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Kinetics and Mechanism of Ring-Exchange Reactions of Nickelocene

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The kinetics of ligand exchange between lithium cyclopentadienide (LiCp) and nickelocene ($NiCp_2$) have been studied in tetrahydrofuran (THF) solution. In the concentration range studied (0.05 to ~0.5 *M*) the rate law suggests that exchange proceeds by two paths. The first path involves rate-determining association of $NiCp_2$ and LiCp and the second involves similar association of $NiCp_2$ with $(LiCp)_2$, a dimer. The dimer reacts at least 40 times faster than the monomer. The interaction of LiCp with *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was also studied in THF, where a stable 1:1 complex, LiCp·(TMEDA), is formed. LiCp·(TMEDA) also exchanges Cp rings with $NiCp_2$ by a bimolecular pathway, with no intervention of dimers, etc. The TMEDA complex is about 40 times more reactive toward exchange than is LiCp, which reflects the generally enhanced reactivities of chelated organolithiums. The exchange of rings between $NiCp_2$ and $MnCp_2$ was studied in benzene solution. The reaction is apparently second order and is much slower than are the $NiCp_2$–LiCp exchanges in THF.

Introduction

Substitution of the π ligand on a metal π complex is an important general method of synthesis. Many examples of such synthetic reactions are cited in recent review articles.[2,3] A special case of substitution involves exchange of one π ring for another, for example arene exchange on M(arene)$_2$ or (arene)M(CO)$_3$.[4-11] The arene exchange reactions in general have been studied at high temperatures,[4-8] in the presence of $AlCl_3$,[9,10] or using irradiation to promote the reactions.[11] At elevated temperatures arene exchange with group VIb arene metal tricarbonyls follows a two term rate law. Each of the reaction paths implied by the rate law is thought to involve associative activation in which the number of coordination sites occupied by the originally bound arene decreases.[12-15]

We have extended the π-exchange studies to cyclopentadienyl exchanges in the metallocene series. We have reported preliminary results of our study of cyclopentadienyl exchanges involving LiC_5D_5 and MCp_2 (Cp = η^5-cyclopentadienyl), M = V, Cr, Mn, Fe, Co, Ni.[16] The reactivity of these metallocenes toward exchange decreases in the order Cr, Mn $\gg$ Ni > V $\gg$ Fe, Co. Ferrocene and cobaltocene, in fact, showed no exchange in tetrahydrofuran (THF) in a month at 25°. Other examples of ring-exchange reactions include the replacement of one ring in ferrocene and its derivatives by arenes, catalyzed by $AlCl_3$.[17-19] Also, Maitlis and Games have prepared $(\eta^4\text{-}C_4Ph_4)(\eta^5\text{-}C_5H_5)Co$ in 12% yield by a ring-exchange reaction between $CoCp_2$ and $[\eta^4\text{-}(C_4Ph_4)PdBr_2]_2$.[20] Reactions to form binuclear compounds, such as the reaction between $NiCp_2$ and $Ni(CO)_4$ to give $[CpNi(CO)]_2$ and $Cp_3Ni_3(CO)_2$,[21] involve ring exchange in one or more steps. We have suggested[16] that ring exchange reactions are potentially important routes to substituted metallocenes, and two such syntheses have been reported. Katz and Action[22] prepared bis(pentalenylnickel) from the reaction of dilithium pentalenide with $NiCp_2$, and an unpublished study has been cited[2] in which a tenfold excess of lithium α-phenyl (dimethylaminoethyl) cyclopentadienide reacts with $NiCp_2$ to produce the substituted nickelocene.

The potentially wide synthetic utility of ring-replacement reactions in the metallocenes and the relative lack of quantitative information concerning M–Cp bond cleavage reactions makes further kinetic studies on these compounds desirable. We chose to study cyclopentadienyl exchanges because the reactions are well-behaved, as there is no net oxidation or reduction and little possibility of side reactions.

We report here the results of our studies of the exchange reactions of $NiCp_2$ with (a) LiC_5D_5, (b) the tetramethylethylenediamine adduct of LiC_5D_5, and (c) $MnCp_2$. Nickelocene was chosen for further study, since our preliminary work[16] had shown that the reactions are clean and that the exchanges proceed at convenient rates.

Experimental Section

All operations involving air-sensitive compounds were carried out in an atmosphere of prepurified nitrogen, generally in a Vacuum/Atmospheres Co. Dri-Train drybox. Nmr spectra were obtained on Varian A-60 or A-60D spectrometers, mass spectra on a Perkin-Elmer Hitachi Model RMU-9D spectrometer, and uv-visible-near-ir spectra on a Cary 14 spectrophotometer. For accurate nmr chemical shift measurements, we used the A-60D equipped with a side band oscillator/frequency counter.

Materials. Reagent grade solvents were used throughout. THF and diethyl ether were further purified by distillation from $LiAlH_4$ under nitrogen; C_6D_6 was purified by distillation from BaO, also

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under nitrogen. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was purified by distillation from sodium metal. Cyclopentadiene was obtained by cracking commercial dicyclopentadiene (Aldrich) from BaO through a 40-cm Vigreux column. A middle cut was taken and the C_5H_6 was used immediately or stored in Dry Ice.

C_5D_6. C_5H_6, KOH, and D_2O–dioxane cosolvent were vigorously stirred for 3 hr in a round-bottom flask equipped with a magnetic stirrer and Dry Ice condenser. (There were always two layers.) The $C_5H_xD_{6-x}$ was then distilled directly from the flask through a 10-cm Vigreux column. The per cent deuteration was obtained by integrating the nmr spectrum of $C_5H_xD_{6-x}$ relative to that of pure C_5H_6. A typical deuteration sequence follows: 75 ml of C_5H_6, 2.0 g of KOH, 45 ml of D_2O, 45 ml of dioxane; 53 ml of $C_5H_xD_{6-x}$, 2.0 g of KOH, 47 ml of D_2O, 45 ml of dioxane; 32 ml of $C_5H_xD_{6-x}$, 2.0 g of KOH, 45 ml of D_2O, 35 ml of dioxane; 23 ml of C_5H_6, 2.0 g of KOH, 65 ml of D_2O, 45 ml of dioxane. Yield: 15 ml of 95 atom % deuterated cyclopentadiene. The C_5D_6 was dried with Linde 3A molecular sieves prior to use.

LiC_5D_5. This compound was always obtained as a powder, rather than as a crystalline solid. Since LiC_5D_5 is very difficult to purify, the best procedure is to obtain the compound in as pure a state as possible. The most successful method of preparation was the reaction of methyllithium (Foote, 5.09% solution in ether, or Ventron, 1.65 *M* in ether) with C_5D_6 in purified ether. A fresh bottle of $(CH_3Li)_4$ was used whenever possible; prior to use the $(CH_3Li)_4$ solution was filtered and analyzed by titration for total base and/or $(MeLi)_4$ by integration relative to a known amount of benzene internal standard.[23] A 500-ml three-necked flask equipped with gas inlets and outlets, magnetic stirrer, and Dry Ice condenser was flushed with N_2 and then charged with 75 ml of ether and 9.2 ml of C_5D_6. Over about an hour 57 ml of 1.7 *F* $(CH_3Li)_4$ in ether was added through a dropping funnel. Solid LiC_5D_5 began to precipitate almost immediately. LiC_5D_5 was filtered in the drybox and dried under vacuum for several days. The best equivalent weight for 92% deuterated material obtained by this method was 76.4 ± 0.1 (calculated, 76.59). Infrared and nmr spectra confirmed the purity of the material, even for batches of LiC_5D_5 with lower equivalent weights than the theoretical. Samples with low equivalent weights gave the same kinetic results as samples with an excellent equivalent weight. The low equivalent weights sometimes observed are attributed to very small amounts of LiOH or Li_2CO_3. The material could not be analyzed for C/H; it is air sensitive and because of its finely powdered nature could not be handled quantitatively in an inert atmosphere. This difficulty in analysis has been experienced before,[24] with LiC_5H_5 prepared by a method similar to ours.

Nickelocene was purchased from Alfa and sublimed twice at 40° (0.5 mm) prior to use.

Perdeuterionickelocene, $Ni(C_5D_5)_2$, was prepared by reacting $NiBr_2(glyme)$[25] with LiC_5D_5 in THF in an inert atmosphere. The reaction was immediate. The THF was evaporated and the residue was extracted with hexane and filtered, followed by removal of hexane, and sublimation. The per cent deuteration was determined as follows: the concentration of total nickelocene species was determined either from the visible spectrum ($\epsilon = 66.0\ M^{-1}\ cm^{-1}$ in THF at 694 nm) or from the known (gravimetric) concentration of the solution; concentration of undeuterated nickelocene was determined from the C–H stretching overtone at 1.644 μm ($\epsilon = 3.97\ M^{-1}\ cm^{-1}$ in THF). The per cent deuteration computed by this method agreed with that of the C_5D_6 (used to prepare the LiC_5D_5) within experimental error.

NaC_5H_5 was prepared from C_5H_6 and NaH in THF by a literature method.[26] **$MnCp_2$** was prepared from $MnBr_2$ and NaCp in THF by the method of Wilkinson, *et al.*[27,28]

Kinetic Studies. Preparation of Solutions. Samples were prepared individually, using volumetric flasks with ground glass stoppers. Each weighing was performed in the laboratory and each transfer of air-sensitive material performed in the drybox. When TMEDA was used in the kinetic runs, the sample was diluted almost to volume in the drybox; then the required volume of TMEDA (density = 0.766 g/mol) was syringed into the flask.

Techniques of the Kinetic Study. The rates of exchange of $NiCp_2$ with LiC_5D_5 in THF were followed by observing the rate of disappearance of the first overtone of the $NiCp_2$ C–H stretching vibration on the Cary 14 spectrophotometer. For $NiCp_2$ in THF this absorbance occurs at 1.644 μm ($\epsilon = 3.97\ M^{-1}\ cm^{-1}$) compared with 1.662 μm ($\epsilon = 0.769\ M^{-1}\ cm^{-1}$) for the corresponding LiC_5H_5 vibration. These C–H overtone assignments are in agreement with those published for other mono- and bis(cyclopentadienyl) compounds.[29] Since ϵ for the LiC_5H_5 overtone is much smaller than for the $NiCp_2$ overtone, and since LiC_5H_5 does not absorb at 1.644 μm, the best results are obtained by observing the $NiCp_2$ peak. Solutions of $NiCp_2$ in THF and benzene and $MnCp_2$ in benzene follow Beer's law in the ranges of concentrations and absorbances used. In benzene solution, the C–H overtone of $MnCp_2$ overlaps that of $NiCp_2$. Hence it was necessary to solve simultaneous equations to determine the distribution of label between Ni and Mn. The extinction coefficients at the appropriate wavelengths in C_6D_6 are, for $NiCp_2$, 1.644 μm (λ_{max}), 4.10 $M^{-1}\ cm^{-1}$; 1.649 μm, 1.82 $M^{-1}\ cm^{-1}$; and for $MnCp_2$, 1.644 μm, 1.45 $M^{-1}\ cm^{-1}$; 1.649 μm (λ_{max}), 3.14 $M^{-1}\ cm^{-1}$.

Between spectral measurements the cells were placed in a constant temperature bath regulated to ±0.05°. Because the reaction is so fast for $NiCp_2$–LiC_5D_5 exchange in the presence of TMEDA, the spectrum was scanned continuously and the cells were thermostated in the cell compartment.

Treatment of Data. The data were treated by means of eq 1, which

$$-\ln(1-\gamma) = R\left(\frac{m[AX_m]_{tot} + n[BX_n]_{tot}}{(mn[AX_m]_{tot})([BX_n]_{tot})}\right)t \qquad (1)$$

is of the same form as that derived by Harris.[30] Here γ is the fraction of exchange that has occurred ($\gamma = 1$ at equilibrium), t is the time, m and n are the number of exchangeable groups X on AX_m and BX_n, respectively, $[AX_m]_{tot}$ and $[BX_n]_{tot}$ are the total concentrations of both labeled and unlabeled AX_m and BX_n, respectively. Assuming no isotope effect, R is the rate exchange of both labeled and unlabeled AX_m or BX_n. According to eq 1, a plot of $-\ln(1-\gamma)$ *vs.* t should be linear, with a slope equal to R times a function of known total concentrations. When $\gamma = 0.5$ we can evaluate R in terms of the half-life $t_{1/2}$

$$R = \frac{0.6931}{t_{1/2}}\ \frac{(mn[AX_m]_{tot})([BX_n]_{tot})}{m[AX_m]_{tot} + n[BX_n]_{tot}} \qquad (2)$$

For LiC_5D_5 exchange with $NiCp_2$ we set $m = 2$ and $n = 1$, and

$$R = \frac{0.6931}{t_{1/2}}\ \frac{2[NiCp_2]_{tot}[LiCp]_{tot}}{2[NiCp_2]_{tot} + [LiCp]_{tot}} \qquad (3)$$

The half-life, $t_{1/2}$, is evaluated from the plot of $-\ln(1-\gamma)$ *vs.* t.

The fraction reacted, γ, is x_t/x_∞, where the reaction parameter x represents the moles of C_5H_5 rings replaced by C_5D_5 rings at time t (x_t) and at equilibrium (x_∞), respectively. Using Beer's law we express the fraction not reacted, $1-\gamma$, as $(A_t - A_\infty)/(A_0 - A_\infty)$, where A_t, A_∞, and A_0 are the absorbances at the C–H overtone at time t, equilibrium, and zero time, respectively. Since $A_0 - A_\infty$ is constant for a given run, a plot of $-\log(A_t - A_\infty)$ is linear and permits ready evaluation of $t_{1/2}$. Using eq 1 or 3, R is computed from the half-life and the initial concentrations. A study of the dependence of R on the initial concentrations of LiC_5D_5 and $NiCp_2$ yields the rate law. In the case of LiC_5D_5–$NiCp_2$ exchange, we found that the reaction proceeds by two paths, such that $R = R_1 + R_2$ in eq 3. It was necessary to show that eq 3 holds rigorously for the case of two parallel paths, and the derivation is done in the Appendix.

For $Ni(C_5D_5)_2$ exchange with $MnCp_2$, plots were made of $-\log([MnCp_2]_t - [MnCp_2]_\infty)$ *vs.* t and of $-\log([NiCp_2]_\infty - [NiCp_2]_t)$ *vs.* t. The half-lives found by the two computations were averaged and used to calculate R.

Results

Lack of H-D Exchange with Solvent. Exchange of D on LiC_5D_5 for H in THF was ruled out. Thus, 92 atom % LiC_5D_5 was equilibrated for 5 weeks in purified THF in the drybox. $[NiBr_2(glyme)]$ was then added and the resulting nickelocene was isolated by evaporation of the THF, followed by sublimation. The isolated nickelocene was found to

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Table I. Visible Spectra of Nickelocene in Different Media

Medium	λ_{max}, nm (ϵ, cm^{-1} M^{-1})
$NiCp_2$ in hexane (0.192 M)	692 (60.3)
$NiCp_2$ in THF (0.170 M)	694 (65.9)
$NiCp_2$ (0.195 M) + LiCp (0.177 M) in THF	692 (66.4)
$NiCp_2$ (0.188 M) + LiCp (0.093 M) + TMEDA (0.092 M) in THF	693 (64.3)

be 92.2% deuterated, indicating no H-D exchange involving THF.

Ring Exchange *vs.* Hydrogen Exchange. To determine whether the entire ring or individual protons exchange, mass spectra were obtained for nickelocene isolated from solutions of $NiCp_2$ and LiC_5D_5 and $NiCp_2$ and LiC_5D_5-(TMEDA). The experimental spectra agree well with those predicted for exchange of the entire ring. Most, if not all, of the observed replacement of H by D proceeds by ring exchange, as indicated by lack of randomization of the label among rings.

Formation of Adducts. An adduct of $NiCp_2$ with LiC_5D_5, with LiC_5D_5-(TMEDA), or with $MnCp_2$ or a formation of a $NiCp_2$ solvate with THF would be possible intermediates for the exchange reactions. Hence visible spectra were recorded of $NiCp_2$ in hexane, in THF, and in THF solutions of various exchanging species. The spectra in the different media are quite similar (see Table I); very little variation in extinction coefficient or λ_{max} was observed in the different media. These experiments, of course, do not rule out the possibility of minute concentrations of adducts or solvates as intermediates or the possibility of species resembling such adducts as transition states in the exchange reactions.

Lithium Cyclopentadienide Exchange with Nickelocene. A typical plot of $-\log (A_t - A_\infty)$ *vs.* t is shown in Figure 1. The results of the exchange reaction between $NiCp_2$ and LiC_5D_5 in THF at 25.0, 30.0, and 35.0° are summarized in Table II, where R is the over-all rate of exchange discussed above. k_{obsd} equals R divided by the product of the initial nickelocene and the initial lithium cyclopentadienide concentrations. The concentrations of LiC_5D_5 and $NiCp_2$ have been varied over only about one order of magnitude, because of the need to counterbalance solubilities, rates of reaction, and accurately measurable absorbance changes. There was generally good agreement between the calculated and observed total changes in absorbance, most final readings being within 10% of the calculated result. Thus, there is no significant isotope effect on equilibrium. k_{obsd} is definitely not constant but increases with increasing concentration of LiC_5D_5. Plots of k_{obsd} *vs.* $[LiCp]_{tot}$ are linear, with an intercept k_0 and a slope k_1. These plots for the three temperatures studied are presented in Figure 2. The values of k_0 and k_1 (Table III) were obtained from a least-squares analysis of the data in Table II. The error limits quoted are one standard deviation. The fact that the error limits in k_0 are larger than on k_1 reflects mainly the difficulty of accurately measuring intercepts of lines. The observed rate law is given by eq 4.

$$\frac{-d[Ni\text{-}C_5H_5]}{dt} = k_0[LiCp]_{tot}[NiCp_2]_{tot} + k_1[LiCp]_{tot}^2[NiCp]_{tot} \quad (4)$$

The tot subscripts on the concentration terms indicate that the rate law is expressed accurately in terms of the total concentration of $NiCp_2$ and LiCp (expressed as monomer), labeled or unlabeled. The activation parameters obtained by a least-squares fit to the plots of $-\log k_0$ *vs.* $1/T$ and $-\log k_1$ *vs.* $1/T$ are presented in Table IV. Again the error limits quoted are one standard deviation.

Table II. Exchange of $NiCp_2$ with LiC_5D_5 in THF

Temp, °C	[LiC_5-D_5], M	[$Ni(C_5$-$H_5)_2$], M	10^6R,[a] M sec^{-1}	10^5k_{obsd},[b] M^{-1} sec^{-1}	$t_{1/2}$, hr
25.0	0.0541	0.207	0.518	4.64	17.8
	0.170	0.0784	0.856	6.43	18.3
	0.251	0.393	7.72	7.81	4.75
	0.258	0.393	7.84	7.73	4.77
	0.279	0.164	3.68	8.02	7.90
	0.375	0.136	4.74	9.30	6.40
	0.421	0.334	14.3	10.2	3.47
	0.424	0.324	14.5	10.5	3.40
30.0	0.0626	0.202	0.741	5.86	14.0
	0.146	0.203	2.36	7.94	8.72
	0.259	0.401	12.2	11.7	3.10
	0.355	0.284	14.1	14.0	2.97
	0.425	0.327	19.8	14.3	2.50
35.0	0.0534	0.200	0.840	7.86	10.8
	0.141	0.199	3.56	12.7	6.90
	0.261	0.399	18.4	17.6	2.06
	0.365	0.297	20.8	19.2	2.08
	0.428	0.327	29.2	20.8	1.70

[a] Rate of exchange of labeled and unlabeled C_5H_5. [b] $k_{obsd} = R/[LiC_5D_5][NiCp_2]$.

Table III. k_0 and k_1 for LiC_5D_5 + $Ni(C_5H_5)_2$ Exchange

T, °C	10^5k_0, M^{-1} sec^{-1}	10^4k_1, M^{-2} sec^{-1}
25.0	3.9 ± 0.2	1.50 ± 0.08
30.0	4.5 ± 0.7	2.5 ± 0.3
35.0	7.4 ± 0.9	3.4 ± 0.2

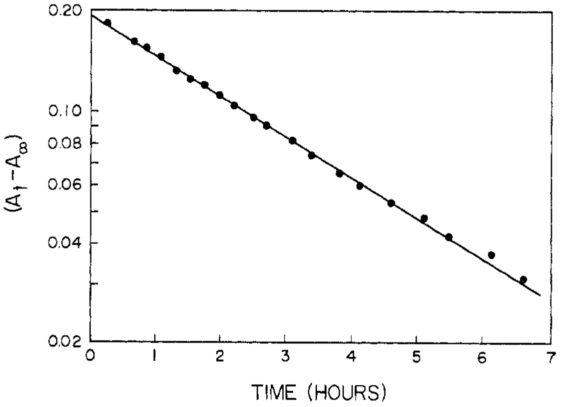

Figure 1. Plot of $-\log (A_t - A_\infty)$ *vs.* t for the system 0.425 M LiCp-0.327 M $NiCp_2$ at 30°.

Stoichiometry of the Complex of LiC_5H_5 and TMEDA. In the absence of TMEDA the nmr absorbance for 0.355 M LiC_5H_5 in THF occurs as a singlet at 95.2 ± 0.2 Hz upfield from internal benzene; in the presence of excess TMEDA the resonance is observed at 90.4 Hz upfield. A plot of the LiC_5H_5 chemical shift (0.355 M) in hertz relative to benzene *vs.* mole fraction of TMEDA is presented in Figure 3. The sudden break in the line at TMEDA mole fraction 0.5 indicates that TMEDA forms a strong 1:1 complex with LiC_5H_5.

Exchange of $NiCp_2$ with LiC_5D_5·(TMEDA). Results are presented in Table V. As shown by the data at 27°, the reaction follows a simple second order rate law

$$\frac{-d[Ni\text{-}C_5H_5]}{dt} = k_2[LiC_5D_5\cdot(TMEDA)][NiCp_2] \quad (5)$$

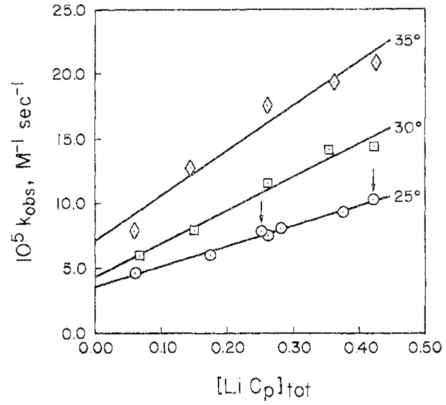

Figure 2. Plots of k_{obsd} *vs.* $[\mathrm{LiCp}]_{tot}$. All runs at 30 and 25°, and the 25° runs indicated by arrows used LiC_5D_5 of equivalent weight 67.4. The rest of the 25° runs used LiC_5D_5 of equivalent weight 76.4.

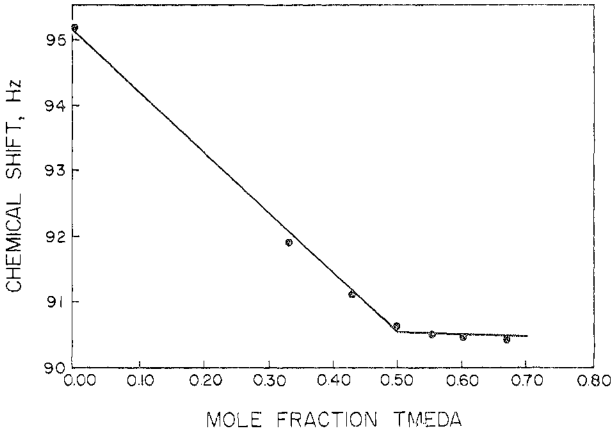

Figure 3. LiC_5H_5 chemical shift (in hertz upfield from internal benzene) *vs.* mole fraction of added TMEDA. $[LiC_5H_5] = 0.355\ M$ in THF.

Table IV. Activation Parameters for $LiC_5D_5 + Ni(C_5H_5)_2$ Exchange

Path	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
k_0	11 ± 3	−40 ± 10
k_1	14 ± 2	−26 ± 6

Table V. Exchange of $Ni(C_5H_5)_2$ with $LiC_5D_5\cdot$(TMEDA) in THF

Temp,[a] °C	$[LiC_5D_5\cdot$(TMEDA)], *M*	$[Ni(C_5H_5)_2]$, *M*	10^5R,[b] *M* sec^{-1}	10^3k_2, M^{-1} sec^{-1}	$t_{1/2}$, min
27	0.0926	0.188	2.15	1.23	40
27.0 ± 0.2	0.140	0.148	2.44	1.18	45.0
	0.229	0.116	3.31	1.24	33.0
	0.332	0.0903	3.28	1.09	41.2
	0.380	0.0804	3.73	1.22	35.0
	0.432	0.0533	2.45	1.06	40.2
19.4 ± 0.1	0.141	0.145	1.43	0.700	76.5
	0.376	0.798	1.85	0.603	71.5
14.6 ± 0.6	0.155	0.155	1.33	0.553	89.7
13.3 ± 0.5	0.390	0.0851	1.29	0.384	106

[a] The sample was thermostated in the beam; hence the temperature variation was greater than with a constant-temperature bath. [b] Rate of exchange of labeled and unlabeled C_5H_5.

Table VI. Exchange of $Ni(C_5D_5)_2$ with $Mn(C_5H_5)_2$ in C_6D_6

Temp, °C	$[Mn(C_5H_5)_2]$, *M*	$[Ni(C_5D_5)_2]$, *M*	10^7R,[a] *M* sec^{-1}	10^6k_3,[b] M^{-1} sec^{-1}	$t_{1/2}$, days
30.0	0.112	0.235	1.17	4.44	10.4
	0.100	0.588	2.51	4.25	5.5
	0.156	0.220	1.50	4.36	9.8
45.0	0.149	0.250	6.17	16.5	2.4
55.0	0.134	0.250	10.7	32.0	1.3

[a] Rate of exchange of labeled and unlabeled C_5H_5. [b] $k_3 = R/[MnCp_2][Ni(C_5D_5)_2]$.

From the temperature dependence of k_2, one obtains the following activation parameters: $\Delta H^\ddagger = 11.5 \pm 0.7$ kcal/mol and $\Delta S^\ddagger = -32 \pm 3$ eu.

Exchange of Manganocene with $Ni(C_5D_5)_2$. The results of these exchange reactions are listed in Table VI. The limited data for manganocene suggest that its exchange with nickelocene follows a second order rate law

$$\frac{-d[Ni\text{-}C_5D_5]}{dt} = k_3[NiCp_2][MnCp_2] \qquad (6)$$

From the temperature dependence of k_3, we find $\Delta H^\ddagger = 15.3 \pm 0.9$ kcal mol^{-1} and $\Delta S^\ddagger = -30 \pm 3$ eu.

Discussion

Nature of Lithium Cyclopentadienide and Its TMEDA Adduct in THF. Since LiCp is insoluble in nondonor solvents, our exchange studies were conducted in THF solution, as were the studies in the presence of TMEDA. Two previous studies[31,32] of LiCp in THF are relevant to the present work.

Ford[31] examined THF solutions of LiCp by uv, ir, and pmr spectroscopy in the concentration range 10^{-3}–1 *M*. The uv spectrum agrees well with the spectrum calculated[33-36] for $C_5H_5^-$, suggesting a delocalized C_5 structure rather than a diene type structure with monohapto-C_5H_5 bound to Li. Similarly the ir spectrum of LiCp in THF also strongly points to a delocalized C_5 structure, as does our observation that the C-H overtone for LiC_5H_5 in THF is a sharp singlet. The pmr spectrum is also a sharp singlet at 5.6–5.7 ppm, depending slightly on concentration. Ford[31] suggested that the concentration dependence might arise from oligomerization or from changes in the nature of the ion pair. On the basis of Smid's spectroscopic[37] and conductivity[38] results for fluorenyllithium, as well as calculations using the Fuoss[39,40] equation, practically no free ions are expected in LiCp solutions in THF in the concentration range 0.05–0.5 *M*.

Cox, *et al.*,[32] have studied the ^7Li nmr of various organolithiums, including LiCp, in THF in the concentration range 0.1–0.4 *M*. The rather large high-field chemical shift for ^7Li in LiCp–THF indicates that the ion pair is "tight" and that the Li sits above the Cp π system, in the shielding region. The ^7Li chemical shift for LiCp is very slightly dependent upon concentration in the range 0.1–0.4 *M*.[32] The available experimental results[31,32] suggest **1** as the probable structure for LiCp in THF. Here an indefinite number of solvent molecules are presumed to be coordinated.

The slight concentration dependencies of ^1H and ^7Li chemi-

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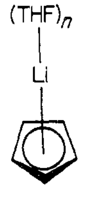


1

cal shifts for LiCp-THF could imply that oligomerization equilibria need to be considered. Oligomerization is common for organolithium compounds,[41] and in general the extent of aggregation decreases with increasing stability of the anion.[42] *n*-Butyllithium, for example, is tetrameric in THF, while in the same solvent fluorenyllithium is dimeric, benzyllithium is monomeric, and allyllithium undergoes a monomer-dimer equilibrium.[42,43] In view of all these observations, equilibration in THF of monomeric LiCp with a dimeric form would not be surprising.

Our results show that LiCp in THF forms a 1:1 complex with TMEDA. X-Ray studies of the TMEDA adducts of triphenylmethyllithium[44] and dilithionaphthelenide[45] bear out the expectation that TMEDA acts as a bidentate chelate toward Li. It is therefore most likely that TMEDA replaces at least two THF's on coordination to **1** and perhaps additional THF molecules due to steric interactions.

Exchange of $\mathrm{LiC_5D_5}$ with $\mathrm{NiCp_2}$. The observed rate law (eq 4) has terms first and second order in $[\mathrm{LiCp}]_{\mathrm{tot}}$. In our interpretation, the k_0 path involves reaction of LiCp monomer, while the k_1 path involves reaction with $(\mathrm{LiCp})_2$, a dimer. This would involve the bimolecular elementary steps of eq 7.

$$\left.\begin{array}{l}\mathrm{NiCp_2 + LiCp} \xrightarrow{k_0}\\ \mathrm{NiCp_2 + (LiCp)_2} \xrightarrow{k'}\end{array}\right\}\text{equilibrium product mixture} \qquad (7)$$

If we express $[(\mathrm{LiCp})_2]$ as $K_{\mathrm{d}}[\mathrm{LiCp}]_{\mathrm{eq}}^2$, where K_{d} is the dimerization constant, the rate law consistent with eq 7 is

$$\frac{-\mathrm{d}[\mathrm{Ni\text{-}C_5H_5}]}{\mathrm{d}t} = k_0[\mathrm{LiCp}]_{\mathrm{eq}} + k'K_{\mathrm{d}}[\mathrm{LiCp}]_{\mathrm{eq}}^2[\mathrm{NiCp}] \qquad (8)$$

Equation 8 appears to have the same form as the experimental rate law (eq 4) with $k_1 = k'K_{\mathrm{d}}$. However, eq 8 is expressed in terms of the actual equilibrium concentration of LiCp, which is unknown, since K_{d} is unknown. Since the plots used to derive eq 4 show no significant deviation from linearity, it must be true that

$$[\mathrm{LiCp}]_{\mathrm{eq}} \approx [\mathrm{LiCp}]_{\mathrm{tot}} \qquad (9)$$

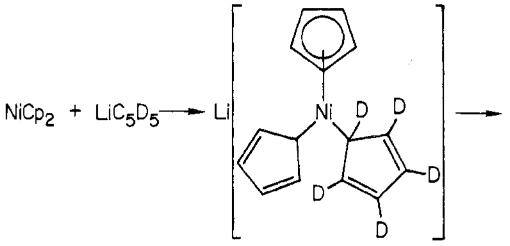
and therefore

$$[(\mathrm{LiCp})_2]^2 = K_{\mathrm{d}}[\mathrm{LiCp}]_{\mathrm{eq}}^2 \approx K_{\mathrm{d}}[\mathrm{LiCp}]_{\mathrm{tot}}^2 \qquad (10)$$

The substitution of $[\mathrm{LiCp}]_{\mathrm{tot}}$ for $[\mathrm{LiCp}]_{\mathrm{eq}}$ in eq 8 gives a rate expression in agreement with eq 4. Our calculations indicate that if $K_{\mathrm{d}} \leqslant 10^{-1}\ M^{-1}$, then eq 9 and 10 hold to within 10%. We therefore take $10^{-1}\ M^{-1}$ as an upper limit to K_{d}.

Intervention of dimeric $(\mathrm{LiCp})_2$ in exchange reaction is perhaps not surprising in view of the comments above concerning organolithium oligomers. The structure of $(\mathrm{LiCp})_2$ in THF is unknown; indeed the present results offer the first clear indication that such a monomer-dimer equilibrium is important in THF. The relatively small derived value for K_{d} is consistent with the earlier general observation[42] on organolithium compounds in THF, that the monomer is favored as the anion becomes more delocalized.

The second order rate law observed for the k_0 (monomer) path suggests associative activation. Although the rather large error limits on our activation parameters for LiCp exchange suggest limitations on their quantitative significance, the apparent large negative $\Delta S^{\ddagger}$ is consistent with an associative exchange. We propose that the exchange process proceeds through a transition state similar to that shown in eq 11. The structure represented in **2** is attractive in that



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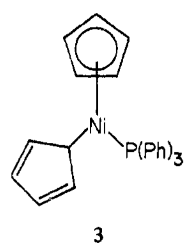
$$\mathrm{Ni(C_5H_5)(C_5D_5) + LiC_5H_5} \qquad (11)$$

nickel achieves the effective atomic number of Kr, and in fact some of the driving force for the reaction may derive from the fact that Ni in $\mathrm{NiCp_2}$ must accommodate 2 more electrons than allowed from EAN considerations. There is considerable precedent for the η^5,η^1,η^1 structure of **2**. In the reaction of $\mathrm{NiCp_2}$ with $\mathrm{PPh_3}$, Ustynyuk, *et al.*,[46] isolated an unstable compound whose chemical reactions are similar to those of $\mathrm{Ni(Cp)(CH_3)(PPh_3)}$, suggesting **3** as the structure for the isolated compound. There is kinetic and spectroscopic evidence for an intermediate of structure **4** in the reaction of $\mathrm{NiCp_2}$ with triethyl phosphite,[3] and **5** was proposed by Ellgen and Gregory as a potential intermediate in $\mathrm{NiCp_2}$



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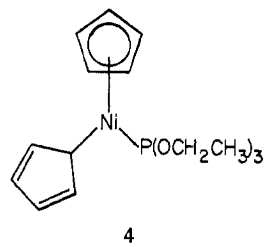

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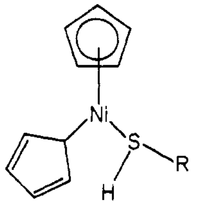

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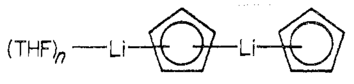
reaction with thiols.[47] In this latter reaction, with C_6H_5SH as an example, the rate law is first order in $NiCp_2$ and first order in C_6H_5SH, with $\Delta H^\ddagger = 13 \pm 1$ kcal/mol and $\Delta S^\ddagger = -26 \pm 4$ eu. These results are more precise than ours but are nevertheless quite similar, which lends support to our mechanistic interpretation.

Activation parameters were also obtained for the k_1 (dimer) exchange process (Table IV). Since in our interpretation $k_1 = k'K_d$, no simple interpretation of the temperature dependence of k_1 can be given. An associative process for the dimer exchange path is preferred in view of what is known about the monomer exchange and also in view of the form of the rate law. We suggested above that a reasonable upper limit for K_d is $10^{-1}\ M^{-1}$, and at 25.0° $k_1 = k'K_d = 1.50 \times 10^{-4}\ M^{-2}\ \text{sec}^{-1}$. Hence k', the true rate constant for the dimer, is $\geqslant 1.50 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$, or at least 40 times greater than the rate constant for the monomer. Actually, the derived value for k' is very similar to the second order rate constants for $NiCp_2$ exchange with LiCp·(TMEDA), and this suggests at least one rather nucleophilic ring in the dimer. In a structure such as **6**, the nonbridging ring might well be more nucleophilic if the bridging Cp is a better donor toward the "sandwiched" Li than were the solvent molecules which are displaced on dimerization. Although Brown[41] has observed that deoligomerization of organolithiums increases reactivity as polymerization catalysts, West, *et al.*,[48] have found that, in the lithiation of Ph_3CH in THF, $(PhLi)_2$ is more reactive than (PhLi), while the opposite is true for allyllithium monomer and dimer. These results suggest that there is probably no general expectation regarding relative reactivities of monomer and oligomers.



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Exchange of LiC_5D_5·TMEDA with $NiCp_2$. The reaction of nickelocene with LiC_5D_5·(TMEDA), also first order in each reagent, is much faster than the reaction with LiC_5D_5. But the similarity of the activation parameters for the LiC_5D_5·(TMEDA) reaction to those for LiC_5D_5 strongly suggests that the two reactions proceed by a similar path, a rate-determining association of the Li species with nickelocene. The simpler rate law in this case presumably results from the presence of only one lithium cyclopentadienide species, namely a 1:1 complex of TMEDA and LiC_5D_5. The simplification of the rate law in the presence of this 1:1 adduct gives convincing support to our interpretation of the two-term rate law for LiC_5D_5 as a monomer-dimer equilibrium.

The over-all polarity of the medium presumably increases with increasing concentration of LiC_5D_5 or LiC_5D_5·(TMEDA). If medium effects are responsible for the complex rate law for LiC_5D_5, one would expect the variation in k_{obsd} with LiC_5D_5·(TMEDA) concentration to be even more dramatic, since we expect the complex to be more basic and polar than LiC_5D_5. Hence the absence of a complex rate law for the exchange of LiC_5D_5·(TMEDA) with nickelocene rules out the possibility of a medium effect on the LiC_5D_5 exchange.

The acceleration of the reaction rate in the presence of TMEDA is probably the result of increased charge separation between Li and Cp in the complex, in comparison with LiCp. Displacement of solvating THF on LiCp·*n*(THF) by the much better donor TMEDA should significantly reduce the affinity of Li for Cp, permitting greater charge build-up on the C_5H_5 moiety. Steric considerations alone would suggest that the separation between the Li and the C_5H_5 ring would be greater in the TMEDA adduct that in LiC_5H_5. The greater reactivity of LiCp·(TMEDA) is analogous to that of other organolithium–TMEDA complexes. The TMEDA complex of *n*-butyllithium, for example, is a much more reactive lithiating agent than is *n*-butyllithium.[49]

It is possible that lithium plays an important role in the LiCp–$NiCp_2$ exchange. A possible role would be stabilization of negative charge on an intermediate anion such as $[Ni(C_5H_5)_3]^-$. If the lithium plays such a role in the reaction, one would expect chelation by the diamine to slow the rate of reaction. Though the acceleration of the rate in the presence of TMEDA does not rule out assistance by Li, these results show that the increased basicity of the Cp ring in LiCp·(TMEDA) outweighs any such effect.

Exchange of $Ni(C_5D_5)_2$ with $MnCp_2$. The large negative $\Delta S^\ddagger$ and the apparent second order rate law in benzene for cyclopentadienyl exchange between $MnCp_2$ and $Ni(C_5D_5)_2$ suggest that this reaction occurs by an associative mechanism similar to that for the LiC_5D_5 and LiC_5D_5·(TMEDA) exchanges with nickelocene. The exchange of $MnCp_2$ with $Ni(C_5D_5)_2$ in benzene is about tenfold slower than the monomeric LiC_5D_5–$NiCp_2$ exchanges in THF. It would be interesting to compare these reactivities in the same solvent; however, LiC_5D_5 is insoluble in benzene, and our preliminary indications are that $MnCp_2$ does *not* exchange with $Ni(C_5D_5)_2$ in THF. It would appear that $MnCp_2$ forms an unreactive THF solvate; in fact a substance of approximate stoichiometry $MnCp_2$·$(THF)_2$ has been isolated.[27]

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Appendix

Derivation of Equation 3 for the Case of Exchange among Three Components. The system under study involves exchange of LiCp and $(LiCp)_2$ with $NiCp_2$, as summarized in eq A1–3.

$$\text{NA} + \text{MA*} \overset{R_1}{\rightleftharpoons} \text{NA*} + \text{MA} \tag{A1}$$

$$\text{NA} + \text{M}_2(\text{A*})_2 \overset{R_2}{\rightleftharpoons} \text{NA*} + \text{M}_2\text{AA*} \tag{A2}$$

$$\text{NA} + \text{M}_2\text{AA*} \overset{R_2}{\rightleftharpoons} \text{NA*} + \text{M}_2\text{AA} \tag{A3}$$

Here N is Ni, M is Li, A is unlabeled Cp, A* is labeled Cp, R_1 is the exchange rate for the monomer path, and R_2 is the exchange rate for the dimer path. We assume that the rate of equilibration of MA and M_2A_2 is fast compared to the R_1 and R_2 exchange rates. If initial concentrations are designated with subscript zero in our system, $[\text{NA*}]_0 = 0$. We now define

$$\text{reaction parameter} = x = [\text{NA*}] \tag{A4}$$

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$$2[\mathrm{NiCp_2}]_0 = n = [\mathrm{NA}]_0 = [\mathrm{NA}] + [\mathrm{NA^*}] \tag{A5}$$

$$\text{total lithium} = m = [\mathrm{MA}] + [\mathrm{MA^*}] + 2[\mathrm{M_2A_2}] + 2[\mathrm{M_2AA^*}] + 2[\mathrm{M_2(A^*)_2}] \tag{A6}$$

$$\text{total label} = a = [\mathrm{MA^*}]_0 + 2[\mathrm{M_2(A^*)_2}]_0 + [\mathrm{M_2AA^*}]_0 \tag{A7}$$

$$\text{total } [\mathrm{LiCp}] = v = [\mathrm{MA}] + [\mathrm{MA^*}] \tag{A8}$$

$$\text{total } [(\mathrm{LiCp})_2] = \mu = [\mathrm{M_2A_2}] + [\mathrm{M_2AA^*}] + [\mathrm{M_2(A^*)_2}] \tag{A9}$$

In terms of these parameters, the amount of label on lithium species at any time is

$$a - x = [\mathrm{MA^*}] + 2[\mathrm{M_2(A^*)_2}] + [\mathrm{M_2AA^*}] \tag{A10}$$

Using a purely statistical analysis, the rate of approach to equilibrium is given by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = R_1 \left\{ \frac{[\mathrm{MA^*}]}{v} \frac{[\mathrm{NA}]}{n} - \frac{[\mathrm{MA}]}{v} \frac{[\mathrm{NA^*}]}{n} \right\} + R_2 \left\{ \frac{[\mathrm{M_2(A^*)_2}]}{\mu} \frac{[\mathrm{NA}]}{n} + \frac{1}{2} \frac{[\mathrm{M_2AA^*}]}{\mu} \frac{[\mathrm{NA}]}{n} - \frac{1}{2} \frac{[\mathrm{M_2AA^*}]}{\mu} \frac{[\mathrm{NA^*}]}{n} - \frac{[\mathrm{M_2A_2}]}{\mu} \frac{[\mathrm{NA^*}]}{n} \right\} \tag{A11}$$

We now make the following substitutions in eq A11

$[\mathrm{NA}] = n - x$

$[\mathrm{NA^*}] = x$

$[\mathrm{MA^*}]/v = (a - x)/m$

$[\mathrm{M_2(A^*)_2}]/\mu = (a - x)^2/m^2$

$[\mathrm{M_2AA^*}]/\mu = 2(a - x)(m - a + x)/m^2$

$[\mathrm{M_2AA}]/\mu = (m - a + x)^2/m^2$

This leads to

$$\frac{\mathrm{d}x}{\mathrm{d}t} = R_1 \left\{ \frac{a - x}{m} - \frac{x}{n} \right\} + R_2 \left\{ \frac{(a - x)^2}{m^2} + \frac{(a - x)(m - a + x)}{m^2} - \frac{x}{n} \right\} \tag{A12}$$

Since R_1 and R_2 are independent, the two bracketed terms in eq A12 must vanish at t_∞. In either case, one finds

$$n = mx_\infty/(a - x_\infty) \tag{A13}$$

The substitution $mx_\infty/(a - x_\infty)$ for n in eq A12 gives

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \left\{ R_1 + R_2 \right\} \left(\frac{a}{m} \right) \left(1 - \frac{x}{x_\infty} \right) \tag{A14}$$

Equation A14 may be integrated to yield eq A15 in terms of $t_{1/2}$

$$R_1 + R_2 = 0.6931mx_\infty/at_{1/2} \tag{A15}$$

Since $x_\infty = na/(m + n)$, eq A15 may be written

$$R_1 + R_2 = 0.6931mn/(m + n)t_{1/2} \tag{A16}$$

Substituting $[\mathrm{LiCp}]_{\mathrm{tot}}$ for m and $2[\mathrm{NiCp_2}]_{\mathrm{tot}}$ for n, we finally get

$$R_1 + R_2 = \frac{0.6931}{t_{1/2}} \frac{2[\mathrm{NiCp_2}]_{\mathrm{tot}}[\mathrm{LiCp}]_{\mathrm{tot}}}{2[\mathrm{NiCp_2}]_{\mathrm{tot}} + [\mathrm{LiCp}]_{\mathrm{tot}}} \tag{A17}$$

Equation A17 is the same as eq 3, showing that eq 3 is appropriate for the present example of exchange by two paths. We found experimentally that R_1 and R_2 may be further expressed as

$$R_1 = k_0[\mathrm{LiCp}]_{\mathrm{tot}}[\mathrm{NiCp_2}]_{\mathrm{tot}} \tag{A18}$$

$$R_2 = k_1[\mathrm{LiCp}]_{\mathrm{tot}}^{\,2}[\mathrm{NiCp_2}]_{\mathrm{tot}} \tag{A19}$$

Registry No. $\mathrm{Ni(C_5H_5)_2}$, 1271-28-9; $\mathrm{LiC_5D_5}$, 37013-18-6; $\mathrm{LiC_5D_5 \cdot (TMEDA)}$, 51464-50-7; $\mathrm{Ni(C_5D_5)_2}$, 51510-35-1; $\mathrm{Mn(C_5H_5)_2}$, 1271-27-8.

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Binding Sites between Platinum(II) and Purine or Pyrimidine Ribosides

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Proton magnetic resonance spectra are reported for the interactions between [Pt(dien)Cl]Cl (dien = $\mathrm{NH_2CH_2CH_2NHCH_2CH_2NH_2}$) and purine or pyrimidine ribosides in aqueous and $\mathrm{D_2O}$ solutions. The binding sites were located by deuteration of the aromatic protons. Both $\mathrm{N_1}$ and $\mathrm{N_7}$ of adenosine and purine riboside are coordinated simultaneously to two different platinum atoms upon mixing the base and [Pt(dien)Cl]Cl in 1:1 ratio. In the case of 6-methylaminopurine riboside, $\mathrm{N_7}$ is significantly favored as a binding site, but $\mathrm{N_1}$ also becomes a binding site when the ratio of [Pt(dien)Cl]Cl to ligand is greater than unity. In cytidine, $\mathrm{N_3}$ is the binding site, whereas uridine does not interact at all with platinum under these conditions.

Introduction

Recently, our work has been centered around platinum nucleoside complexes[1,2] because of their antitumor activity. In an earlier work,[2] we found that guanosine (G), inosine (I), and xanthosine (X) act as monodentate ligands using $\mathrm{N_7}$ as a binding site. Adenosine (A), however, behaves as a bidentate ligand with both $\mathrm{N_1}$ and $\mathrm{N_7}$ coordinated to two platinum atoms. This result led us to consider $\mathrm{N_1}$ of adenosine as a

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