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XVII*. THE ORIENTATION OF THE π-ALLYL LIGAND IN π-CYCLOPENTADIENYL AND π-INDENYL COMPLEXES OF IRON AND RUTHENIUM

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Summary

Only one isomer has been found for π-allyl derivatives of π-C_5H_5-π-$C_3H_5M(CO)$ and π-C_9H_7-π-$C_3H_5M(CO)$ (M = Fe, Ru) in purified samples This isomer does not convert to the other on prolonged standing in solution and it has been assigned the configuration where the *anti* protons are away from the ring.

Studies of π-cyclopentadienyl-π-allylmolybdenum dicarbonyl and its derivatives have shown the presence of conformational equilibria between two species differing principally in the orientation of the allyl moiety [1 - 4]. We have recently presented a reliable method for assigning given configurations based upon the large magnetic anisotropies found to be associated with indenyl derivatives [1,2]. An investigation of some analogous iron and ruthenium complexes has been attempted to determine whether similar equilibria can exist for the monocarbonyl complexes π-C_5H_5-π-$C_3H_5M(CO)$ (where M = Fe or Ru). Indenyl derivatives have also been synthesized in order to assign configurations on the basis of the magnetic anisotropies.

The preparation of π-cyclopentadienyl-π-allyliron carbonyl was previously reported in 1963 [5]. Recently King has reported the synthesis of the ruthenium analog [6] and indicated that both isomers (presumed to be similar to those observed in molybdenum and tungsten) were present. The two isomers differ in the orientation of the allyl moiety, as seen in Fig. 1.

We have synthesized both the cyclopentadienyl and indenyl complexes of π-allyl-iron and -ruthenium and also the cyclopentadienyl-π-methallyliron. The complexes are highly air-sensitive and decompose rapidly in solution unless sealed under a vacuum or an inert atmosphere. The problems encountered in

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[*] For part XVI see ref 1.

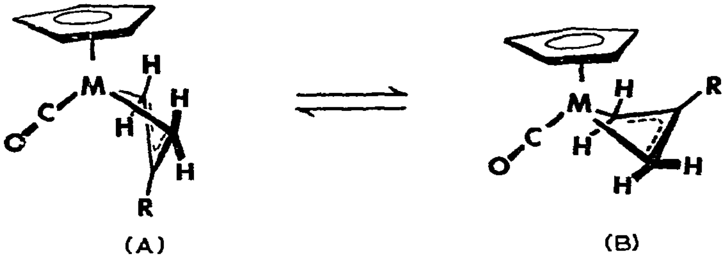

Fig 1

the stability of these complexes appear more pronounced in the indenyl derivatives; hence, extensive preparation of homologs was not pursued

Contrary to the findings of King and Ishaq [6], throughout this series of compounds we have observed only one isomer to be present in the final products. The carbonyl stretching frequencies contain only one band for each compound, all occurring around 1950 cm^{-1} This is in contrast to the molybdenum and tungsten cases, where a mixture of isomers was evidenced by separate carbonyl bands for each, differing by about 10 cm^{-1} Furthermore, the NMR spectra show only one pattern of proton resonances

On the basis of the chemical shifts and coupling constants in the NMR spectra, all of the complexes appear to have the configuration (B), in which the central carbon of the allyl is oriented toward the aromatic ring In comparing the cyclopentadienyl and indenyl compounds, an upfield shift is expected for protons which approach nearest the ring, i.e. the *anti* protons of the allyl in (A) and the central proton in (B) [1,2]. Both iron and ruthenium complexes show a much greater upfield shift for the central proton, identifying the isomers as (B). For ruthenium the upfield shift is +1.22 ppm, while for iron it is +0.94. The chemical shifts may be found in Table 1. The assignment of the complexes as isomer (B) can be inferred from the observed *syn—anti* coupling of the allylic protons. In the complexes of molybdenum and tungsten, a coupling of ≈2 Hz was observed in isomers where the allyl was oriented as in (B) of Fig. 1 [1] For isomer (A), the splitting was found to be <0.6 Hz. The observed splittings must be interpreted in terms of coupling constants with care because of the complications introduced by the AA'BB'X spin system Nevertheless, the larger splittings are readily observed in the iron and ruthenium allyls (see Table 2). Assuming the same trends as in the molybdenum complexes, these couplings suggest that configuration (B) is present. It is particularly significant that the

TABLE 1

NMR AND INFRARED DATA FOR SOME π-ALLYL COMPLEXES

M	Allyl	Ring	*central*[a]	*syn*[a]	*anti*[a]	ν(CO)[b]	$\nu(^{13}CO)$[b]
Fe	π-Allyl	C_5H_5	4.35	2.71	0.49	1953	1932
Fe	π-Allyl	C_9H_7	3.41	2.26	0.10	1944	1924
Ru	π-Allyl	C_5H_5	3.94	2.80	1.18	1955	1935
Ru	π-Allyl	C_9H_7	2.72	2.37	0.95	1950	1931
Fe	2-Methallyl	C_5H_5	(1.98)[c]	2.63	0.47	1947	1928

[a] Chemical shifts are given in ppm downfield from TMS at 100 MHz in CS_2 at room temperature [b] Carbonyl stretching frequencies are given in cm^{-1} as observed in cyclohexane solutions [c] Methyl resonance

TABLE 2

COUPLING CONSTANTS (Hz)

M	Allyl	Ring	N^a	$J(H_cH_a)$	$J(H_cH_s)$
Fe	π-Allyl	C_5H_5	2 4	11 1	6 9
Fe	π-Allyl	C_9H_7	b	10 5	7 0
Ru	π-Allyl	C_5H_5	2 4	10 5	6 8
Ru	π-Allyl	C_9H_7	2 0	10 5	7 1
Fe	2-Methyallyl	C_5H_5	2 4		

[a] N is the observed splitting between the outer lines of an AA'BB' spectrum and corresponds to $J(H_{sa}) + J(H_{sa'})$ In an AA'BB'X spectrum additional splittings are observed, so that N is an approximate expression Paramagnetic impurities prevented the measurement of N

methallyl derivative also appears to be (B), as substitution on the central allyl carbon of the methyl group provided enough interaction in the case of the molybdenum analogs to drastically favor the (A) configuration [1].

The magnitude of the upfield shift for the (B) isomer of the molybdenum allyl is much greater (δ_{anis} +3.46 ppm) than that of the iron (+0 94 ppm) or ruthenium (+1 22 ppm). Presumably these shifts can be attributed to the "ring current" of the six-membered ring of the indenyl group. Using the model which proved successful for the molybdenum complexes [1], calculation of the maximum shift for the iron or ruthenium systems is approximately 2 0 ppm as compared to 4.5 ppm for the molybdenum system. This difference arises from the adjustment of angle parameters to those appropriate for structures of the type π-$C_5H_5M(CO)L$ (M = Fe or Ru). The loss of a preferred orientation is characterized by a reduction in magnitude of the indenyl-induced shifts and a splitting of the equivalency of the 4, 5, 6, and 7 indenyl protons. For the molybdenum system the 4,7 and 5,6 protons were separated by nearly 0.3 ppm A similar splitting of these protons was found in both π-C_9H_7-π-$C_3H_5Ru(CO)$ (0.18 ppm) and π-C_9H_7-π-$C_3H_5Fe(CO)$ (0.16 ppm) This suggests that the geometric arrangement about Fe or Ru produces less steric interaction of the allyl with the ring and electronic factors influencing ring orientation are less pronounced than in the molybdenum and tungsten systems The upfield shift of the central proton is significantly larger than that of either the *syn* or *anti* protons Furthermore, the *anti* protons resonate at rather high field, a characteristic noted for the (B) isomer with molybdenum Although the assignment of configuration in the iron and ruthenium compounds is not as secure as in the case of the molybdenum analogs, all evidence indicates no significant presence of any isomer other than the (B) isomer in carefully purified samples, even on prolonged standing at room temperature

The absence of a second isomer (<0.5%) precludes the detection of the barrier to rotation of the allyl, since no NMR line broadening would be observed even if the rate were relatively rapid. Although we expect that the barrier to interconversion of the (A) and (B) isomers would be rather high* our results do not allow us to demonstrate this position Our method of preparation differs from that of King and Ishaq [6] in that vacuum distillation was used to purify the samples, consequently, it is probable that the (B) isomer was separated from any (A) that may have been present. It is clear, however, that

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* A π—σ—π rearrangement may well be the lowest energy path The spectra provided for us by Professor King show both isomers and no evidence for rapid rearrangement

one isomer is relatively stable and the other tends to decompose or interconvert. Therefore, it appears that the 4/1 ratio of isomers suggested by King and Ishaq represents, at most, a kinetically controlled ratio and not the relative thermodynamic stabilities This suggests that the (A) isomer only exists as a transient intermediate in the iron system These results, however, do not preclude the possibility of isolating the pure (A) isomer. With sufficient steric interactions in substituents to stabilize the (A) form or trapping it by using low temperatures with ruthenium or osmium complexes, it should be possible to isolate the pure (A) isomer.

Experimental

Preparations, reactions and purifications were carried out under nitrogen or on a vacuum line. Chromatographic separations utilized low activity alumina (Fisher A-540). NMR spectra were obtained using a Varian HA—100 and IR spectra were obtained from cyclohexane solutions using a Perkin—Elmer 421 calibrated with gaseous DCl, NMR samples were prepared via vacuum line techniques to avoid paramagnetic broadening (typical line widths ≈0.3 Hz)

π-C_5H_5-π-$C_3H_5Fe(CO)$

Following the procedure of Green and Nagy [5], π-$C_5H_5Fe(CO)_2$ dimer was reduced with sodium amalgam. Allyl chloride was then treated with the sodium salt to yield the σ-complex, which was converted to the desired π-complex by ultraviolet irradiation. A typical reaction involved stirring 10 g of dimer in tetrahydrofuran with a 1% amalgam (3 g Na) for three hours, during which the color of the solution changed from deep red to amber. The solution of the sodium salt was added dropwise to an excess of allyl chloride (20 ml) in THF, stirred at —78° for one-half hour and then allowed to warm to room temperature The excess allyl chloride and THF were removed in vacuo and the residue, predominantly π-C_5H_5-σ-$C_3H_5Fe(CO)_2$ (ν(CO) 2010,1957 cm^{-1}) and sodium chloride, was extracted with cyclohexane (200 ml), filtered and placed in a 1000 ml Pyrex flask. The deep orange solution was cooled to —78°, the flask evacuated, and the solution irradiated with a sun lamp for about six hours at room temperature. At this point IR indicated a predominance of the π-allyl complex and a lesser amount (~10%) of the starting dimer. The solvent was evaporated and the residue chromatographed on a 10 in. alumina column. A broad yellow band containing the desired compound was eluted with petroleum ether. The solvent was evaporated and the air sensitive brown residue was transferred to a vacuum line. The yellow-orange compound was sublimed directly into an NMR tube attached to a U-tube and maintained at 0° Carbon disulfide and TMS (5%) were distilled into the tube, which was sealed and stored at 0° The compound decomposed at 65° and showed one carbonyl stretching frequency at 1953 cm^{-1} (lit. [5], dec 65°, 1950 cm^{-1})

π-C_5H_5-π-$C_4H_7Fe(CO)$

The procedure was the same as that for the unsubstituted allyl except that the ultraviolet irradiation time was about ten times longer (55 hours). The σ-complex showed IR absorptions at 2006 and 1952 cm^{-1}.

π-C_9H_7-π-$C_3H_5Fe(CO)$

The procedure for the σ-allyl derivative followed that of the cyclopentadienyl analog, with the exception that smaller quantities ($\approx$3 g) of the π-indenyl dimer [7,8] were used. After addition of the anion to the allyl chloride, the mixture was stirred until it warmed to 0°. The solvent was removed maintaining the 0° temperature. The σ-allyl complex (ν(CO) 2005, 1951 cm^{-1}) was extracted with 350 ml of cyclohexane and the solution placed in a jacketed tube, which was evacuated and maintained between 5 and 10° by circulating water through the outer jacket. The tube was irradiated with a 200 W incandescent light bulb and the solution agitated with a magnetic stirrer. Carbon monoxide was periodically removed under vacuum and after ten hours, IR spectroscopy showed significant (ca. 60%) conversion to the π-complex The cyclohexane was evaporated and the residue chromatographed on alumina The π-complex eluted slowly with petroleum ether as an orange band Solvent was removed and the complex crystallized as red-orange needles from pentane in Dry Ice The complex was extremely air-sensitive and decomposed rapidly in CS_2.

π-C_5H_5-π-$C_3H_5Ru(CO)_2$

The procedure used was similar to that for the iron complex The ruthenium dimer [8] was reduced and added to allyl chloride to give the σ-complex, which showed carbonyl bands at 2020 and 1961 cm^{-1} (lit. [6], 2015, 1970 cm^{-1}) The σ-complex was purified by vacuum distillation into a 0° trap (this required approximately ten hours) A cyclohexane solution of the yellow oil was irradiated with a sun lamp filtered by glass to reduce the ultraviolet radiation. After eight hours, the IR of the reaction mixture indicated $\approx$40% conversion to the π-complex and 30% conversion to other carbonyl-containing species (approximately fifteen other CO bands). Chromatography on alumina with petroleum ether gave a yellow band which indicated a 4/3 ratio of π-complex to σ-complex and contained approximately 5% of an unidentified product having three carbonyl bands (2006, 1965, and 1943 cm^{-1}). Vacuum distillation into a 0° trap gave a mixture of a yellow oil and white crystals, for which the IR spectrum indicated less than 1% of any species other than the σ- and π-complexes (2020, 1961, 1955, ^{13}CO, 2005, 1935 cm^{-1}) Crystallization from pentane effected separation of the two complexes. Recrystallization from pentane gave white crystals melting at 45° (lit. [6] 44-45°) This complex appeared to be considerably more stable than any of the iron complexes

C_9H_7-π-$C_3H_5Ru(CO)$

The dimer [7,8], $[C_9H_7Ru(CO)_2]_2$, was treated with sodium amalgam in THF and the sodium salt subsequently was added to an excess of allyl chloride. The solvent was evaporated and the residue chromatographed on alumina where 25/75 petroleum ether/benzene eluted the π-complex in low yield as an air-sensitive pale yellow oil Irradiation was not necessary as the π-complex apparently formed readily from the σ-complex under the conditions employed

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