

Preliminary communication

CATIONIC η^3 -R,2,3- η^5 -5,6-2R-BICYCLO[2.2.1]HEPTA-2,5-DIENE-R-YL
 (R = CH₂, CHCH₃) COMPLEXES OF RHODIUM AND IRON

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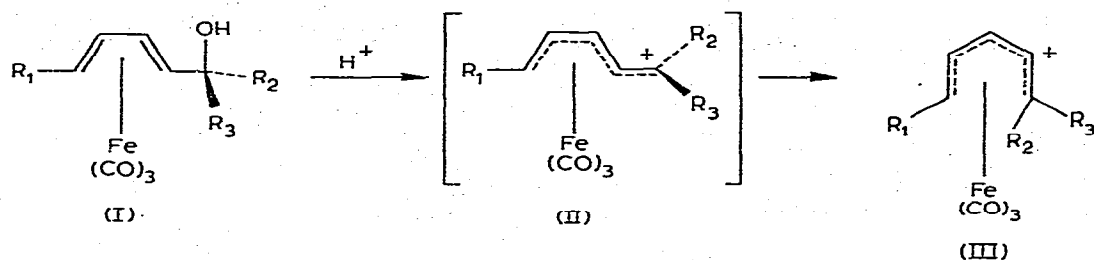
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Summary

The title compounds were isolated as PF₆⁻-salts by treating carbinols (IVa—c) with concentrated H₂SO₄ and subsequent addition of aqueous NH₄PF₆, and were characterized by ¹H NMR spectra.

During dehydration of carbinols (I) the initially formed *trans*-dienyl cations (II) [1,2] are rapidly rearranged into *cis* isomers (III), which are isolable as stable crystalline solids [3].



It was interesting to investigate the cations generated by complexes of unconjugated dienols. Carbinols (IVa—c) containing a rigid norbornadienyl ligand were synthesized according to Scheme 1.

Treating carbinols (IVa—c) with concentrated sulphuric acid results in the formation of cationic complexes which are isolated as stable hexafluorophosphate salts [(C₇H₇R)Rh(C₅H₅)]PF₆ (Va, R = CH₂; Vb, R = CHCH₃) and [(C₇H₇CHCH₃)Fe(CO)₃]PF₆ (Vc)*.

In the PMR spectra of the cationic complexes Va—c (see Table 1) all the bicyclic ligand protons exhibit separate signals. Signals of the exocyclic methine protons of Vb and Vc are observed at the lowest field, δ 6.80 and

*Satisfactory elemental analysis was carried out for all new compounds.

SCHEME 1

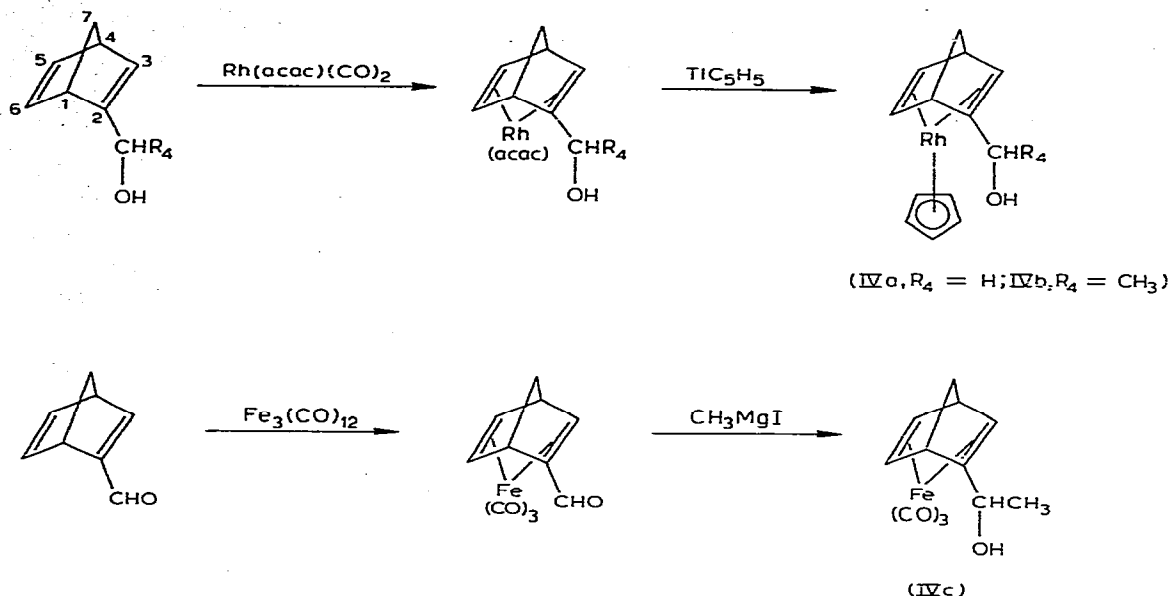


TABLE 1

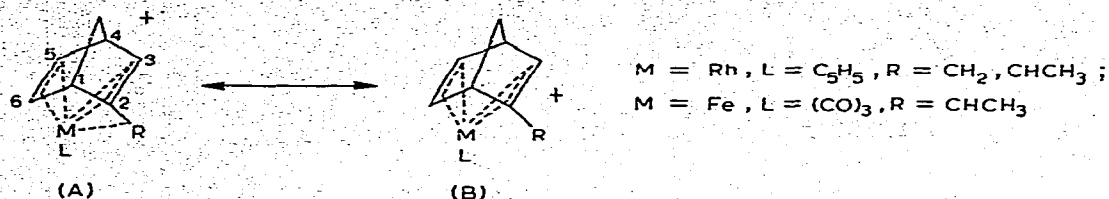
PMR SPECTRA OF COMPLEXES Va-c IN ACETONE-d₆

Complex	Chemical shift, δ (ppm) (multiplicity, coupling constant (Hz)) ^a										
	H(8)	CH ₃	H(3)	H(5,6)	H(1,4)	H(7 α)	H(7 β)	C ₃ H ₅			
Va	3.98 (bs)	5.40 (bs)	4.90	4.30	4.56	3.56	3.78	1.67	1.80	5.98 (d, 1.1) ^b	
Vb	6.80 (q, 6.5) ^c	1.62 (d, 6.5)	4.74	4.29	4.88	3.28	3.80	1.59	1.75	5.80 (d, 0.8) ^b	
Vc	1.20 (q, 7)	1.74 (d, 7)	5.83	4.50	7.72	3.67	4.10	^d	^d		

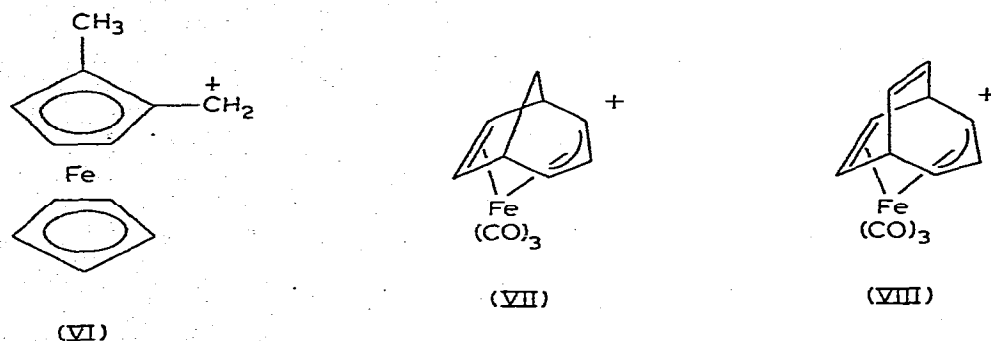
^aIn the cases where the coupling constant is not given, signals are observed as complex multiplets. ^bCoupling constant $J(\text{Rh}-\text{H})$. ^cAdditional splitting is observed with $J \sim 1.5$ Hz. ^dSignals of these protons are superimposed by the signal of acetone, present in the solvent as an admixture.

7.20 ppm respectively. Slightly broadened singlets (in contrast to the other multiplets of the bicyclic ligand) of the exocyclic methylene group of cation Va are observed at δ 3.98 and 5.40 ppm. Such a difference in the chemical shifts of geminal protons at an exceedingly low coupling constant* is typical of *syn-anti* protons in π -allylmetal complexes. It is known that the value of this constant usually does not exceed 1.5 Hz [4]. Consequently, structure A may be assigned to cationic complex Va, according to which the bicyclic ligand is attached to the metal atom by a π -olefinic and π -allylic bond involving the exocyclic carbon atom. The tilting of the C(2) — C(8) bond towards the metal atom, which is probable in the rigid bicyclic system, should favour formation of a metal—C(8) bond in the cationic complexes Va—c.

* The broadening of *exo*-methylene signals in Va may be due, at least partly, to coupling of these protons with the rhodium atom. Thus, in the ¹³C spectrum of Vb splitting of the *exo*-carbon C(8) signal into a doublet is observed, $J(\text{Rh}-\text{C}(8)) = 5.3$ Hz.



The 2-substituted norbornadiene complexes IVa–c and Va–c are chiral. Therefore, for example, the methylene protons of the CH₂OH group in IVa are diastereotopic and exhibit *AB* doublets at δ 3.82 and 3.39 ppm, $J_{AB} = 11.3$ Hz. Similar nonequivalence of geminal protons is observed in the chiral carbenium ion (VI) where the methylene protons give a pair of doublets at 5.80 and 6.12 ppm [5]. Therefore, as an alternative complex Va may be considered as a carbenium ion (B). However the low value of the coupling constant of *exo*-methylene protons mentioned above at a substantial difference in chemical shifts ($\Delta\delta = 1.42$ ppm) agrees more with the π -allyl (A) rather than with the carbenium ion structure (B). This conclusion is supported by the fact that the magnitude of the chemical shift nonequivalence of *exo*-methylene protons in Va is temperature independent in the range 30–150°C in nitrobenzene, and by its remarkably high stability.



Unlike the known cations VII [6] and VIII [7], the π -allyl moiety in Va–c is not symmetrical, and is partly included in the cyclic system. This results in asymmetrical distribution of the positive charge along the π -allyl fragment. Thus, in the PMR spectra of Vb and Vc H(8) appears at a much lower field than in the case of H(3) (6.80 and 4.74 for Vb, and 7.20 and 5.83 ppm for Vc, respectively). Therefore the cationic complexes Va–c may be considered as resonance hydrides (A) \leftrightarrow (B), with predominance of the π -allyl structure. One can expect, however, that the introduction of stronger electron-donating substituents at C(8) will increase the contribution of the carbenium ion structure.

References

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