Ring Exchange Reactions of First Transition Series Metallocenes

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Summary The first ring exchange reactions involving first transition series metallocenes show that chromocene, manganocene, and nickelocene are quite labile.

The metallocenes, MCp_2($Cp = \pi$-C_5H_5), may be considered the prototype compounds for much of organometallic chemistry. Ligand exchange reactions of cyclopentadienyls or cyclopentadienides with metallocenes could lead to important applications in the synthesis of mixed ligand compounds, and to new insight into the effects of electron configuration on reactivity in an isostructural organometallic series. We have studied two types of exchange reactions, (a) the reaction of $Li(C_5D_5)$ with MCp_2 in THF, M = V, Cr, Mn, Fe, Co, and Ni; and (b) the reaction of $Ni(\pi$-$C_5D_5)_2$ with MCp_2 in heptane (M = V, Cr, Co) or benzene (M = Mn) (see Table). Most reported ligand exchanges with "sandwich" complexes have involved arene substitutions, often under extreme conditions in the presence of catalysts.[2] However, Maitlis *et al.* have reported "cyclopentadienylation" by $CpFe(CO)_2Br$, and π-Ph_4C_4 exchange by such compounds as $[\pi$-$Ph_4C_4PdBr_2]_2$.[3]

Table. *Exchange half-times for* $M(\pi$-$C_5H_5)_2 + M'(C_5D_5)_n$

M	$M(\pi$-$C_5H_5)_2$ (molar)	M	*n*	$M'(C_5D_5)_n$ (molar)	Solvent	Temp.	$t_{\frac{1}{2}}$
V	0·34	Li	1	0·42	THF	25·0	75 h
Cr	”	”	”	”	”	32	$\leqslant$ 2 min
Mn	0·0419	”	”	0·0520	”	32	$\leqslant$ 2 min
Fe	0·468	”	”	0·268	”	25·0	no reaction[a]
	0·289	”	”	0·380	”	25·0	no reaction[b]
Co	0·34	”	”	0·42	”	25·0	no reaction[c]
Ni	”	”	”	”	”	25·0	3·5 h
V	0·157	Ni	2	0·0608	n-heptane	51·3	no reaction[d]
Cr	0·142	”	”	0·0625	”	”	25 h
Mn	0·146	”	”	0·0628	benzene[e]	”	28 h
Co	0·092	”	”	0·031	”	”	no reaction[f]

[a] After 5 weeks; [b] after $2\frac{1}{2}$ weeks; [c] after 2 weeks; [d] after $3\frac{1}{2}$ weeks; [e] poor solubility of $Mn(\pi$-$C_5H_5)_2$ in heptane; [f] after 5 weeks.

The $Li(C_5D_5)$ reactions were followed by observing the rate of disappearance of the first overtone of the metallocene C–H stretching vibration at about 1·64μ. The exchanges of $Ni(\pi$-$C_5D_5)_2$ with MCp_2 were followed by sublimation of $NiCp_x(\pi$-$C_5D_5)_{2-x}$ after destruction of the other metallocenes. The isolated $NiCp_x(\pi$-$C_5D_5)_{2-x}$ was then analysed for C–H by the near i.r. method. The kinetic data were treated as is usual with isotope exchanges;[4] the plots of log $(A_t - A_\infty)$ *vs.* time were linear for several half-lives. Mass spectral analysis of $NiCp_x(\pi$-$C_5D_5)_{2-x}$, isolated from the reactions of $NiCp_2$ with $Li(C_5D_5)$ or $Ni(\pi$-$C_5D_5)_2$ with $CrCp_2$, verified the results of the near i.r. method, and proved that the entire cyclopentadienyl moiety exchanges. Preliminary kinetic studies of the $NiCp_2$–$Li(C_5D_5)$ system show a dependence of the rate on the concentrations of both reactants, implying that this reaction is at least second order.

The visible spectra of the MCp_2 complexes in hexane were compared to the corresponding spectra in THF and to spectra in THF containing $Li(C_5D_5)$. The near identity of spectra in each case rules out formation of a large concentration of $Li(C_5D_5)/MCp_2$ adducts and/or $MCp_2 \cdot (THF)_x$ solvates (excepting $MnCp_2$).

We find the same order of reactivity of MCp_2 toward both $Li(C_5D_5)$ and $Ni(\pi$-$C_5D_5)_2$ (see Table). This similarity suggests a similar mechanism, or at least the importance of similar factors in reactivity. We observe that the compounds which do exchange with $Li(C_5D_5)$ either have valence orbital vacancies (according to the effective atomic number rule) to accept additional electrons from $Li(C_5D_5)$ (M = V, Cr, Mn), or additional electrons to donate to Li

(M = Ni). It is not clear why vanadocene, with the largest number of valence orbital vacancies, reacts the slowest with $Li(C_5D_5)$ or why cobaltocene is inert toward substitution. In addition, we observe that "electron-rich" $Ni(\pi\text{-}C_5D_5)_2$ reacts only with the "electron-deficient" metallocenes (M = Cr, Mn). We expect more detailed mechanistic studies to clarify these relative rate data.

The relative labilities of the metallocenes toward substitution by $Li(C_5D_5)$ parallel those toward $FeCl_2$–THF[5] and the general substitution chemistry of the metallocenes. Vanadocene, ferrocene, and cobaltocene are generally inert toward loss of a ring;[5–7] and ring loss is characteristic of chromocene, manganocene and nickelocene.[5,6,8–10] Our systems should yield more definitive information on relative labilities since the same basic reaction is studied for each metallocene, and no redox reactions are involved.

We thank the Donors of the Petroleum Research Fund of the American Chemical Society, the Research Corporation and the University of California Intramural Fund for financial support and Standard Oil of California for a fellowship (1969–70) (to M.E.S.). We thank Professor Paul C. Ellgen for helpful discussions.

(*Received*, 23*rd March* 1972; *Com.* 483.)

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