follows from the fact that the Cope rearrangement of these fluxional molecules no longer interchanges C_1 and C_5 (or $C_{2,8}$ and $C_{4,6}$). Of course, the pairs of valence isomers of **1f–i** should have nearly identical oxidation potentials so that their rates of quenching are essentially determined by their equilibrium concentrations.

Conclusion

The radical cations of the bridged bicyclooctadienes **1b–e,h–j** have been recognized as bis-homoaromatic structures, the first class of homoaromatic radical cations, and only the second class of open-shell homoaromatic systems. The influence of the substituted *exo*-methylene groups in **1e–i** on the radical cation structure is an unusual and unprecedented manifestation of molecular orbital effects in radical cation chemistry.

The intermediates **1b–e,h–j** are also of interest because their structure type is different, in principle, from that of the parent molecules. The latter have two-well potential energy surfaces, whereas the radical cations have a single minimum corresponding to the transition state for the degenerate rearrangement of the parent molecules. This qualifies the radical cations as further examples of the family of nonvertical radical cations, to which we have previously assigned the one-electron oxidation products of *endo*-dicyclopentadiene,[27] 1,1-diphenyl-2-methylenecyclopropane,[28] and a pentamethyl-substituted 5-methylenebicyclo[2.2.0]hex-2-ene.[26] We are actively pursuing further examples of this interesting class of radical cations.

Isomerization of 1-Butene Catalyzed by (η^6-Arene)NiR_2. A Very Active Homogeneous Catalyst System

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Abstract: (η^6-Arene)NiR_2 (R = $SiCl_3$, SiF_3, C_6F_5) complexes exhibit very high catalytic activity for the isomerization of 1-butene, especially in bromobenzene solution. The isomerization is generally first order in both 1-butene and Ni complex. The catalytic activity decreases in the order $SiCl_3 > SiF_3 > C_6F_5$. The reaction rate in toluene solution increases with increasing 1-butene concentration below a ratio of $1\text{-}C_4H_8/Ni = 100$ but decreases at higher ratios apparently due to induced decomposition of the Ni complex. However, the rate is not adversely affected by high $1\text{-}C_4H_8$ concentration in bromobenzene solution. The ratio of *cis*-2-butene to the trans isomer is also dependent on solvent, suggesting that an important step in the mechanism is the involvement of solvent in the catalytic cycle. The reaction of ethylene with (η^6-arene)$Ni(SiCl_3)_2$ gives vinyltrichlorosilane and ethyltrichlorosilane. A mechanism is proposed which involves the intermediacy of nickel hydride species generated by the insertion of 1-butene into the Ni–R bond followed by β-hydride elimination.

The synthesis, structure, and reactivity of π-arene complexes of late transition metals have been of great interest.[1-3] The π-arene ligand bound to groups 8–10 metals is often quite labile in solution allowing for unique reactivity at the metal center.[1-5] Three coordination sites are opened by the loss of an η^6-arene, and the interconversion from $\eta^6 \rightarrow \eta^4 \rightarrow \eta^2 \rightarrow \eta^0$ facilitates catalytic cycles for H–D exchange and hydrogenation of arenes.[5]

In previous papers we have reported on the synthesis and reactivity of π-arene nickel(II) and cobalt(II) systems.[4,6] Complexed arenes in (η^6-arene)MR_2 (M = Ni, Co; R = $SiCl_3$, C_6F_5) are easily displaced by ligands such as CO, R_3P, dienes, and THF. In addition, (η^6-toluene)$Ni(C_6F_5)_2$ catalyzes the oligomerization of 1,3-butadiene, the polymerization of norbornadiene, and the hydrogenation of toluene.[4a] We now report a detailed study of 1-butene isomerization by these interesting homogeneous catalysts.

Experimental Section

Materials. 2-Methylallyl chloride, *n*-heptane, bromobenzene, iodobenzene, anisole, 2-chlorotoluene, and a mixture of 3- and 4-bromotoluene (1:3) were purchased from Fisher and Aldrich Chemicals and used without further purification. Nickel metal, cobalt metal, and nickel bromide were purchased from J. T. Baker, Matheson, and Aldrich Chemicals. Diethyl ether and tetrahydrofuran (THF) were refluxed over sodium benzophenone ketyl and distilled before use. Methylene chloride and toluene were refluxed over calcium hydride and distilled. Chlorobenzene and fluorobenzene were refluxed over phosphorus pentoxide and distilled. 3-Chlorotoluene was distilled just before use. All solvents were stored in a nitrogen atmosphere. 1-Butene was purchased from Matheson Co. and ethylene-d_4 (99%) was obtained from Merck and Co.

Preparation of (η^6-Arene)NiR_2 (Arene = Benzene, Toluene, Mesitylene; R = $SiCl_3$ SiF_3, C_6F_5). Bis(2-methylallyl)nickel was prepared from nickel bromide and 2-methylallylmagnesium chloride in ether.[7] (η^6-Toluene)$Ni(SiCl_3)_2$ and (η^6-toluene)$Ni(SiF_3)_2$ were prepared from bis(2-methylallyl)nickel and $SiHCl_3$ ($SiHF_3$) as described earlier.[8] (η^6-Toluene)$Ni(C_6F_5)_2$ was prepared from nickel vapor, C_6F_5Br, and toluene as described earlier.[4a,9] (η^6-Benzene)- and (η^6-mesitylene)$Ni(SiCl_3)_2$ were prepared by displacement of toluene from the η^6-toluene complex with excess benzene and mesitylene, respectively.

Isomerization of 1-Butene with (η^6-Toluene)NiR_2. (η^6-Toluene)NiR_2 (0.1 mmol) was placed in a 100-mL three-necked flask. A solvent (15 mL) was added and the solution was frozen in liquid nitrogen. 1-Butene (10 mmol) was added. The flask was immersed in an ice-water bath and the mixture was stirred magnetically. The start of the reaction was taken to be the time the frozen mixture was completely thawed. At intervals, 0.3–0.5-mL aliquots were withdrawn and analyzed on a Varian 940 gas chromatograph with a 24-ft 25% bis(2-methoxyethyl) adipate on chromosorb-P column operating at room temperature.

Reaction of Ethylene with (η^6-Toluene)$Ni(SiCl_3)_2$ or (η^6-Toluene)$Ni(C_6F_2)_2$. (η^6-Toluene)$Ni(SiCl_3)_2$ or (η^6-toluene)$Ni(C_6F_5)_2$ (0.2 mmol) was placed in a 100-mL three-necked flask. Nitrogen head gas was removed under vacuum and then the complex was exposed to ethylene gas (2.0 mmol) and the system allowed to stand for 42 h at room tem-

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Table I. Isomerization of 1-Butene Catalyzed by (η^6-Toluene)Ni($SiCl_3$)$_2$ at 0 °C

solvent	[Ni], 10^{-3} M	1-C_4H_8/Ni	k', s^{-1} M^{-1}	cis/trans[a]
bromobenzene	1.6	430	12	0.40
	1.1	1000	12	0.33
3- and 4-bromotoluene (1:3)	3.2	200	3.6	0.39
2-chlorotoluene	3.0	220	2.6	0.28
chlorobenzene	3.2	200	0.55	0.40
3-chlorotoluene	3.0	220	0.20	0.28
toluene	7.1	97	0.17	0.26
tetrahydrofuran	7.6	91	8.7×10^{-3}	0.30
n-heptane	6.8	100	2.4×10^{-2}[f]	0.72
iodobenzene	6.7	100	(93%)[b,c]	1.01
anisole	6.8	100	(89%)[b,d]	0.29
fluorobenzene	7.0	95	(6.8%)[b,c]	0.32
methylene chloride	14	58	NR[e]	

[a] The rate for cis → trans isomerization is at least 10 times lower than the 1-butene → 2-butene reaction. Therefore these ratios reflect only the cis/trans ratio formed directly from 1-butene. [b] A first-order plot was not obtained. [c] Conversion after 10 min (98% conversion at equilibrium). [d] Conversion after 4.5 min. [e] Black precipitates were formed and no reaction occurred. [f] Although the complex did not dissolve in *n*-heptane, an approximate first-order reaction was observed, and the rate constant was estimated on the basis of the amount of Ni complex present.

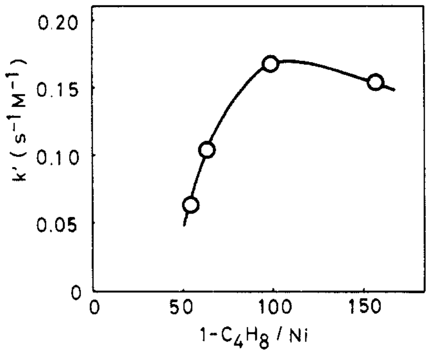

Figure 1. Effect of 1-butene concentration on the rate of 1-butene isomerization in toluene ([Ni] = 6.7×10^{-3} M) with (η^6-toluene)Ni($SiCl_3$)$_2$ at 0 °C.

perature. Volatile materials were distilled in vacuo into a −196 °C trap and analyzed by GLC (15% SE-30 on chromosorb-P, 10 ft, 60–80 °C). Ethylene-d_4 was allowed to react with nickel complexes in a similar manner.

Results

Effect of Solvents on the Isomerization of 1-Butene with (η^6-Toluene)Ni($SiCl_3$)$_2$. Solvents studied with the (η^6-toluene)Ni($SiCl_3$)$_2$ systems are listed in Table I. The complex dissolved well in all solvents but *n*-heptane (completely insoluble) to give yellow solutions. The isomerization in toluene required a 10-min induction period after which the reaction proceeded smoothly to equilibrium in 1 h if the 1-C_4H_8/Ni ratio was below 100. Higher 1-C_4H_8/Ni ratios shortened the introduction period, but excessively high ratios caused partial decomposition of the Ni complex with formation of a black precipitate and a decrease in reaction rate. These data indicte that 1-butene is involved in the initiation step leading to the catalytically active species, but too much 1-butene can cause decomposition of the intermediate in a later step. Figure 1 attempts to illustrate this behavior.

The isomerization in toluene was first order in 1-butene, and the rate was proportional to the concentration of the Ni complex (Figure 2). The second-order rate constants k' are listed in Tables I–III. The isomerization in halobenzenes was much more rapid

$$-d[1\text{-}C_4H_8]/dt = k_{obsd}[1\text{-}C_4H_8] \qquad (1)$$

$$k_{obsd} = k'[Ni] \qquad (2)$$

and no induction period was required. Equilibrium was attained in 7 min even when the concentration of the Ni complex was as low as 1.1×10^{-3} mol L^{-1} and the ratio of 1-C_4H_8/Ni was 1000. In bromobenzene the rate constant was found to be very high, exceeding even that reported for the Ni[P(OEt)$_3$]$_4$–H_2SO_4 at 25 °C, the most active homogeneous catalyst for 1-butene isomerization yet reported.[10] The rate constants in bromobenzene were found to be almost independent of 1-butene concentration, while the ratio of *cis*-2-butene to *trans*-2-butene decreased with an increase in 1-butene concentration.

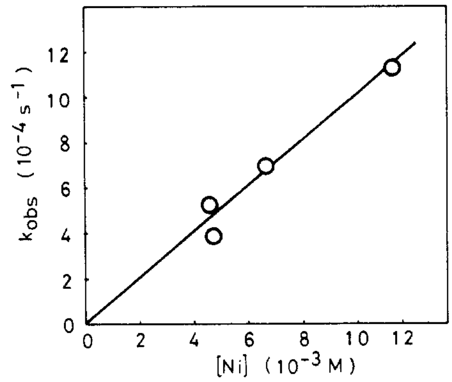

Figure 2. Effect of Ni concentration on the rate of 1-butene isomerization in toluene (1-C_4H_8/Ni = 63–68) with (η^6-toluene)Ni($SiCl_3$)$_2$ at 0 °C.

Table II. Isomerization of 1-Butene Catalyzed by (η^6-Arene)Ni($SiCl_3$)$_2$ at 0 °C

arene	solvent	k', s^{-1} M^{-1}	cis/trans
benzene[a]	chlorobenzene	0.67	0.48
toluene[a]		0.55	0.40
mesitylene[a]		0.32	0.30
benzene[b]	bromobenzene	13	0.42
toluene[b]		12	0.40
mesitylene[b]		5.4	0.39

[a] Reactions were carried out at [Ni] = 3.1–3.4 × 10^{-3} M and 1-C_4H_8/Ni = 200–220. [b] Reactions were carried out at [Ni] = 1.5–1.8 × 10^{-3} M and 1-C_4H_8/Ni = 370–470.

Table III. Isomerization of 1-Butene Catalyzed by (η^6-Toluene)Ni(SiF_3)$_2$ and (η^6-Toluene)Ni(C_6F_5)$_2$ at 0 °C

solvent	[Ni], 10^{-3} M	1-C_4H_8/Ni	k', s^{-1} M^{-1}	cis/trans
	(η^6-Toluene)Ni(SiF_3)$_2$			
toluene	6.9	100	NR[a]	
methylene chloride	16	44	8.2×10^{-4}	0.27
bromobenzene	3.3	210	1.9	0.40
	(η^6-Toluene)Ni(C_6F_5)$_2$			
toluene	6.9	100	1.8×10^{-4}	0.54
bromobenzene	7.1	96	0.23	0.40

[a] The yellow solution turned pale yellow with precipitation of black solids and no reaction was observed after 2 h.

The first-order rate law was not followed in fluorobenzene and iodobenzene solvents. Conversions were measured after 10 min and are shown in Table I. In fluorobenzene a colorless solution formed quickly, whereas in iodobenzene a brown solution was maintained although a small amount of brown precipitate formed. The catalytic activity decreased over time. This cis/trans ratio in iodobenzene was the highest among the solvents investigated.

For the chloroarenes the rate decreased in the order 2-chlorotoluene > chlorobenzene > 3-chlorotoluene. No difference in cis/trans ratios was observed. Methyl-substituted derivatives of bromobenzene gave slower rates than bromobenzene itself, but no change in cis/trans ratio was observed.

(η^6-Toluene)Ni($SiCl_3$)$_2$ is not stable in THF at 0 °C, probably due to reaction with the $SiCl_3$ groups (as well as by displacement

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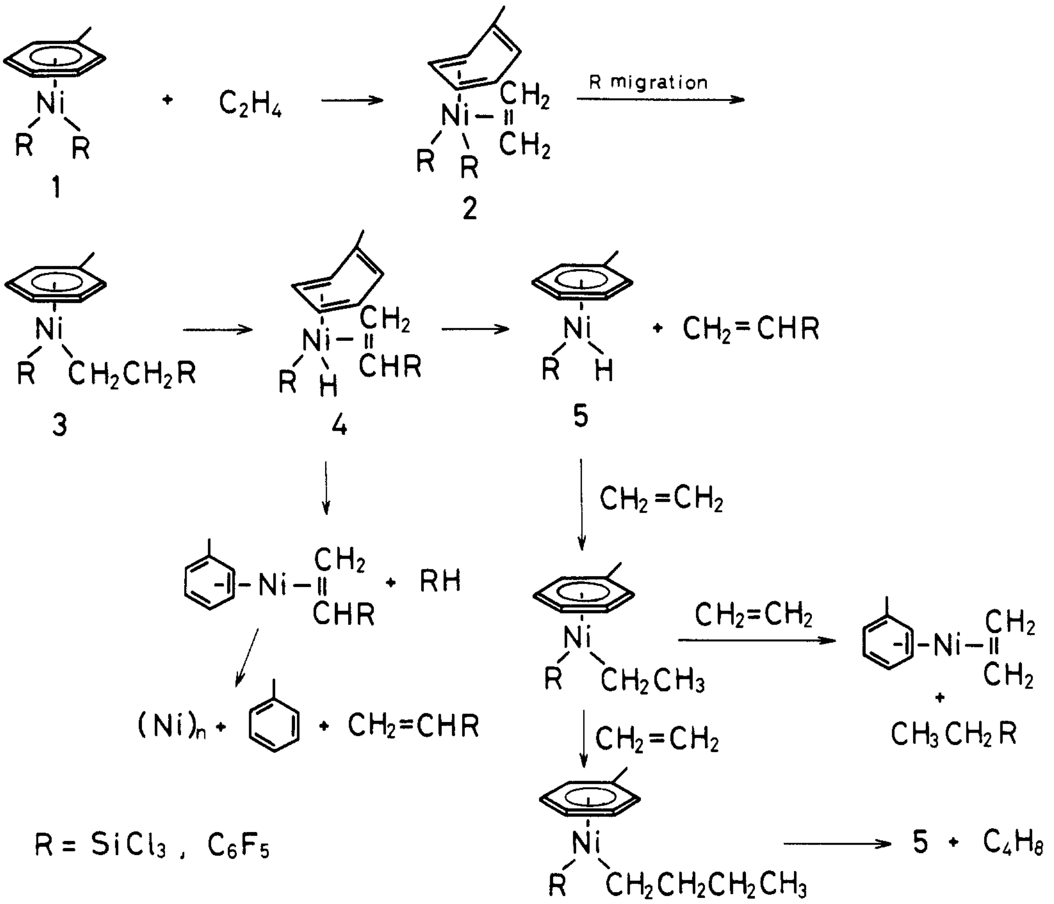
(10) (a) Tolman, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 2994. (b) Tolman, C. A.; Faller, J. W. "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 49–53.

Scheme I



of the complexed toluene). It is known that M–SiCl$_3$ complexes have a high affinity toward the oxygen in ether and carbonyl compounds.[11] When 1-butene was added to the THF/Ni complex solution, a black precipitate formed while isomerization proceeded very slowly, following the first-order rate law.

In anisole solution (η^6-anisole)Ni(SiCl$_3$)$_2$ formed quickly. Upon 1-butene addition the solution lost its color and a white solid precipitated. The conversion of 1-butene was more rapid in anisole than in toluene. A similar reactivity trend has been observed in the dehydrohalogenation of alkyl halides with (arene)Cr(CO)$_3$.[12]

In methylene chloride (η^6-toluene)Ni(SiCl$_3$)$_2$ dissolved and was stable. However, when 1-butene was added a black precipitate and colorless solution formed immediately. Although the solid had not been characterized, its solubility in CH$_2$Cl$_2$–EtOH (with air exposure) indicates that it is not Ni metal.

The toluene–Ni complex is not soluble in *n*-heptane, but 1-butene isomerization did proceed for more than 1 h, following a first-order rate law. The solid complex slowly turned black and the cis/trans ratio was higher than normally observed.

Effect of Water. Since Ni–Si bonds are susceptible to cleavage to yield Ni–H species,[13] we decided to investigate the effects of water. The addition of water in a 0.5:1 H$_2$O:Ni ratio to (η^6-toluene)Ni(SiCl$_3$)$_2$ in toluene solution shortened the induction time for 1-butene isomerization and increased the rate by 1.5. Addition of 1.0 mol of water per Ni complex shortened the induction time further but the rate increase dropped to 1.2.

Effect of Arenes in (η^6-Arene)Ni(SiCl$_3$)$_2$. The benzene, toluene, and mesitylene complexes were prepared and the isomerization reaction was examined in chlorobenzene and bromobenzene solutions (Table II). It is known that increasing methyl substitution on the complexed arene stabilizes the Ni–arene bond and the arene becomes less labile.[4] The same trend has been observed with other M–arene systems.[5a,14] Therefore, if η^6-arene lability is important in the catalytic cycle or in generation of the catalytic species, the order of catalytic activity should be benzene > toluene > mesitylene, and this is what was observed. The cis/trans ratio was also affected, especially in chlorobenzene.

Isomerization of 1-Butene with (η^6-Toluene)Ni(SiF$_3$)$_2$ and (η^6-Toluene)Ni(C$_6$F$_5$)$_2$. These complexes were less active than the SiCl$_3$ derivative (Table III). No isomerization took place with (η^6-toluene)Ni(SiF$_3$)$_2$ in toluene solution. Upon 1-butene addition the yellow solution turned pale green with formation of a black solid. In methylene chloride slow isomerization took place, whereas in bromobenzene the rate was greatly increased up to one-sixth of that of the SiCl$_3$ derivative. No differences in cis/trans ratios were observed.

The relative isomerization rates with (η^6-toluene)Ni(C$_6$F$_5$)$_2$ vs. the SiCl$_3$ derivative are 1:940 in toluene and 1:52 in bromobenzene, again showing the considerably higher activity of the SiCl$_3$ species. In toluene solution the cis/trans ratio was higher for the C$_6$F$_5$ derivative than for SiF$_3$ and SiCl$_3$. However, in bromobenzene no difference was observed.

Reaction of Ethylene with (η^6-Toluene)Ni(SiCl$_3$)$_2$ and (η^6-Toluene)Ni(C$_6$F$_5$)$_2$. Ethylene was allowed to react with (η^6-toluene)Ni(SiCl$_3$)$_2$ in the solid state, yielding vinyltrichlorosilane, ethyltrichlorosilane, and butenes (eq 3, percent values indicate mass balance based on starting complex):

$$\mathrm{C_2H_4} + (\eta^6\text{-toluene})\mathrm{Ni(SiCl_3)_2} \xrightarrow[42\ \mathrm{h}]{\mathrm{rt}} \underset{14\%/\mathrm{SiCl_3}}{\mathrm{CH_2{=}CHSiCl_3}} + \underset{23\%/\mathrm{SiCl_3}}{\mathrm{C_2H_5SiCl_3}} + \underset{98\%/\mathrm{Ni}}{\text{toluene}} + \mathrm{C_4H_8} \quad (3)$$

Note the near quantitative release of toluene and that no tri-

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(12) Tsonis, C. P.; Hwang, J. S. *J. Mol. Catal.* **1984**, *26*, 219.

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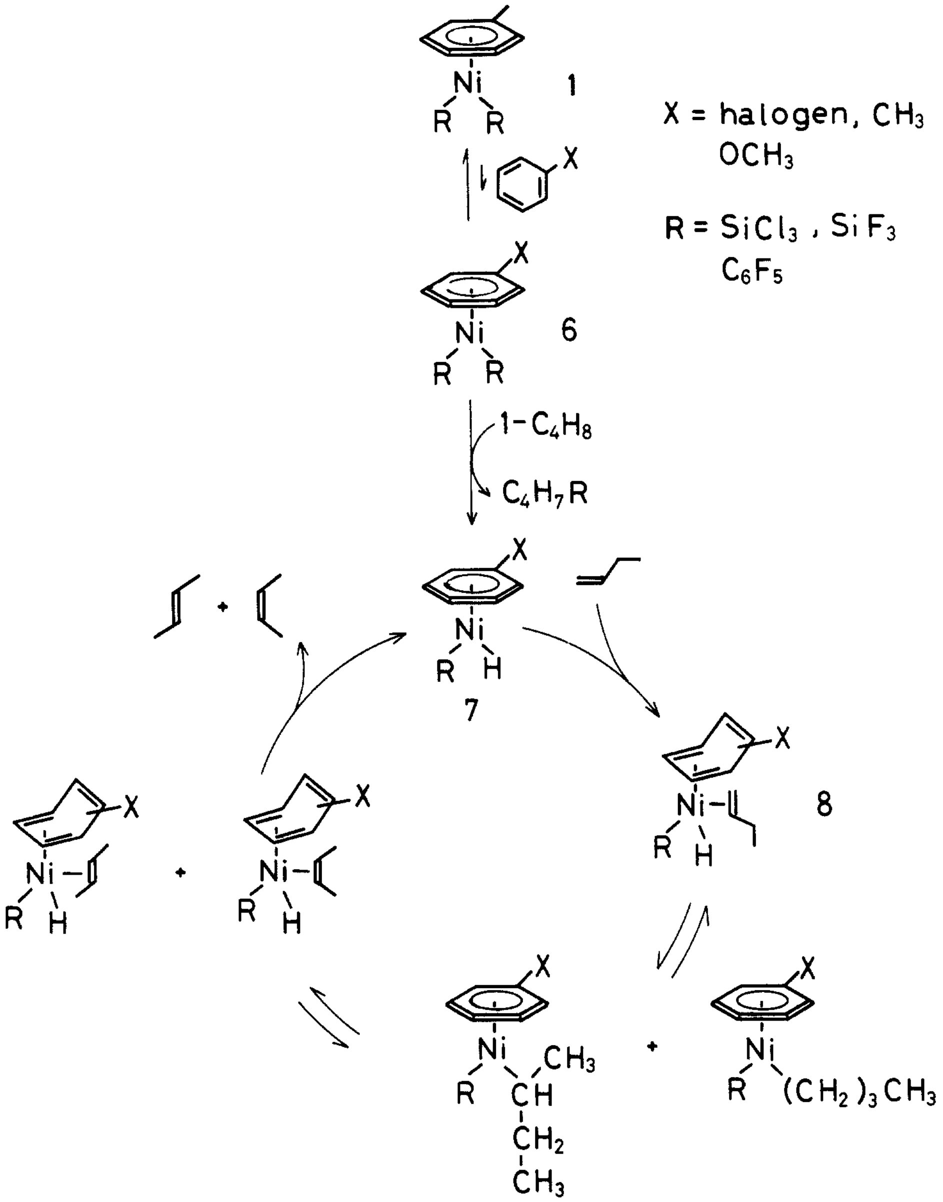
Scheme II



chlorosilane was produced. A black solid precipitated until the complex completely reacted.

In the same manner (η^6-toluene)Ni(C_6F_5)$_2$ was treated with ethylene, yielding pentafluorobenzene, pentafluorostyrene, and butenes (eq 4, percent values indicate mass balance based on starting complex):

$$C_2H_4 + (\eta^6\text{-toluene})Ni(C_6F_5)_2 \xrightarrow[40\ h]{rt} \underset{53\%/C_6F_5}{C_6F_5H} + \underset{0.32\%/C_6F_5}{CH_2{=}CHC_6F_5} + \underset{59\%/Ni}{\text{toluene}} + C_4H_8 \quad (4)$$

About 40% of the toluene was not recovered. No ethylpentafluorobenzene or decafluorobiphenyl were formed.

When ethylene-d_4 was used the products were fully deuterated. Furthermore, H–D scrambling of C_2H_4 and C_2D_4 occurred readily with (η^6-toluene)Ni($SiCl_3$)$_2$ as catalyst.

Discussion

Ethylene with (η^6-Toluene)NiR$_2$. A likely mechanistic sequence is shown in Scheme I. It is proposed that η^6-toluene slips to η^4, with ethylene coordination to give **2** followed by R migration to yield **3**. Then β-hydride elimination would yield **4**, and loss of $CH_2{=}CHR$ would yield **5**.[15] Complex **5** is a likely species to catalyze the dimerization of ethylene to yield butenes. Alternatively a reductive coupling from **4** would yield RH and release Ni metal, toluene, and $CH_2{=}CHR$. The species **5** may also be involved in the production of CH_3CH_2R by interaction with **3**.[16]

With the $SiCl_3$ derivative, pathways leading to $CH_3CH_2SiCl_3$ and $CH_2{=}CHSiCl_3$ are favarable. In the case of the C_6F_5 derivative the reductive coupling mode is favored, yielding mainly C_6F_5H.[17] Most importantly, both systems must yield **5** since both systems catalytically dimerize C_2H_4. The intermediacy of **5** also can explain the H–D scrambling in C_2H_4/C_2D_4 and the general lability of the C–H bond in C_2H_4 in this environment.

1-Butene Isomerization Mechanism. The results of the ethylene experiments coupled with the water addition experiments strongly imply that a Ni–H species is an important intermediate in the 1-butene isomerization reaction. This species could be formed

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in a manner analogous to those shown earlier for ethylene, that is, butene complexation and insertion into the Ni–R bond followed by β-hydride elimination. Similar proposals have been expressed earlier for the dimerization of ethylene by (η^1-aryl)NiBr-$(PPh_3)_3$–BF_3OEt_2 where a Ni–H species was formed from the dissociation of ethylene (coordinated ethylene did not insert into the η^1-aryl–Ni bond).[18]

Our experiments have also shown that the reaction rate is very sensitive to solvent and that electron-demanding arene solvents cause the fastest reaction. This requires that the solvent be involved in the coordination sphere but that the solvent molecule be highly labile. This is indeed the case for η^6-halobenzenes on Ni(II) and Co(II).[4]

The cis/trans ratio is dependent on solvent and on the 1-C_4H_8/Ni ratio. This would imply a steric effect of the solvent and a sensitivity to whether more than one butene molecule is coordinated. Actually, high concentrations of 1-C_4H_8 not only affect the cis/trans ratio but also cause decomposition of the Ni complex. Apparently the coordination of a second butene molecule changes the reaction pathway significantly.

The original η^6-arene affects both the rate and the cis/trans ratio (in the same solvent). This observation suggests that the original arene is only partially displaced by solvent arene. Indeed, our earlier work has shown that very large excesses of halobenzenes are necessary to displace even a small amount of η^6-benzene or η^6-toluene.[4b] Thus, if the toluene complex were placed in a bromobenzene solvent, a small amount of toluene, perhaps less than 1%, would be displaced at equilibrium.

The cis/trans ratio under similar conditions does not change when comparing SiF_3 and $SiCl_3$ derivatives. However, the C_6F_5 derivative does yield a higher cis/trans ratio when all are compared in toluene solution. However, in bromobenzene solution the differences disappear, indicating that the active catalyst in bromobenzene is not as sensitive to steric factors as the active catalyst in toluene.

The activity order of (η^6-arene)NiR_2 ($R = SiCl_3 > SiF_3 > C_6F_5$) reflects in part the strength of the η^6-arene–M bond (where $R = SiCl_3$ the η^6-arene–Ni bond is longest).[19] The fact that (η^6-arene)$Co(C_6F_5)_2$ is not active while (η^6-arene)$Ni(C_6F_5)_2$ is somewhat active also reflects the strength of the η^6-arene bond, the Co system having a shorter stronger η^6-arene–M bond than the Ni system.[20]

The following mechanistic sequence (Scheme II) attempts to account for all of the observations, which summarized are the following:[21] (1) more strongly bound original arene affects the rate, (2) ethylene and water experiments suggest a Ni–H intermediate, (3) arene solvents strongly affect the rate (electron demanding and thereby weakly π-bonding arene solvents give higher rates), (4) only one butene molecule is involved in the coordination sphere (in the absence of high concentrations of 1-butene), (5) 1-butene is involved in both an initiation step (therefore an induction period) and a termination step (decomposition of the catalytic species, especially at higher 1-butene concentrations), and (6) steric effects cause changes in the cis/trans product ratio.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

Registry No. (η^6-Toluene)$Ni(SiCl_3)_2$, 80410-01-1; (η^6-benzene)$Ni(SiCl_3)_2$, 89389-59-3; (η^6-mesitylene)$Ni(SiCl_3)_2$, 100909-73-7; (η^6-toluene)$Ni(SiF_3)_2$, 88083-21-0; (η^6–toluene)$Ni(C_6F_5)_2$, 66197-14-6; 1-butene, 106-98-9; bromobenzene, 108-86-1; 3-bromotoluene, 591-17-3; 4-bromotoluene, 106-38-7; 2-chlorotoluene, 95-49-8; chlorobenzene, 108-90-7; 3-chlorotoluene, 108-41-8; toluene, 108-88-3; tetrahydrofuran, 109-99-9; *n*-heptane, 142-82-5; iodobenzene, 591-50-4; anisole, 100-66-3; fluorobenzene, 462-06-6; methylene chloride, 75-09-2.

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(21) Attempts to characterize intermediate Ni–H species by ^1H and ^{13}C NMR were not successful. This is probably due to the short lifetime of such species, or due to intermediate paramagnetic species present that would severely broaden NMR resonances (paramagnetic materials are present according to ESR studies of precipitated decomposition products).

Intramolecular General Acid and General Base Catalyses in the Hydrolysis of 2-Halotryptophans and Their Analogues

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Received September 16, 1985

Abstract: Radical halogenation of protected L-tryptophan, and of related indoles, leads to the corresponding 2-halo derivatives in high yield; enzymatic removal of the blocking groups provides the new amino acid analogues. In the concentration range 0.01–3.0 M $HClO_4$, hydrolysis to oxindoles of the fully protected 2-halotryptophans, as well as of 2-halo-3-(*R*)-indoles in general ($R = CH_3$, CH_2CO_2Et, $CH_2CH_2CO_2Me$), increases linearly with acidity (h_0) and gives extrapolated intercepts $\cong 0$. Protonation of the indole at C-3 is relatively fast and addition of water to the resulting 2-haloindoleninium ion is rate-limiting. For α-*N*-acyl-2-halotryptophans and 2-haloindole-3-propionic *acids*, the extrapolated intercepts are >0 and additional pathways for hydrolysis must be invoked. For the latter compounds, k_{obsd} is much greater than for 2-haloskatoles in weakly acidic media, the factor increasing with pH to $>10^5$ at pH 5. In the pH region −0.5 to 1.5, enhanced hydrolysis is due, primarily, to intramolecular general base catalysis of water addition by carboxylate ion; above pH 1.5, such catalysis becomes so effective that indole protonation is now rate-limiting. Above pH 4, intramolecular proton transfer from the carboxyl group (general acid catalysis) is more effective than transfer from external hydronium ion by a factor of 127 M. On the other hand, the effective molarity for intramolecular general base catalysis of water addition is estimated to be $>10^{12}$. In the case of 2-haloindole-3-acetic acids, the transition-state geometry for general base catalysis is even more favorable and water addition to the protonated indolenine is so fast that indole protonation remains rate-limiting even in 1 M acid.

The widespread occurrence of indoles in both plant and animal metabolites has provided the primary stimulus in the search for novel or more effective drugs based on this ring system. A lack of synthetic routes has limited the number of 2-substituted bioindoles available for study;[1,2] halo derivatives have been particularly inaccessible, both because of their labilities in acid media[3]

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