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Preliminary communication

REGIOSPECIFIC CARBON—CARBON BOND FORMATION BY OXIDATIVE COUPLING OF η^1-ALLYL OR η^1-PROPARGYL LIGANDS OF ORGANOIRON COMPLEXES

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Summary

Novel and regiospecific coupling reactions of η^5-$C_5H_5(CO)_2Fe(\eta^1$-allyl) and (η^5-$C_5H_5(CO)_2Fe(\eta^1$-propargyl) complexes due to oxidation by silver hexafluorophosphate are reported. The mono- and bi-nuclear products contain (substituted) hexadiene and hexatetraene ligands while variable amounts of protonation products are also formed.

Previously, we have reported that several neutral binuclear iron complexes containing unsaturated bridging organic ligands are readily oxidized by trityl or silver salts to mono- or bi-nuclear cationic complexes containing the η^2-cyclobutadiene [1,2], η^2-7,8-benzocyclobutadiene [3,4] or η^2-1,2-butatriene [5,6] ligands.

Herein, it is reported that Fp(η^1-allyl)*(Ia—Id) and Fp(η^1-propargyl) (VI) complexes undergo novel and regiospecific couplings through the γ-carbon of the σ-bonded ligand when oxidized by silver hexafluorophosphate. The resulting products are mono- and bi-nuclear complexes containing 1,5-hexadiene, substituted 1,5-hexadiene, or substituted 1,2,4,5-hexatetraene ligands. Variable amounts of the protonation products were formed also. The products and yields of the coupling reactions are given in Table 1.

The relative amounts of the mono- and bi-nuclear hexadiene complexes formed during the oxidation of I are dependent on the nature of the substitution at the γ-carbon of the η^1-allyl ligand. Thus, Ia afforded primarily the mononuclear complex IIa and considerably lesser amounts of the binuclear complex IIIa. (Since IIIa is stable under the reaction conditions it is unlikely that this complex is the precursor of IIa). Complex Ib gave the mononuclear complex IIb as the only coupling product. In contrast to these results the *trans*-cinnamyl

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*Fp = η^5-$C_5H_5(CO)_2Fe$

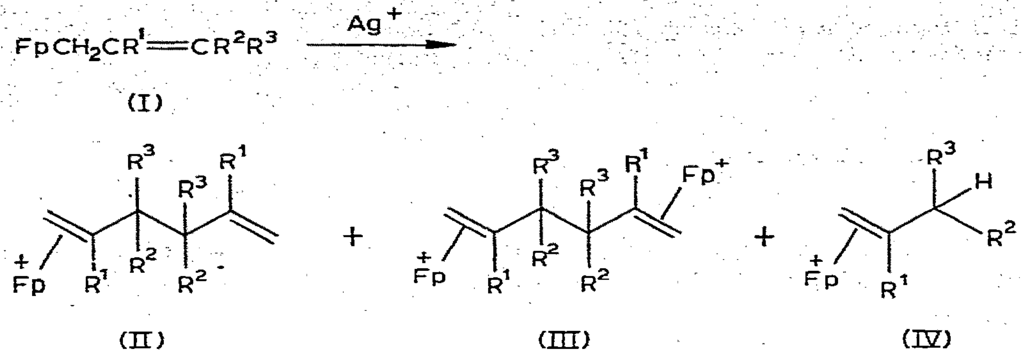


TABLE 1

PRODUCTS[a] RESULTING FROM THE OXIDATION OF $FpCH_2CR^1{=}CR^2R^3$ BY SILVER HEXAFLUOROPHOSPHATE[b]

	R^1	R^2	R^3	Equivalents of Ag^+	Products and yields		
Ia	H	H	H	0.5	IIa(35%)	IVa(10%)	IVa(1%)
Ib	Me	H	H	0.5	IIb(30%)	IIIb(0%)	IVb(36%)
				1.0	IIb(30%)	IIIb(0%)	IVb(36%)
Ic	H	Me	Me	1.0	IIc([c])	IIIc(35%)	IVc(35%)
Id	H	Ph	H	1.0	IId(1%)	IIId(60%)	IVd(0%)

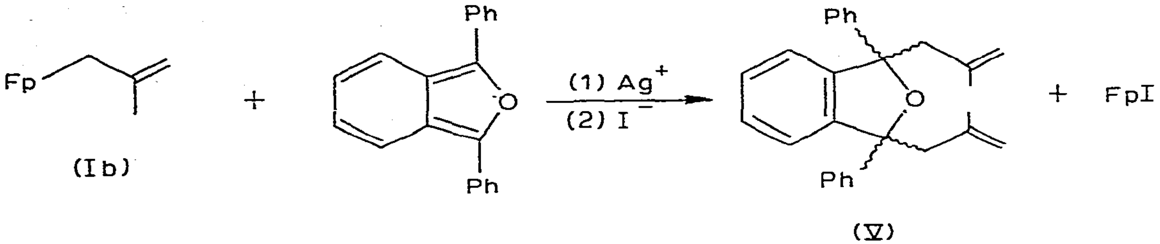
[a] The new complexes (including VII) were isolated as hexafluorophosphate salts and with the exception of IIb, IIc, IIIc and IIId, they were characterized by PMR and IR spectroscopy and iron analyses. The remaining new complexes were characterized spectroscopically because of contamination with a side product (IIb and $Fp(isobutylene)^+ PF_6^-$), low yield (IId) or thermal instability (IIc, IIIc). Both IIIc and IIId were decomposed to yield 3,3,4,4-tetramethyl-1,5-hexadiene and 3,4-diphenyl-1,5-hexadiene, respectively. These dienes were characterized by comparison of their spectroscopic properties to the literature values [7,8]. [b] Methylene chloride or 1,2-dichloroethane solutions of the reactants were mixed at −78°C and then allowed to warm to 24°C. [c] The yield of IIc was small and variable.

complex Id gave the binuclear complex IIId and only a trace of a substance thought to be the mononuclear complex IId. Oxidation of Ic afforded both IIc and IIIc. Since both IIc and IIIc are labile and decompose within minutes in nitromethane at 24°C it is not clear how much IIc is derived from IIIc. With the exception of Id, the oxidation of I gave varying amounts of $Fp(alkene)^+ X^-$ (IVa—IVc) containing the propene, isobutylene or 3-methyl-1-butene ligand.

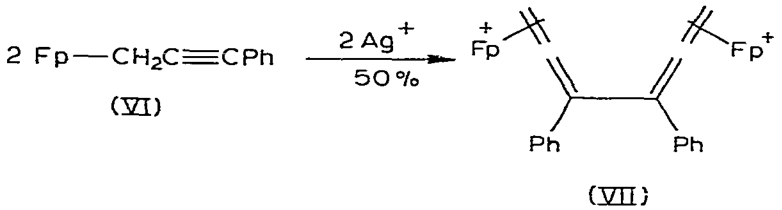
It is particularly significant that the oxidative couplings of the allyl ligands are regiospecific resulting in carbon—carbon bond formation between the most highly substituted carbons of the allyl fragment. This is dramatically illustrated by the oxidation of Ic during which two tertiary carbons are coupled to form two adjacent quaternary carbons. This mode of coupling has not been reported for the reactions between allyl Grignard reagents and allyl halides [9—11], or for the reductive coupling of allyl halides by zinc [12].

The oxidative coupling of I appears to be non-stereospecific. Thus, the 3,4-diphenyl-1,5-hexadiene obtained by reductive demetallation of IIId by NaFp is a mixture of the *meso* and *d,l*-isomers.

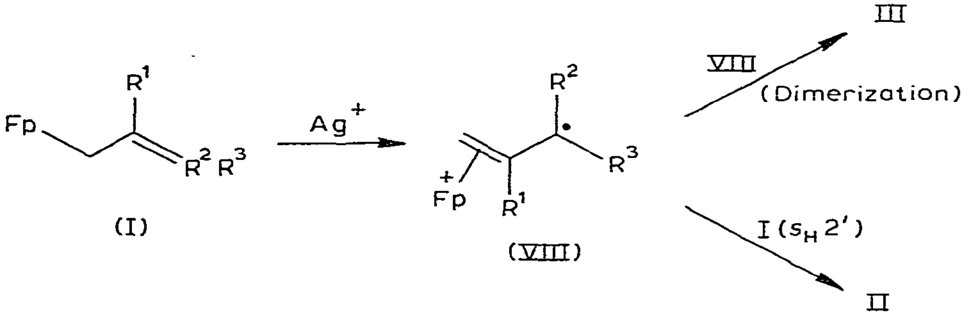
In an important variant of this reaction the 2-methylallyl ligand of IIb has been oxidatively transferred to 1,3-diphenylisobenzofuran. The adduct was obtained in 60% yield after treatment of the reaction mixture with sodium iodide.



The oxidative coupling reaction of I is not restricted to allyl complexes. The phenylpropargyl complex VI is regiospecifically coupled to afford the binuclear complex VII containing the bridging 3,4-diphenyl-1,2,4,5-hexatetraene ligand.



Although information pertaining to the mechanism of these oxidations is scant the yields and nature of the oxidation products suggests that two related mechanisms, one that gives primarily mononuclear products and another that affords primarily binuclear products, are operative. At present we believe that these reactions involve cation-radicals (i.e. VIII) resulting from oxidation of the allyl or propargyl complexes by Ag$^+$. Dimerization of these radicals affords the binuclear complexes III. An S_H2' reaction between VIII and the parent complex affords the mononuclear complexes II. (Studies of the reactions between Fp(η^1-allyl) and carbon tetrachloride indicate that the S_H2' reaction is an important degradative pathway for these complexes) [13].



Acknowledgment

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