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Novel Reaction of Coupling of π-Allyl and π-acetylene Ligands Coordinated to Metal Atom

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Numerous reactions of acetylenes resulting in the formation of cyclobutadiene [1] and arene ligands [2] are well reviewed in the literature. Information concerning the formation of cyclopentadienyl compounds by reactions of alkynes with transition-metal complexes is restricted to several examples [3].

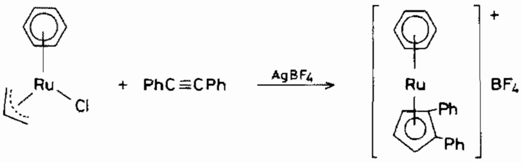
In our study of the reactivitiy of cationic allyl-arene complexes of Ruthenium with different neutral ligands we have observed a novel reaction of intramolecular condensation of π-allyl and π-tolane ligands abbording a π-arene-π-cyclopentadienyl derivative of Ruthenium.

The reaction of π-C_3H_5-π-C_6H_6-RuCl with tolane in acetone in inert atmosphere under ambient conditions in the presence of silver tetrafluoroborate gave a stable pale yellow crystalline solid which proved not to be π-C_6H_6-π-C_3H_5-Ru-π-C_2Ph_2 as expected. The Raman spectrum of the product obtained showed the absence of the band corresponding to coordinated diphenylacetylene.

The ^1H NMR spectrum of the compound (in CD_3CN) consists of a multiplet at δ 7.4 ppm corresponding to phenyl protons, a single resonance of protons of π-arene ring at δ 6.13 ppm, a doublet at δ 5.76 ppm (J_{H-H} 2.5 Hz) and a triplet at δ 5.52 ppm. The intensity ratio of bands (10:6:2:1) indicates that the reaction is accompanied by the loss of two hydrogen atoms.

The ^{13}C NMR spectrum* (in CD_3CN) exibits a set of signals corresponding to phenyl carbon atoms in the region of 128.3–129.9 ppm, a singlet at δ 101.7 ppm and three doublets at δ 87.7, 81.2 and 78.5 ppm. The low field doublet may be assigned to the carbon atoms of π-arene ligand while the other two must represent resonances of π-allyl ligand. However doublet splitting of these signals shows that these atoms are bonded only to one proton while terminal allylic carbon atoms are bonded to two hydrogen atoms.

All these results indicate that the product obtained is π-benzene-π-(1,2-diphenylcyclopentadienyl)-Ruthenium-tetrafluoroborate**, *i.e.* condensation of π-allyl ligand with tolane occurred:



Conclusive proof of the structure was obtained from X-ray crystallographic investigation***. Preliminary results demonstrate that the reaction may be of general interest and analogous complexes have been prepared for other platinum metals.

References

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*Doublet structure of ^{13}C signals is observed in Off Resonance Decoupled spectra.

**The formulation is supported by elemental analysis.

***Results will be published later.