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Preliminary communication

INTRAMOLECULAR REARRANGEMENT IN DIENETRICARBONYLRUTHENIUM AND OLEFINTETRACARBONYLRUTHENIUM TYPE COMPLEXES

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Summary

Variable temperature ^{13}C NMR spectra of dienetricarbonylruthenium and olefintetracarbonylruthenium type complexes are reported. It is shown that the molecules are fluxional and that the rearrangement in (ethyl acrylate)-tetracarbonylruthenium is consistent with a coupled olefin rotation—Berry pseudorotation type mechanism.

We are witnessing a current, active interest in the study of intramolecular rearrangement in five coordinated dienetricarbonyliron [1,2] and olefintetracarbonyliron [3,4] complexes. Our interest in the subject led us to examine the analogous ruthenium complexes in an effort to identify the metal dependence of the rearrangement. In this report we wish to communicate on results of a limited number of complexes* which nevertheless clearly establish two things: first, the ruthenium complexes are fluxional, second, the activation barriers are slightly higher in ruthenium than in the analogous iron complexes. Indeed our report appears to offer the first unambigous demonstration of this. In previous studies on $(\eta\text{-}C_5H_5)M(CO)_2\text{-}(\eta^1\text{-}C_5H_5)$ [5,6] the differences in activation energies, albeit higher for ruthenium complexes, are very close [5] or within [6], the experimental errors of the measurement.

Table 1 summarizes ^{13}C chemical shift data in the carbonyl region and the associated activation parameters for rearrangement in the reported complexes. For sake of comparison the iron complexes are also included in Table 1.

The low temperature limiting spectrum is consistent with square pyramidal arrangement with one apical and two equivalent basal CO groups for dienetricarbonylmetal and trigonal bipyramidal geometry with olefin occupying

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*It is to be remembered that such ruthenium complexes are still very rare and that the only olefintetracarbonylruthenium reported to date is that of the unstable ethylenetetracarbonylruthenium [7] identified only by its IR spectrum.

TABLE 1 [d]

^{13}C NMR SPECTRA OF THE REPORTED COMPLEXES $\delta(^{13}CO)$ (TMS = 0 ppm)

Compound	Low temperature limit (°C)	High temperature limit (°C)	$\Delta H^{\neq}$ (kcal/mole)	$\Delta S^{\neq}$ (eu)	$\Delta G^{\neq}_{298}$ (kcal/mole)
(Ethyl acrylate)tetracarbonyliron (I)	209.8, 208.9, 208.2 207.4 (−80)	208.8 (+10)	10.7 ± 0.3	−0.1 ± 1.3	10.7 ± 0.5
(Ethyl acrylate)tetracarbonylruthenium (II)	197.8, 195.7, 194.8, 193.7 (−60)	195.6 (+25)	11.9 ± 0.3	−0.7 ± 1.1	12.1 ± 0.4
(Diethyl fumarate) tetracarbonyliron (III)	206.6, 204.8, (−30)	205.8 (+20)	13.8 ± 0.5	3.4 ± 2	12.8 ± 0.8
(Diethyl fumarate) tetracarbonylruthenium (IV)	194.1, 191.5 (0)	192.7 (+60)	17.6 ± 0.4	7.6 ± 1.3	15.4 ± 0.6
Tetrakis(trifluoromethyl)cyclopentadienonetricarbonyliron (V) [a]	202.4, 199.6 [c] (−70)	200.5 (35)	9.7 ± 0.4	−4.8 ± 1.9	11.1 ± 0.5
Tetrakis(trifluoromethyl)cyclopentadienone tricarbonyliron (VI) [b]	197.9, 186.3 [c] (−60)	187.2 (−17)	11.8 ± 0.7	−1.3 ± 3.0	12.2 ± 0.8

[a] Prepared according to ref. 10 [b] Prepared according to ref. 11. [c] First entry (intensity = 1) assigned to the axial CO, second entry (intensity = 2) to the basal CO's. [d] ^{13}C NMR of II, IV recorded in toluene-d_8; I, III in CD_2Cl_2 and V, VI in acetone-d_6. $\Delta H^{\neq}$, $\Delta G^{\neq}_{298}$ were obtained from full line shape analysis as described previously [1,3].

an equatorial site for olefintetracarbonylmetal complexes[*]. The high temperature singlet implies rearrangements which will average out the different carbonyl environments.

As we pointed out earlier [1] this can be accomplished in the case of dienetricarbonylmetal by diene rotation or carbonyl scrambling. The essentially identical activation energies of butadiene- and tetrakis(trifluoromethyl)cyclopentadienonetricarbonyliron [1] speak against diene rotation. Whether this prevails in the ruthenium complexes is not yet known.

The observation of single lines at high temperatures for the two olefintetracarbonylruthenium complexes again rules out simple olefin rotation as sole operator and indicates that the previously observed [3,4] coupled olefin rotation—Berry rearrangement is also operating here. As expected for the above mechanism, the barrier to rearrangement increases with the π-acidity of the olefin, i.e. ethylacrylate < fumarate. It is also interesting to observe that on going from iron to ruthenium we see a larger coordination shift of the bound olefin[**] which most probably reflects larger metal—$\pi^\star$ interaction in the ruthenium—olefin bond [8,9] with concomitant increase in the rearrangement barrier, again consistent with the above proposed mechanism. Finally, experimental and computer generated spectra of II in the exchange region are shown in Fig.1. In the slow exchange region (K = 2-12 sec^{-1}) all four resonances collapse at exactly the same rate, consistent with a Berry type process. The highest field resonance (an axial CO) in the analogous iron complex (I) remains sharp in this slow exchange region and implies mechanistic distinctions between iron and ruthenium[***]. Of the six possible assignments of the four resonances to axial and equatorial sites in II, (eeaa = aaee (1), aeea = eaae (2), and eaea = aeae (3)), a choice between only 3 cases can be made because of the invariance of the NMR experiment to labelling. The assignment (eeaa) is consistent with the observed collapse pattern at intermediate exchange rates (K = 30 sec^{-1}) and with the necessity to assign axial CO's to high field[****].

The compounds olefintetracarbonylruthenium (olefin = ethylacrylate, fumarate) were synthesized by the method of Lewis [7] by photolysis of $Ru_3(CO)_{12}$ in the presence of excess ethyl acrylate and diethyl fumarate in heptane for ~60 hours. The complexes II and IV were isolated as orange liquids after filtration and removal of the solvent under high vacuum.

The new complexes were characterized by IR, ^{13}C NMR and mass spectroscopy.

Carbonyl stretching frequencies in heptane. II: 2119 w, 2047 s, 2032 s, 2006 s (cm^{-1}); IV: 2131 vw, 2063 s, 2049 w, 2016 m (cm^{-1}).

Mass spectra. II: 314 (Parent ion); and successive loss of 4 CO; IV: 358 (Parent ion — CO); and successive loss of 3 CO.

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[*] Of course such ground state geometry in the solid state is well established for the iron compounds.

[**] Upfield shifts of the olefin on coordination in ppm are: 89.1 for III, 96.4 for IV, 68.7 ($=CH_2$) and 84.6 (=C(H)(COOEt)) for I, 78.7 ($=CH_2$) and 92.4 (=C(H)(COOEt)) for II.

[***] Further work to prove this point is being carried out.

[****] The axial ^{13}CO resonance to high field of the equatorial ^{13}CO resonance has been observed and can be unambiguously assigned in a number of (olefin)Fe$(CO)_4$ complexes(olefin = diethylmaleate, hexafluorocyclobutene, 1,1-difluoroethylene).

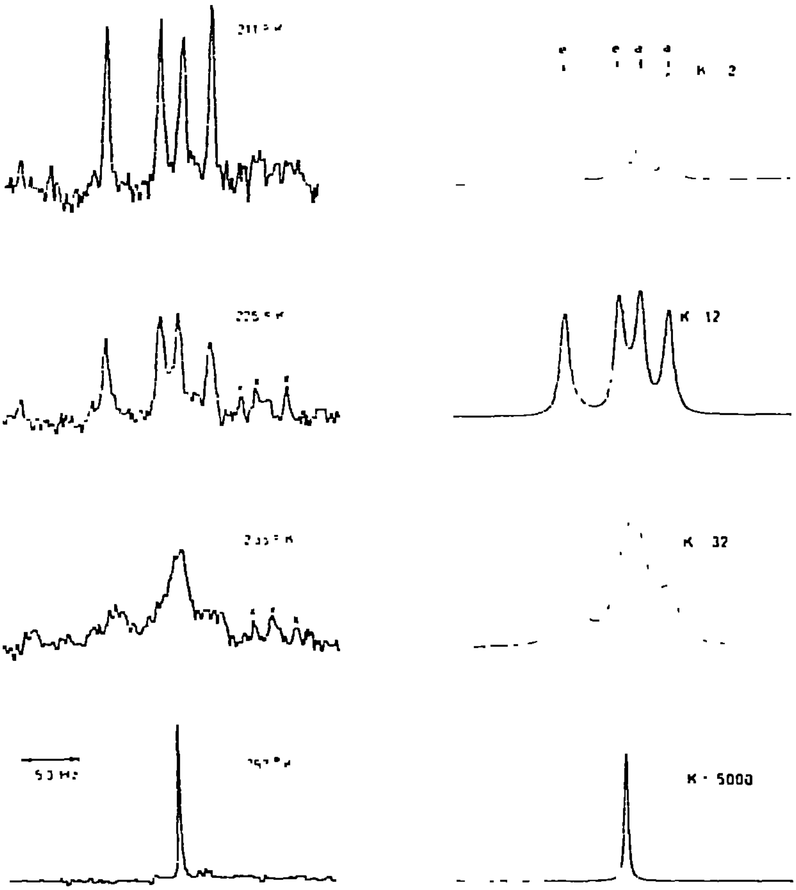

Fig. 1. Observed and calculated temperature dependent ^{13}C NMR spectra of (ethylacrylate)Ru(CO)$_4$ in the CO region. Peaks marked with x are unknown impurities. *K* in sec^{-1}.

We have also prepared the corresponding diethyl maleate complex. However quite unexpectedly this complex undergoes facile thermal (50°C) conversion to the fumarate complex, whereas irradiation brings about this conversion in the iron complex. This contrasting behavior and the rearrangement in related olefintetracarbonylruthenium complexes is currently under investigation.

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