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Stereochemistry of the Cycloaddition Reaction of 1,2-Dicyano-1,2-bis(trifluoromethyl)ethylene with Transition Metal-Propargyl Complexes

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Transition metal-propargyl complexes react with a number of electrophilic molecules (E = Nu) to afford (3+2) cycloaddition products.[1-3] To elucidate further the proposed two-step mechanism involving a dipolar intermediate, we undertook a stereochemical study at the E–Nu bond of this reaction using *cis-* and *trans-*1,2-dicyano-1,2-bis(trifluoromethyl)ethylene ($C_6F_6N_2$). The two isomeric olefins had been employed previously as a stereochemical probe.[4-6]

Results and discussion

The complexes $MCH_2C{\equiv}CC_6H_5$ ($M = \eta^5$-C_5H_5-$Fe(CO)_2$, $Mn(CO)_5$, and $Re(CO)_5$) react smoothly at room temperature with each of *cis-* and *trans-*$C_6F_6N_2$ in organic solvents to afford crystalline 1:1 adducts in high yields (*Anal.* Calcd for $C_{22}H_{12}F_6FeO_2N_2$: C, 52.17; H, 2.37. Found: C, 52.30; H, 2.41. Mass spectrum: calcd P^+, m/e 506; observed P^+, m/e 506. Satisfactory elemental analyses and mass spectra were obtained also for the other new compounds). The infrared ν_{CO} absorptions of these products agree well with those expected for metal-vinyl derivatives, Ia and Ib, sketched in Fig. 1a (*e.g.*, for Ib, $M = \eta^5$-$C_5H_5Fe(CO)_2$, ν_{CO} 2033 and 1983 cm^{-1} in CH_2Cl_2 soln.). The ^1H NMR spectra show signals of the methylene protons between 6.38 and 6.72 τ compared to 6.30 and 6.41 τ for the analogous tetracyanoethylene cycloadducts of $MCH_2C{\equiv}CC_6H_5$ ($M = Mn(CO)_5$ and η^5-$C_5H_5Fe(CO)_2$,[7] respectively). The ^{13}C NMR spectral data, to be presented in our full account of this work, also support the proposed formulations.

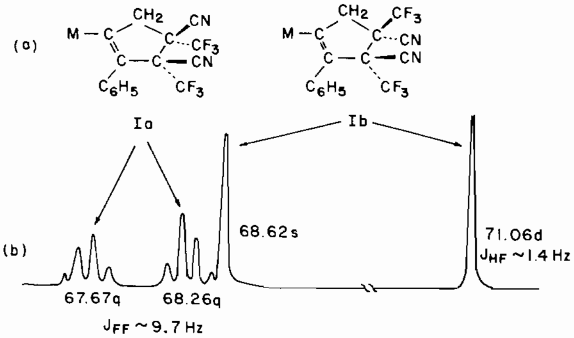


Fig. 1. (a) Structures of the cyclopentenyl ring of the two diastereomeric products of reaction between $MCH_2C{\equiv}CC_6H_5$ and *trans*-$C_6F_6N_2$. (b) ^{19}F NMR spectrum of a 1:1 mixture of Ia and Ib, $M = \eta^5$-$C_5H_5Fe(CO)_2$, in $CDCl_3$ (chemical shifts in ppm relative to $CFCl_3$).

The ^{19}F NMR spectrum of a 1:1 mixture of Ia and Ib, $M = \eta^5$-$C_5H_5Fe(CO)_2$, is presented in Fig. 1b. The spectra of the other complexes Ia and Ib are very similar. The assignment of resonances to the proper isomeric structure, Ia or Ib, is easily made from the observation[8] that nonequivalent *cis*-CF_3 groups on adjacent carbons have larger J_{FF} than do corresponding *trans*-CF_3 groups. Thus the pair of quartets can be assigned to Ia, and the pair of singlets to Ib.

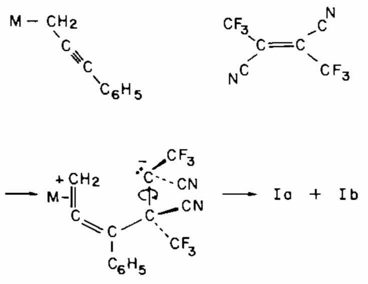
The stereochemical results for the reactions of *trans*-$C_6F_6N_2$ are listed in the Table. The corresponding study with *cis*-$C_6F_6N_2$ is complicated by isomerization to *trans*-$C_6F_6N_2$ under the reaction conditions.

The observation of both isomers, Ia and Ib, from the reactions of *trans*-$C_6F_6N_2$ with all three metal-propargyl complexes requires that the cycloaddition be non-concerted. Thus these data are consistent with

TABLE. Stereochemical Data for Reactions of $MCH_2C{\equiv}CC_6H_5$ with *trans*-$C_6F_6N_2$

M	Solvent	Reaction Time	% Diastereomers in Product Mixture		%Stereoselectivity
			trans (Ib)	*cis* (Ia)	
η^5-$C_5H_5Fe(CO)_2$	Benzene	5 min	91	9	82
	Benzene	45 min	84	16	68
$Mn(CO)_5$	Benzene	44 hr	66	34	32
	Acetonitrile	5.5 hr	70	30	40
$Re(CO)_5$	Acetonitrile	5 min	70	30	40

the previously proposed two-step mechanism, shown below. The loss in stereochemistry would result from rotation of 180° about the C–C (E–Nu) bond in the zwitterionic intermediate which occurs before ring closure. The appreciable enhancement of the rate for $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ on going from benzene to the more polar acetonitrile solvent (see the Table) is in accord with such a two-step mechanism.



Hence, from this and previously presented evidence,[9] it appears very likely that transition metal-σ-allyl and -propargyl complexes undergo cycloaddition reactions with electrophiles through strictly analogous pathways.

Acknowledgment

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