation.
- 4 F. Morandini, G. Consiglio, B. Straub, G. Ciani and A. Sironi, *J. Chem. Soc., Dalton Trans.*, (1983) 2293.
- 5 M.I. Bruce and A.G. Swincer, *Aust. J. Chem.*, 33 (1980) 1471.
- 6 A. Davison and D.L. Reger, *J. Am. Chem. Soc.*, 94 (1972) 9237.
- 7 R. Benn and G. Guenther, *Angew. Chem.*, 95 (1982) 381 and ref. therein; see also L.W. Jelinski; *Chem. Eng. News*, (1984) 26.
- 8 E.D. Becker, *High Resolution NMR*, 2nd edit., Acad. Press, New York, 1980, p. 102.
- 9 J.I. Seeman and S.G. Davies, *J. Chem. Soc., Chem. Commun.*, (1984) 1019.
- 10 H. Lehmkuhl, J. Gründke, and R. Mynott, *Chem. Ber.*, 116 (1983) 159, G. Consiglio, F. Morandini and V. Lucchini, *Organometallics*, 4 (1985) 1202.
- 11 G. Consiglio, F. Morandini, G. Ciani and A. Sironi, *Angew. Chem.*, 95 (1983) 322.