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Preliminary communication

BUTADIENERUTHENIUM TRICARBONYL

XIV*. ^{13}C NMR SPECTROSCOPY

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Summary

The synthesis of 1,3-butadieneruthenium tricarbonyl from 1,5-cyclooctadieneruthenium tricarbonyl and butadiene is described. A comparison of H,H and C,H spin coupling data reveals that very similar distortions of the diene ligand occur in 1,3-butadieneruthenium tricarbonyl and the corresponding iron complex.

The ruthenium and osmium analogues of 1,3-butadieneiron tricarbonyl (I) have not previously been described. The reaction of 1,3-butadiene with $Ru_3(CO)_{12}$ in refluxing benzene was reported not to give butadieneruthenium tricarbonyl, but instead a hydridoruthenium cluster $HRu_3(CO)_9C_4H_5$ [2]. 1,4-Disubstituted and 2,3-disubstituted butadienes [2,3], however undergo a direct reaction with $Ru_3(CO)_{12}$ to yield the expected mononuclear ruthenium tricarbonyl complexes.

In the course of our studies on the structure of tricarbonyliron complexed dienes, we have analysed the high-resolution proton-coupled ^{13}C spectrum of butadieneiron tricarbonyl [1]. The combination of vicinal C,H and H,H coupling constants as well as other spin coupling constants were shown to provide detailed information about the distortion of the complexed diene ligand. The question now arises to which extent this distortion depends upon the nature of the transition metal. Therefore, we were interested in synthesizing the unsubstituted butadieneruthenium tricarbonyl (III) and analysing its proton and carbon NMR spectra.

1,5-Cyclooctadieneruthenium tricarbonyl (II) [4] was previously shown to react with various diene systems in ligand exchange reactions [5]. Thus we treated II with 1,3-butadiene in benzene (sealed tube) for 1 h at 100°C. The

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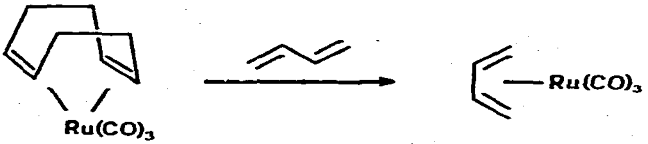
[*] For part XIII see ref. 1.

product was purified by chromatography (silica/pentane) to give 1,3-butadieneruthenium tricarbonyl (III) as a colourless oil in 50% yield.



II

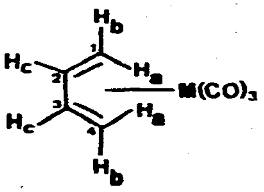
III

After short-path distillation at 20°C (0.005 Torr) on to a coldfinger, the complex showed an m.p. of ~10°C. Further characterization was achieved by elemental analysis, mass spectrum, IR, and ^{1}H and ^{13}C NMR spectroscopy. IR: CO stretching frequencies (in n-hexane) 2069s, 2006vs, 1995s cm^{-1}. Mass spectrum (70 eV): 240 (20, M^+), 212 (45, $M^+ - $ CO), 184 (12, $M^+ - $ 2CO), 156 (100, $M^+ - $ 3CO), 130 (42), 102 (32), 54 (63). ^{1}H NMR (C_6D_6, 100 MHz): 0.12 (2H), 1.44 (2H), 4.88 ppm (2H); H,H coupling constants see Table 1. ^{13}C NMR (C_6D_6, 25.2 MHz): 32.74, 86.31, 197.50 ppm; C,H coupling constants see Table 1.

TABLE 1

H,H AND C,H COUPLING CONSTANTS OF I AND III[a]

		III (M = Ru)	I (M = Fe)
J(H,H)	1a,2c	8.65	9.33
[Hz]	1b,2c	6.94	6.93
	2c,3c	4.60	4.70
	1a,1b	−2.77	−2.42
	1a,4a	−0.30	−0.31
	1a,4b	−0.13	−0.09
	1a,3c	−1.10	−1.11
	1b,3c	1.10	1.14
	1b,4b	0.02	0.05
J(C,H)	1,1a	159.62	161.52
[Hz]	1,1b	156.17	157.97
	1,2c	3.64	3.39
	1,3c	7.66	7.75
	1,4a	0.69	0.37
	1,4b	1.64	1.71
	2,1a	−0.02	−0.02
	2,1b	−0.82	−0.90
	2,2c	168.16	169.12
	2,3c	2.67	2.30
	2,4a	3.93	4.12
	2,4b	8.94	9.37



[a] The error for J(H,H) and J(C,H) is ± 0.02 Hz, as reported also for complex I [1].

The six-spin proton spectrum of III is of the type AA'MM'XX'. It was analysed starting from a set of coupling constants obtained from the iron complex. Subsprectral analysis and iterative computer simulation (LAOCOON-3) on 122 experimental line frequencies then gave the final set of parameters listed in Table 1. In the proton-coupled ^{13}C spectrum 48 lines could be resolved of the terminal carbon C(1) and 32 lines of the central carbon C(2).

These spectra were analysed by a procedure closely analogous to that used for the iron complex [1]. In particular, the assignment and relative signs of the geminal coupling constants $J_{2,1a}$, $J_{2,1b}$, $J_{2,3c}$ as well as the negative sign of the geminal H,H coupling constant $J_{1a,1b}$ were taken from ref. 1.

A comparison of C,H and H,H spin couplings in the butadieneiron tricarbonyl (I) and the butadieneruthenium tricarbonyl (III) (Table 1) shows, in general, very similar data for both complexes. The difference in the electronegativities* of Fe and Ru does not appear to be reflected in the coupling constants. Significant differences are observed in the ^1J(C,H), ^3J(C,H), ^3J(H,H) and ^2J(H,H) data. The ^1J(C,H) coupling constants which are known to increase upon complexation of the parent hydrocarbon by a tricarbonyliron moiety show a small (1—2 Hz) but significant decrease upon going from the iron to the ruthenium complex. In the H,H coupling constants, the selective decrease of $^3J_{1a,2c}$ suggests that H_a is more twisted below the plane of the carbon skeleton than in the iron complex. This is equivalent to a slight rehybridization at C(1), and is also reflected in ^2J(H,H), which becomes more negative. The negative sign of this coupling constant (in contrast to that of uncomplexed butadiene) has been interpreted, in the case of the iron complex, in terms of a substantial rehybridization towards sp^3, i.e., a decrease in the HCH bond angle. This model, when applied to the structure of the ruthenium complex, may account for the decrease in the ^1J(C,H) coupling constants of the terminal carbon atom. The *cis* and *trans* vicinal C,H coupling constants ($J_{2,4a}$, $J_{2,4b}$) across the terminal C,C bond are both about 5% smaller than in the iron complex. It is known from X-ray analysis of several dieneruthenium tricarbonyl complexes [6] that the terminal C,C bond is longer (1.41—1.45 Å) than the central C,C bond (1.39—1.41 Å). For tricarbonyliron complexes the two bond lengths are very close with an average value of 1.41 Å [7]. Thus, the decrease in the vicinal C,H coupling constants may indicate an increased C(1)—C(2) bond length in butadieneruthenium tricarbonyl. Further work on various ruthenium complexes is in progress, including the study of one-bond C,C coupling constants**.

Acknowledgement

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References

1 K. Bachmann and W. von Philipsborn, Org. Mag. Res., 9 (1977) in press.
2 O. Gambino, M. Valle, S. Aime and G.A. Vaglio, Inorg. Chim. Acta, 8 (1974) 71.
3 B.F.G. Johnson, R.D. Johnston, P.L. Josty, J. Lewis and I.G. Williams, Nature, 213 (1967) 901.
4 F.A. Cotton, A.J. Deeming, P.L. Josty, S.S. Ullah, A.J.P. Domingos, B.F.G. Johnson and J. Lewis, J. Amer. Chem. Soc., 93 (1971) 4624.
5 A.J.P. Domingos, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 49 (1973) C33.
6 F.A. Cotton and R. Eiss, J. Amer. Chem. Soc., 91 (1969) 6593; R. Goddard, A.P. Humphries, S.A.R. Knox and P. Woodward, J. Chem. Soc., Chem. Commun., (1975) 507; K.W. Muir and R. Walker, Ibid., (1975) 698.
7 S.M. Johnson and I.C. Paul, J. Chem. Soc. B, (1970) 1783. A. Immirzi, J. Organometal. Chem., 76 (1974) 65. G.I. Birnbaum, J. Amer. Chem. Soc., 94 (1972) 2455. K.B. Birnbaum, Acta Cryst. B, 28 (1972) 161.

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*Fe (1.6), Ru (1.4) (Allred—Rochow); Fe (1.8), Ru (2.2) (Pauling).

** *Note added in proof.* Meanwhile the direct synthesis of III has been achieved in 35% yield from