

If the η^4 -arene represents a much lower energy, as suggested by E° data, for **1**⁰ and **2**⁰, then it is interesting that $[\text{C}_6(\text{C}_6\text{H}_5)_6]_2\text{Fe}$,^{35,48} $[\text{C}_5(\text{CH}_3)_5]_2\text{Co}$,^{32,33} and $[\text{C}_6(\text{CH}_3)_6]_2\text{Co}$ ⁴⁹ all retain the η^6 -coordination of the arene and are 20e complexes. Apparently, the stabilization energy gained by Jahn-Teller distortion to the 18e η^4 -arene complexes⁴⁷ is less than the destabilization resulting from loss of arene aromaticity in these cases. The E° data, as well as the structurally characterized 20e η^6 -arene complexes, suggest that in many cases η^4 -arene complexes are not sufficiently likely as intermediates to warrant their being so frequently proposed, especially for first-row metal complexes lacking strongly electron-withdrawing groups.

Conclusions

(1) The mixed-sandwich rhodium and iridium complexes **2a** and **2b** represent only the second class of complexes that undergo $\eta^6 \rightleftharpoons \eta^4$ change in arene coordination on change of the oxidation state of the metal.

(2) Electrochemical investigations of the electron-transfer reactions and the concomitant structural changes provide a good method for a systematic probe of the redox reaction.

(48) Michaud, P.; Mariot, J. P.; Varret, F.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1982**, 1383.

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(3) The separation of the E° values of the reductions decreases and the tendency toward formation of η^4 -arene complexes increases for $(\text{C}_6\text{Me}_6)\text{M}(\text{C}_6\text{Me}_6)^{2+}$ complexes on descending the periodic table.

(4) The electron-transfer kinetics of the complexes do not suggest in which step the structure change occurs, but the E° data indicate that the structure change occurs predominantly between the cationic metal d^7 and neutral metal d^8 species. This is consistent with the earlier suggestion⁸ that $[(\text{C}_6\text{Me}_6)_2\text{Ru}]^{n+}$ undergoes its η^6 -arene $\rightarrow \eta^4$ -arene change when the complex is reduced from $n = 1$ to $n = 0$.

Investigation of a variety of $(\text{Cp})\text{M}(\text{arene})^{2+}$ is being pursued to study the effect of the arene substituents on the structure change.

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Registry No. **2a**²⁺·(PF₆)₂, 12715-84-3; **2a**²⁺, 51539-75-4; **2a**⁺, 97732-09-7; **2a**⁰, 97732-08-6; **2b**²⁺, 51539-74-3; **2b**⁺, 97732-11-1; **2b**⁰, 97749-34-3; **3**, 97732-10-0; $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Co}(\text{PF}_6)$, 79973-42-5; $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Co}$, 74507-62-3; $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$, 1277-43-6; Pt, 7440-06-4; Hg, 7439-97-6; Au, 7440-57-5; dichloromethane, 75-09-2; acetonitrile, 75-05-8; acetone, 67-64-1; *N,N*-dimethylformamide, 68-12-2; dimethyl sulfoxide, 67-68-5.

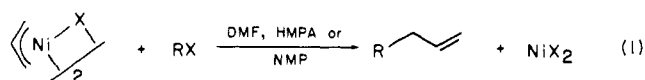
Reactions of Organic Halides with (π -Allyl)nickel Halide Complexes: A Mechanistic Study

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Abstract: The mechanism of allyl transfer reactions between (π -allyl)nickel halides and organic halides was studied. Extensive redistribution of (π -2-methallyl)nickel bromide (**1**) occurs in dimethylformamide (DMF), producing an equilibrium which involves nickel(II) bromide, bis(π -methallyl)nickel, and a symmetrical (π -methallyl)nickel bromide species. The degree of allyl redistribution is a function of temperature and total nickel concentration—decreasing the temperature or addition of nickel(II) bromide to the solution suppressed the formation of bis(π -methallyl)nickel. The position of this equilibrium affects the rate of cross-coupling reactions between **1** and organic halides since the rate of product formation increases when nickel(II) bromide is dissolved in the reaction mixture. Initiation of cross-coupling results when catalytic amounts of reducing agent are added to the reaction mixture or when it is exposed to a source of light. The presence of less than 1 mol % of *m*-dinitrobenzene inhibits the formation of cross-coupled material regardless of the type of organic halide used. The evidence indicates that the cross-coupling reaction proceeds by an electron transfer catalyzed mechanism. A mechanism utilizing common nickel(I⁺) intermediates in the reactions of alkyl, aryl, and vinyl halides and not involving free carbon-centered radicals has been proposed.

(π -Allyl)nickel halide complexes¹ (**1**) undergo facile reaction with organic halides to substitute the allyl group for the halogen (eq 1).² This process has an unusual order of reactivity, with aryl and vinyl halides being substantially more reactive than alkyl halides, and with a substrate halide reactivity order of $\text{I} > \text{Br} \gg \text{Cl}, \text{OTs}$. This coupling reaction requires the use of a polar,



coordinating solvent such as dimethylformamide (DMF), hexa-

methylphosphoramide (HMPA, $(\text{Me}_2\text{N})_3\text{PO}$), or *N*-methylpyrrolidone (NMP). Since a wide variety of (π -allyl)nickel halide complexes can be readily prepared and since a wide range of organic halides are suitable substrates, this process has been used extensively in organic synthesis.³ Recent examples include the synthesis of perillenal from furanyl halides,⁴ myrcene, tagetol, and

(3) For extensive reviews on the applications of (π -allyl)nickel complexes in organic synthesis see: (a) Heimbach, P.; Jolly, P. W.; Wilke, G. *Adv. Organomet. Chem.* **1970**, 8, 29. (b) Semmelhack, M. F. *Org. React.* **1972**, 19, 115. (c) Baker, R. *Chem. Rev.* **1973**, 73, 487. (d) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1975; Vol. 2. (e) Hegedus, L. S. *J. Organomet. Chem. Lib.* **1976**, 1, 329. (f) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry", University Science Books: Mill Valley, CA, 1980; pp 692-701.

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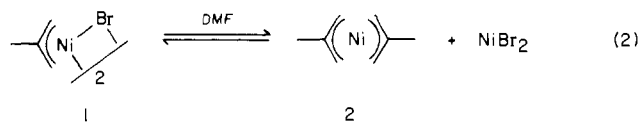
(1) For a detailed treatment of the chemistry of this class of compounds see: Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974; Vol. 1 and 2.

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Table I. ^1H and ^{13}C NMR Spectra of Complexes **1** and **2** in $\text{DMF-}d_7$ at 26 °C

complex	δ ^1H			δ ^{13}C		
	anti H	CH_3	syn H	C_4	$\text{C}_{1,3}$	C_2
1	1.70	2.24	2.56	22.8	53.4	113.2
<i>cis</i> - 2	2.09	1.46	3.32	24.1	51.6	124.2
<i>trans</i> - 2	1.64	1.70	3.45	24.3	50.8	123.0

β -farnesene with use of unsaturated (π -allyl)nickel halides⁵ and indoles from *o*-allylanilines prepared by using (π -allyl)nickel halides.⁶ Although this reaction has been used synthetically for over 15 years, little is known of its mechanism. This is in part because, although the products of the reaction are simple, the process appears to be complex. (π -Allyl)nickel halide complexes are subject to a number of dynamic processes including allyl exchange processes⁷ and the allyl redistribution reaction shown in eq 2.⁸ Early studies from these laboratories showed that the reaction described in eq 1 was a radical chain process which was



completely inhibited by addition of 1 mol % *m*-dinitrobenzene, that chiral secondary halide substrates racemized upon conversion to products, but that vinyl halides maintained their geometry.⁹ Herein we report a considerably more detailed examination of these processes.

Results

Spectroscopic Studies. Central to an understanding of the mechanism of the allylation reaction in eq 1 was a clear understanding of the nature and amounts of (π -allyl)nickel species present at the start of the reaction. The allylation reaction only proceeds in polar, coordinating solvents, the same solvents that promote the allyl redistribution process (eq 2). Further, the bis(π -allyl)nickel species **2** itself does *not* react with organic halides.⁸ Thus, the position of the redistribution equilibrium will have an effect on the amount of the reactive species (**1**) present, and hence on the course of the reaction. Since complexes **1** and **2** have distinctive ^1H and ^{13}C NMR spectra, NMR spectroscopy was used to determine the position of the redistribution equilibrium and its sensitivity to changes in solvent and temperature. Preparation of a solution of **1** in $\text{DMF-}d_7$ (0.32 M) followed immediately by acquiring a 360-MHz ^1H NMR spectrum showed the solution to contain a mixture of (π -allyl)nickel halide **1** as well as bis(π -allyl)nickel **2** in a ratio (by integration) of 45:55 (complex **2** was a mixture of *cis* and *trans* isomers, with a *trans/cis* ratio of 79:21).¹⁰ The ratio of products did not change with time. Thus the redistribution equilibrium was rapidly established and lay to the side of the unreactive bis(π -allyl)nickel complex **2**.

The position of this redistribution equilibrium was sensitive to a number of factors. Dilution favored complex **2**, as seen by the change in the ratio of **1** to **2** from 45:55 at 0.32 M to 39:61 at 0.30 M and 37:63 at 0.25 M. The redistribution was strongly solvent dependent. *No* bis(π -allyl)nickel complex (**2**) was observed in chloroform- d_1 , acetonitrile- d_3 , or benzene- d_6 (solvents in which

Table II. Allyl Redistribution as a Function of Solvent Composition

no. of equiv of DMF/Ni	solvent ratio (v/v) benzene- d_6 :DMF- d_7	1:2	2 <i>trans</i> : <i>cis</i>
(A) DMF- d_7 Added to Benzene- d_6 Solution of 1 (Initial Concentration 0.13 M)			
0	100:0		
1	98:2	93:7	3:1
2	96:4	79:21	2.7:1
3	94:6	60:40	2.8:1
4	93:7	55:45	2.9:1
6	90:0	48:52	3.1:1
9	85:15	43:57	3.1:1
10	83:17	43:57	3.2:1
20	71:29	43:57	2.9:1
30	62:38	40:60	2.8:1
40	56:44	42:58	2.6:1
(B) Benzene- d_6 Added to a DMF- d_7 Solution of 1 (Initial Concentration 0.32 M)			
43	59:41	38:62	2.8:1
43	54:46	40:60	2.9:1
43	48:52	37:63	2.8:1
43	42:58	40:60	2.9:1
43	34:66	43:57	3.2:1
43	24:76	42:58	3.0:1
43	16:84	43:57	3.2:1
43	2:98	42:58	3.1:1
43	0:100	45:55	3.7:1

Table III. Radical Clock Reactions

Initial Radical	Resulting Radical	k_r
		$1 \times 10^5 \text{ sec}^{-1}$ (ref 11)
		$1 \times 10^6 \text{ sec}^{-1}$ (ref 12)
		$1.3 \times 10^8 \text{ sec}^{-1}$ (ref 13)

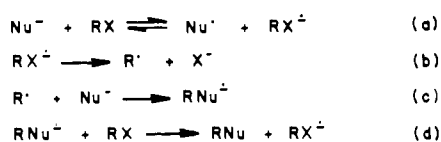
Table IV. Reaction of Unsaturated Halides with Complex **1**

halide	products	apparent rate constant of radical trapping, $\text{M}^{-1} \text{s}^{-1}$
$\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_4\text{I}$	98:2 linear/cyclic	4.9×10^6
$\text{H}_2\text{C}=\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{Br}$	57:43 linear/cyclic	1.3×10^6
	100% linear	$<6.8 \times 10^6$

the allylation reaction did not proceed). However, stepwise addition of DMF to a benzene solution of **1** rapidly established the redistribution reaction (Table II). The most profound changes occurred between 1 and 3 equiv of added DMF. These are likely to be due to the solvation of nickel(II) bromide by DMF, favoring the right side of the redistribution equilibrium. Once 9 equiv of DMF were present, little change in this equilibrium occurred. Similarly, addition of benzene to a DMF solution of **1** did not greatly alter the ratio of **1**:**2**. Addition of nickel(II) bromide (1.55 equiv) to a DMF solution of **1** (0.25 M) changed the ratio of **1**:**2** from 37:63 to 62:38, as would be expected if the redistribution reaction is truly an equilibrium. Finally, this redistribution equilibrium could be approached from the right as well as the left. Addition of 1 equivalent of nickel(II) bromide to 1 equiv of bis(π -allyl)nickel complex **2** in DMF resulted in the same equilibrium mixture of **1** and **2** (45:55) as did dissolution of (π -allyl)nickel bromide (**2**) alone in DMF, although equilibrium was somewhat slow to be achieved (8 h) by this method.

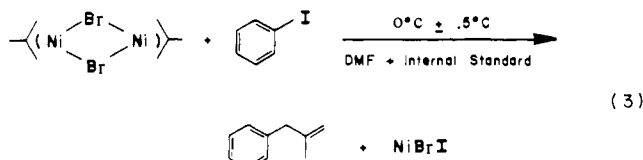
Radical Clock Experiments. Previous studies from these laboratories had implied that free organic radicals were involved in the allylation of alkyl halides by (π -allyl)nickel halides (eq 1). To probe both the existence and lifetime of these radicals a series

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Scheme I. Generalized $S_{RN}1$ Pathway

of "radical clock" experiments were conducted. A number of free radicals which decompose by intramolecular pathways with known absolute rate constants are available.¹¹ By using halide precursors to these as substrates, it is, in principal, possible to assess the lifetime of the free radicals involved by merely measuring the ratio of products formed by the intramolecular process of known rate to those formed by intermolecular reaction. The radical clocks studied are shown in Table III, and results of their reactions with (π -2-methylallyl)nickel bromide (**1**) are shown in Table IV. These results seem to indicate that with alkyl halide substrates, carbon-centered radicals having lifetimes of approximately 1 μ s were involved.¹⁴ These results stand in contrast to those obtained earlier with vinyl halides,⁹ for which allylation with *retention* of stereochemistry was observed. Since free vinyl radicals undergo inversion¹⁵ with rate constants of $\sim 10^8$, either free radicals were not involved in this process or vinyl radicals combine much more rapidly with the (allyl)nickel intermediates than do alkyl radicals. Any proposed mechanism must take this into account.

Kinetic Studies. At this stage the reaction of organic halides with (π -allyl)nickel halides had many of the features common to $S_{RN}1$ -type reactions¹⁶ (Scheme I), including chain interruption by radical scavengers, an abnormal reactivity pattern for halide substrates, racemization of chiral alkyl substrates upon conversion to products, and apparent detection of radicals by internal trapping (radical clock studies). Kinetic investigations were thus undertaken to determine if other characteristics of this coupling reaction were consistent with the features typically observed for $S_{RN}1$ processes. The specific reaction studied is shown in eq 3. Because the radical-chain nature of the process,¹⁷ the unknown nature of the chain initiating step, and the existence and sensitivity to minor changes in conditions of the redistribution equilibrium (eq 2), made



the accurate assessment of the concentration of **1** impossible, and because of the air sensitivity of the system, rigorous kinetic studies were not attempted. Rather, the effects of changes in reaction conditions on the overall rate of product formation were measured. Product concentrations as a function of time were determined by withdrawing aliquots of the reaction mixture, quenching at -20°C , extracting into hexane, and analyzing the organic layer

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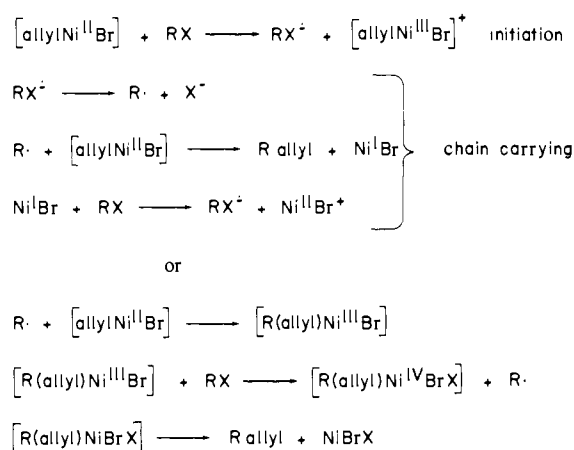
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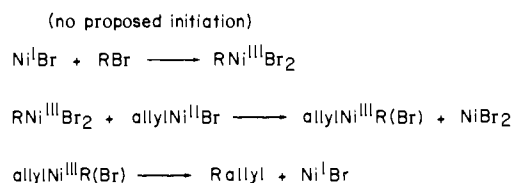
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(17) "The rate laws for most free-radical reactions are overall three-halves order in reactants. Rate laws for free-radical chain reactions are of limited value in determining the general mechanism of the reaction"; Huiser, E. S. "Free Radical Chain Reactions"; Wiley-Interscience: New York, 1970; p 45.

Scheme II. Original Proposed Mechanism



Scheme III. Alternate Mechanism



(appearance of methallylbenzene vs. mesitylene as internal standard) by quantitative gas-liquid chromatography. The reaction rates were sufficiently slow to be followed under pseudo-first order conditions, often with a 20-fold excess of iodobenzene present. The results of these experiments are shown in Figure 1.

These data illustrate several important features of the reaction. Under pseudo-first-order conditions in the dark with either limiting complex **1** or limiting iodobenzene the reaction was very slow to start, having an induction period of about 2 h. (The small, constant amount of methallylbenzene noted initially was likely formed upon quenching the aliquots prior to analysis.) Once under way, it proceeded at a modest rate. Irradiation of the reaction mixture with tungsten illumination for 5 min, followed by continuing the reaction in the dark led to substantial increase in rate (~ 2 -fold), indicating that the process was photoinitiated. Irradiation for 65 min resulted in an approximate eightfold increase in rate. Whatever the initiating species formed on irradiation, it is relatively long lived. Irradiation of the nickel complex **1** in DMF in the *absence* of iodobenzene for 5 min followed by covering the flask with aluminum foil and adding the substrate iodobenzene 2 min after returning the reaction to the dark resulted in a reaction rate comparable to that resulting from a 5-min irradiation in the presence of iodobenzene. The dark reaction was also initiated by reducing agents such as sodium naphthalenide.¹⁸ After 150 min in the dark an equimolar mixture of complex **1** and iodobenzene (0.02 M) in DMF showed no reaction to produce methallylbenzene. Addition of a small amount of sodium naphthalenide immediately started product formation, which then proceeded, albeit slowly. Finally, the addition of nickel(II) bromide (20-fold excess) also led to a substantial increase in rate (~ 5 -fold). Part of this increase may be due to the shifting of the redistribution equilibrium toward complex **1** (the reactive species). However, the effect was too large to be solely due to this. The reaction in the presence of excess nickel bromide was also completely inhibited by addition of 1% dinitrobenzene.

Discussion

The experimental evidence presented above clearly indicates that the reaction of (π -allyl)nickel halide complexes with organic halides proceeds by a radical chain mechanism that can be initiated

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Scheme IV. Unified Mechanism

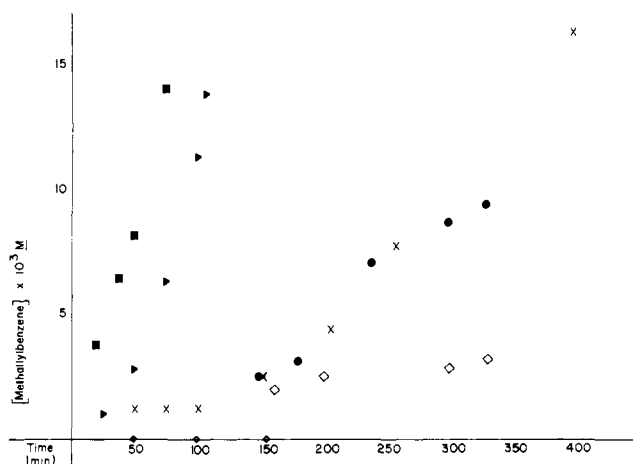
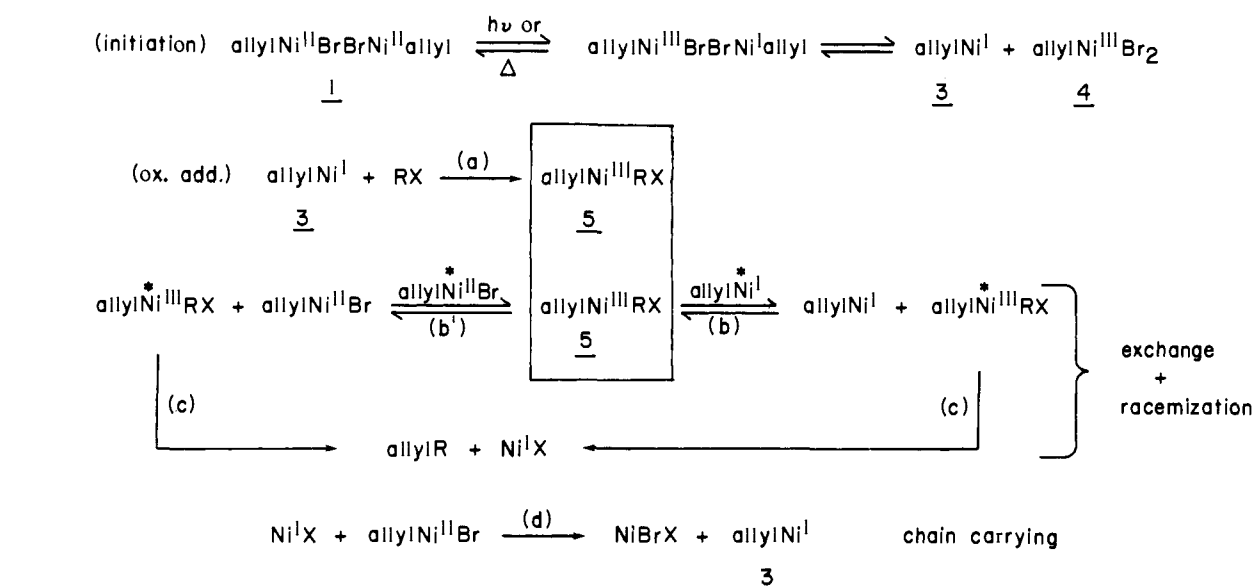


Figure 1. Effect of reaction conditions on observed rate of reaction of (π -methallyl)nickel bromide with iodobenzene. Pseudo-first-order conditions, excess iodobenzene: (x) 0.02 M **1**, 0.40 M PhI, DMF, DARK; (●) 0.20 M **1**, 0.02 M PhI, DMF, DARK; (▲) 0.02 M **1**, 0.40 M PhI, DMF, 5 min; (■) 0.02 M **1**, 0.40 M PhI, DMF, 0.40 M NiBr_2 , DARK; (◇) 0.02 M **1**, 0.02 M PhI, DMF, 1 mol % of sodium naphthalenide added to a DARK reaction of $T = 155$ min.

by heat, light, or reducing agents and that can be inhibited by small amounts of *m*-dinitrobenzene. Although the reaction has many features in common with $\text{S}_{\text{RN}}1$ -type processes, the magnitude of the effects of initiation on the rate of reaction was small compared to those normally observed in $\text{S}_{\text{RN}}1$ processes.^{16d} Further, there is an *apparent* intervention of free carbon-centered radicals with alkyl halides as substrates but not with vinyl halide substrates. In addition, extensive, solvent-dependent redistribution of the allyl groups among both reactive and unreactive allylnickel species occurs. Although the redistribution affects the rate of the reaction by influencing the concentration of the reactive complexes present and accounts for the strong solvent dependence of the reaction, it does not appear to be *directly* involved in the coupling process.

In our original study (1975)⁹ a mechanism involving nickel(I) and/or nickel(III) intermediates and *free* organic radicals was proposed for reactions of aryl, alkyl, and allyl halides (Scheme II). No explanation was offered for vinyl halides. Subsequently (1978) Kochi^{19,20} offered a mechanism for the reaction of vinyl (and aryl) halides which involved a "2 equiv" oxidative addition

without the intermediacy of free carbon-centered radicals (Scheme III) which nicely accounted for the maintenance of stereochemistry of vinyl halides in the reaction. Thus, two different mechanisms were required to describe the reactions of (π -allyl)nickel halides with organic halides, one for alkyl halides and one for aryl and vinyl halides.

However, it is possible to propose a *single* mechanism, for *all* substrates, that avoids the intermediacy of free carbon-centered radicals, yet is consistent with the racemization of chiral 2° alkyl halides upon reaction, and with the behavior of radical clock substrates. Such a mechanism is shown in Scheme IV. In this mechanism, the radical chain features of the process are solely due to the role of the nickel(I) species, generated in the initiation step (for example, by inner-sphere intramolecular electron transfer²¹ within the dimeric (π -allyl)nickel halide which then fragments to generate (π -allyl)nickel(I) species **3**) and again in the reductive elimination step c. These nickel(I) species are the key chain-carrying intermediates, (as they are in Schemes II and III), and the observed inhibition results by removal of one of these by the radical trap.

For *all* classes of substrates, a "2 equiv" oxidative addition of the organic halide to **3** generates the nickel(III) species **5** (step a). Reductive elimination (step c) gives the coupled product and nickel(I) halide, which reacts with more of the starting complex **1** (step d) to generate more (π -allyl)nickel(I) species **3** to carry the chain. With vinyl halides, both the oxidative addition (step a) and the reductive elimination (step c) occur with retention of olefin geometry,^{22,23} resulting in the observed retention in the coupling product. With alkyl halides, the oxidative addition step is likely to occur with inversion of configuration in an $\text{S}_{\text{N}}2$ -type process.²³ Reductive elimination should go with retention, leading to an overall inversion of stereochemistry. However, rapid exchange of **5** (alkyl group transfer) with either **3** (path b) or **1** (path b¹) with inversion would produce *racemic* complex **5**, and hence *racemic* product upon reductive elimination as is observed. Path b corresponds to a "self-exchange" reaction of a metal alkyl complex with its lower oxidation state precursor, a process well documented for Rh(I)–Rh(III) and Co(I)–Co(III) systems²⁴ and proposed for the observed racemization of chiral Pd(II)–benzyl complexes.²⁵ Path b¹ corresponds to an alkyl group transfer from

(21) Monomeric (π -allyl)nickel complexes such as (allyl)nickel acetylacetonate also react with organic halides. In these cases, bimolecular disproportionation may be the initiation step.

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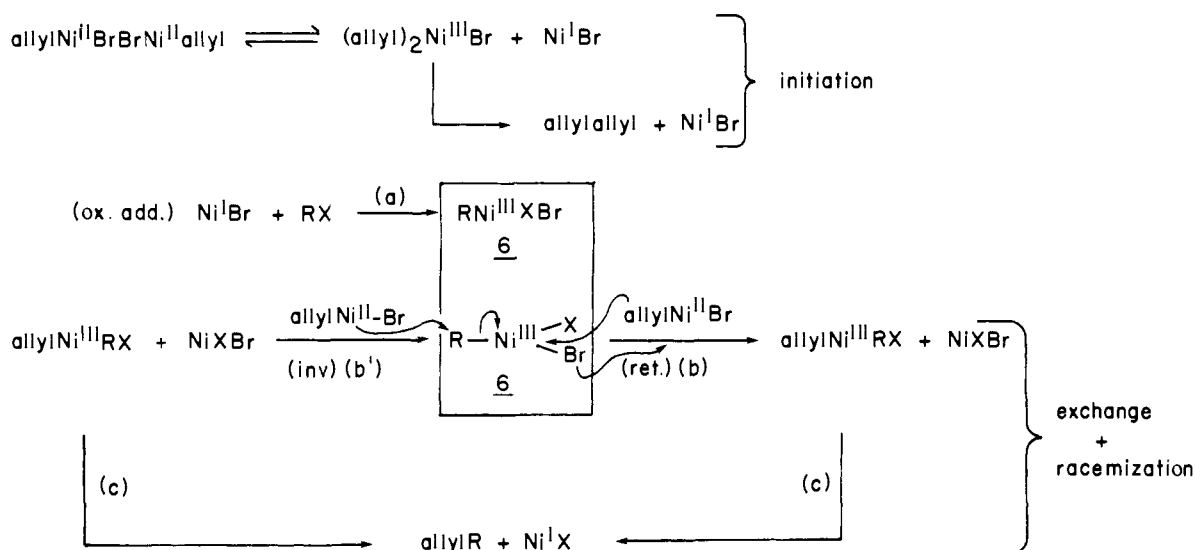
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(19) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; p 403.

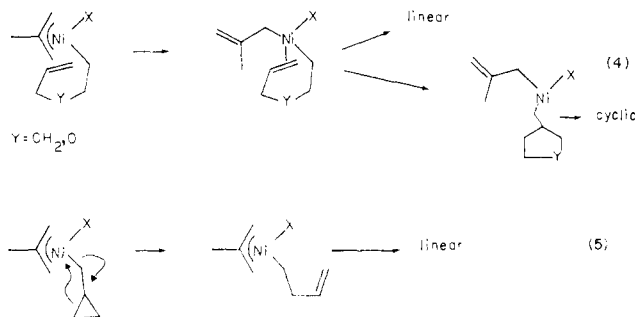
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Scheme V. Modified Alternate Mechanism



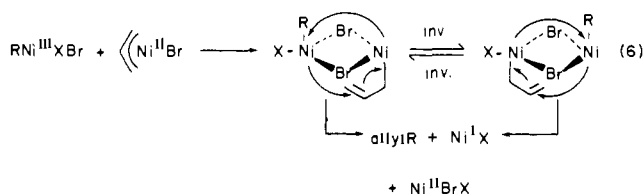
nickel(III) species **5** to the starting nickel(II) complex **1**. (A similar alkyl group transfer from nickel(III) to nickel(II) is central to Kochi's proposed mechanism for reactions of *vinyl* halides, Scheme III). Of the two exchange processes, *b'* is more likely because of the higher concentrations of **1** relative to **3**. Thus, racemization can result without the intervention of free radicals. There remains the results of the radical clock experiments.

Insertion of olefins into metal-carbon σ -bonds, including those of Ni, is a well-known process, extensively used in organic synthesis.²⁶ All three radical clock substrates in this study have remote unsaturation. The observed partitioning between linear and cyclic products will result if insertion is competitive with reductive elimination.²⁷



Finally, the proposed initiation step is attractive since the process should be independent of substrate.²⁸ Since the (π -allyl)nickel complex is quite stable to irradiation in the absence of substrates, and since radical decomposition products are not observed, initiation processes which irreversibly generate allyl radicals and/or nickel(I) species are less likely.²⁹ It also provides a species that can be the active chain carrying species for *all* classes of reactive halides. For the vinyl and aryl halide pathway, oxidative addition of these halides to nickel(I) species are well documented, and the order of substrate reactivity ($\text{ArI} > \text{ArBr} > \text{ArCl}$) parallels that observed in these nickel(I) oxidative addition processes.²⁰ Thus, Scheme IV accommodates all available experimental data and provides a unifying mechanism for all reactive substrates.

Finally, incorporating reasonable exchange processes into the mechanism in Scheme III allows *this* mechanism to account for all experimental observations with all substrates. The necessary modifications are shown in Scheme V.³⁰ The key step involves reaction of nickel(III) intermediate **6** with the starting (π -allyl)nickel(II) complex **1**. This may occur by either transfer of an allyl group from **1** to **6** (path *b*) followed by reductive elimination to give coupling with retention of stereochemistry at the allyl group or transfer of the R group from **6** to **1** (*b'*) followed by reductive elimination to give inversion of stereochemistry. This would result in an overall racemization. Rapid exchange of alkyl and allyl groups through a bridged dimer (as in eq 6) prior to reductive elimination would also result in racemization.



Experimental Section

General. All experiments were performed by using Schlenk techniques and maintaining an atmosphere of argon unless otherwise noted. Transfers of solid air-sensitive materials were performed under an atmosphere of nitrogen in a glovebag (I^2R Co.) or drybox. These solids were then thoroughly degassed with six cycles of vacuum and argon. All hydrocarbon and ethereal solvents were freshly distilled under a nitrogen atmosphere from sodium benzophenone ketyl. Baker Reagent Grade *N,N*-dimethylformamide (DMF) was fractionally distilled from calcium hydride or barium oxide at 100 mmHg. It was stored in a two-neck flask fitted with a septum and stopcock over Linde size 4A molecular sieves with an argon atmosphere. Acetonitrile was distilled from phosphorus pentoxide (P_2O_5) to calcium hydride (CaH_2) and redistilled under nitrogen prior to use. Other commercially obtained liquid organic compounds were vacuum distilled from CaH_2 , P_2O_5 , or other appropriate drying agents and stored over 4A molecular sieves with an atmosphere of argon. Halocarbon starting materials were treated in the same fashion, except that the storage flask was covered with foil and stored in the dark. Solid organic materials were recrystallized or sublimed when possible. Anhydrous nickel bromide (Aldrich Gold Label) was heated for 30 min under vacuum with a drying pistol to drive off any adsorbed water before use. Ceric ammonium nitrate (Baker Reagent Grade), *p*-iodobenzonitrile (Pfaltz and Bauer), *p*-iodoanisole (Aldrich), magnesium turnings (Baker), silver tosylate (Aldrich), and sodium iodide (Aldrich) were used without further purification.

Analytical gas-liquid chromatography (GC) was carried out with a Varian Series 2400 gas chromatograph equipped with flame-ionization

(25) See: Stille, J. K.; Lau, K. S. Y. *J. Am. Chem. Soc.* **1978**, *98*, 5832.

(26) For insertion of olefins into (π -allyl)nickel(II) complexes see: Mori, M.; Ban, Y. *Tetrahedron Lett.* **1976**, 1803; **1979**, 1133.

(27) We thank a referee for suggesting the possibility, although not the details, for this process.

(28) A previous proposal involved a one-electron reduction of the substrate halide by the (π -allyl)nickel species, see ref 9.

(29) (a) DePoorter, B.; Muzard, J.; Pete, J.-P. *Organometallics* **1983**, *2*, 1494. (b) Kormer, V. A.; Skelokhneva, L. F.; Kartsvadze, R. *Akad. Nauk SSSR Dokl. (Chem.)* **1978**, *239*, 102.

(30) We thank Professor M. F. Semmelhack for suggesting this.

detectors, a Hewlett-Packard 3370B integrator and one of the following columns, (A) $1/8$ in. \times 10 ft stainless steel 10% Carbowax on Chromosorb W (100/120), (B) $1/8$ in. \times 12 ft stainless steel 10% SE-30 on Chromosorb NAW (100/120), (C) $1/8$ in. \times 10 ft stainless steel 5% SE-30 Chromosorb NAW (100/120), or a Varian Series 3700 gas chromatograph equipped with a 50-m capillary column, flame-ionization detector, and integrator. Preparative-scale separations were accomplished with a Perkin-Elmer 3920 GC fitted with a $3/8$ in. \times 8 ft aluminum 20% OV-17 on Chromosorb A (45/60) column and thermal conductivity detector.

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a Varian EM-360, Varian T-60, JEOL FX-100 with variable temperature probe, IBM WP-270, or Nicolet NT-360 instruments. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were obtained on the JEOL FX-100 at 25.05 MHz. All chemical shifts are relative to tetramethylsilane (Me_4Si). NMR spectra of oxygen-sensitive solutions were recorded in 5-mm NMR tubes which were loaded in a glovebag, drybox, or high vacuum line. Samples to which additional reagents were added were stopped with rubber septa, wrapped with Teflon tape, and degassed. Samples prepared on the high vacuum line were sealed by flame.

Infrared (IR) spectra were recorded with Beckman IR 4210 or Perkin-Elmer 983 infrared grating spectrophotometers. Elemental analysis were performed by M-H-W Laboratories, Phoenix, AZ.

Preparation of Nickel Complexes. μ -Dibromo-bis(η^3 -2-methallyl)-nickel (**1**). This was prepared by the method of Semmelhack^{3b} from nickel tetracarbonyl and 2-methyl-1-bromoprop-2-ene bromide in 96% yield.

Bis(η^3 -2-methallyl)nickel (2**).** This was prepared by the method described in Wilke et al.¹⁰

^1H and ^{13}C NMR. Spectroscopic Studies of (Allyl)nickel Systems. (A)

Spectra of Nickel Complexes in Pure Solvents. (1) **Benzene- d_6 .** Complex **1** (0.0220 g, 0.059 mmol) was placed in a 5-mm NMR tube with a septum and dissolved in 0.45 mL of degassed benzene- d_6 (solution A). ^1H NMR (100 MHz): δ 2.61 (s, 2, syn H), 1.83 (s, 3, CH_3), 1.61 (s, 2, anti H).

(2) **Acetonitrile- d_3 .** Complex **1** (0.060 g, 0.161 mmol) was weighed into an NMR tube and dissolved in 0.61 mL of degassed acetonitrile- d_3 in a drybox. After two cycles of freeze-thaw degassing of this solution on a high-vacuum line the tube was flame sealed. ^1H NMR (100 MHz): δ 3.01 (s, 3, syn H), 2.19 (s, 3, CH_3), 2.15 (s, 2, anti H). ^{13}C NMR: δ 122.6 (C_2), 58.0 (C_1 , C_3), 22.7 (C_4).

(3) **Acetone- d_6 .** Complex **1** was dissolved in degassed acetone- d_6 and transferred to a degassed NMR tube by syringe. ^1H NMR (100 MHz): δ 2.86 (s, 2, syn H), 2.31 (s, 3, CH_3), 1.96 (s, 2, anti H). ^{13}C NMR: δ 119.2 (C_2), 56.4 (C_1 , C_3), 22.7 (C_4).

(4) **Dimethylformamide- d_7 (DMF- d_7).** Complex **2** (0.054 g, 0.322 mmol) was dissolved in 0.53 mL of degassed DMF- d_7 in a septum-capped NMR tube (solution B). ^1H NMR (100 MHz): δ 3.45 (s, 2, trans-syn H), 3.32 (s, 2, cis-syn H), 2.09 (s, 3, cis-anti H), 1.70 (s, 3, trans CH_3), 1.64 (s, 2, trans-anti H), 1.46 (s, 3, cis CH_3). ^{13}C NMR: δ 124.2 (cis C_2), 123.0 (trans C_2), 51.6 (cis C_1 , C_3), 50.8 (trans C_1 , C_3), 24.3 (trans C_4), 24.1 (cis C_4). Trans:cis ratio by integration of ^1H NMR spectrum was approximately 3:1.

Complex **1** (0.114 g, 0.305 mmol) was weighed into a degassed NMR tube with a serum cap and dissolved in 0.95 mL of DMF- d_7 (solution C). Three (allyl)nickel species (complex **1**) and complex **2**, (trans and cis isomers) were detected. ^1H NMR (360 MHz): δ 3.45 (s, 2, trans-syn H), 3.32 (s, 2, cis-syn H), 2.56 (br s, 2, complex **1**-syn H), 2.24 (br s, 3, complex **1**- CH_3), 2.09 (s, 2, cis-anti H), 1.70 (s, 5, complex **1**-anti H and trans CH_3), 1.64 (s, 2, trans-anti H), 1.46 (s, 3, cis CH_3). Trans:cis and 2:1 ratios were 3.7 and 1.2 by integration, respectively.

(B) **Spectra of Complex 1 in Mixed Solvents.** (1) **Additions of DMF- d_7 to a Benzene- d_6 Solution of Complex 1.** Sequential additions of DMF- d_7 were made by microliter syringe to solution A while monitoring the changes in the ^1H NMR spectrum at 30 $^\circ\text{C}$. The changes in relative proportions of (allyl)nickel species appear in Table II.

(2) **Additions of Benzene- d_6 to a DMF- d_7 Solution of Complex 1.** Changes in the ^1H NMR spectrum were recorded after additions of benzene- d_6 to solution C were made in a manner similar to that described in section B.1 above. Table II cites the changes in (allyl)nickel product ratios.

(C) **Additions of Nickel Bromide to DMF- d_7 Solutions of (π -Methallyl)nickel Species.** (1) **Complexes 1 + NiBr_2 .** Anhydrous nickel(II) bromide (0.043 g, 0.197 mmol) was dissolved in 0.53 mL of DMF- d_7 by heating the mixture under vacuum in a 10 mm \times 150 mm vacuum hydrolysis tube (Kontes Glass Co.) for 12 h in an 80 $^\circ\text{C}$ oil bath. This solution was filtered (in a glovebag) through a fine frit into a serum capped vial and freeze-thaw degasses three cycles before use (solution D). Complex **1** (0.0474 g, 0.127 mmol) was weighed into an NMR tube and dissolved in 0.50 mL of DMF- d_7 . ^1H NMR indicated trans:cis and 2:1 ratios of 3.6 and 1.7, respectively. Solution D was added via gas-tight

syringe in three portions. Addition of 0.44 equiv of NiBr_2 per equiv of complex **1** immediately changed the trans:cis ratio to 3.5 and 2:1 ratio to 2.1. One equivalent of NiBr_2 per equivalent of Complex **1** produced 2.4 (trans:cis) and 2.0 (2:1) ratios shortly after the addition of more solution D. When 1.55 equiv of nickel bromide had been added, 2.4 (trans:cis) and 1.3 (2:1) ratios were observed several minutes after the addition of solution D. These proportions had changed to ca. 2 trans:cis and 0.6 2:1 after storage at -10 $^\circ\text{C}$ for 17 h.

(2) **Complex 2 + NiBr_2 .** Solution E (0.069 g, 0.316 mmol of NiBr_2 in 0.44 mL of DMF- d_7) was prepared in the same manner as solution D. Half of solution E was added to solution B via gas-tight syringe and the changes in the ^1H NMR spectrum monitored as a function of time. ^1H NMR after 25 min indicated that trans:cis and 2:1 ratios were 3.5 and 12.6, respectively. The second half of solution E was transferred 30 min after the first addition. Thirty two hours later the ratios had changed to 2.7 trans:cis and 1.40 2:1. ^1H NMR (100 MHz): δ 3.45 (s, 2, trans-syn H), 3.32 (s, 2, cis-syn H), 2.60 (s, 2, complex **1**-syn H), 2.21 (s, 3, complex **1**- CH_3), 1.70 (br s, 5, complex **1**-anti H and trans CH_3), 1.64 (s, 2, trans-anti H), 1.46 (s, 3, cis CH_3). ^{13}C NMR: δ 124.0 (cis C_2), 122.8 (trans C_2), 114.7 (complex **1**- C_2), 53.4 (complex **1**- C_1 , C_3), 51.6 (cis C_1 , C_3), 50.8 (trans D_1 , C_3), 24.3 (trans D_4) 22.9 (complex **1**- C_4).

(D) **Radical Clock Experiments.** (1) **Cyclopropyl Methyl Bromide.** The substrate (0.096 g, 0.709 mmol) was used as obtained, except that it was freeze-thaw degassed for three cycles before addition of a solution containing complex **1** (0.176 g, 0.473 mmol) in DMF by syringe. This reaction mixture was irradiated in the light box until there was no complex **1** color apparent (ca. 6 h). The reaction vessel was fitted with a short path distillation head, and the volatile organic materials were flash distilled (using a 120 $^\circ\text{C}$ oil bath) to a collection flask cooled to 0 $^\circ\text{C}$. ^1H NMR (360 MHz in CDCl_3): δ 5.84 (m, 1, $\text{C}=\text{CHC}$), 4.98 (m, 2, $\text{C}=\text{CH}_2$), 4.70 (br s, 2, (C_2) $\text{C}=\text{CH}_2$), 2.05 (m, 4, allylic CH_2), 1.74 (s, 3, CH_3), 1.53 (m, 2, homoallylic CH_2). The sample contained 1% or less cyclopropyl coupled product based on the NMR assignments made by Manning and Kropp for 1-cyclopropyl-3-methyl-2-butene.³¹

(2) **1-Iodo-2-ethyl Allyl Ether.** This iodide was prepared as described by Bergman,¹² except that it was purified by drying over anhydrous calcium chloride and then fractionally distilling under 0.5 torr of vacuum.

Complex **1** (1.20 g, 3.11 mmol) was weighed into a degassed 100-mL Airlessware flask. The iodide (1.12 g, 5.28 mmol) was weighed into a 50-mL two-neck round-bottomed flask fitted with a vacuum adapter and septum. Degassed DMF (30 mL) was added to the flask containing the substrate and freeze-thaw degassed for three cycles before transferring by cannula to the vessel with complex **1**. This solution was exposed to light until the reaction was complete (24 h). A small amount of nickel black was observed before the reaction was quenched with 50 mL of water and extracted with 4 \times 60 mL of pentane. The combined pentane layer was washed (2 \times 50 mL of water and 2 \times 50 mL of saturated NaCl solution), dried over anhydrous MgSO_4 , and concentrated as a rotary evaporator at 0 $^\circ\text{C}$, wt = 0.653 g, colorless liquid. Proton NMR indicated a linear:cyclic coupled materials ratio of 57:43 by integration of the terminal vinyl methylene signals. Capillary GC (with no correction for response ratio) showed a 53:47 linear:cyclic ratio. Isolation (Chromatotron, 2-mm plate, 5:1 petroleum ether:ether) yielded a 58:42 ratio of linear:cyclic materials. Fraction 1 (0.317 g of colorless liquid with a sweet odor, density 1.03 g/mL, 97% pure by capillary GC) was purified further by preparative-scale GC at 160 $^\circ\text{C}$: ^1H NMR (270 MHz in CDCl_3) δ 5.92 (m, 1, $\text{C}=\text{CHC}$), 5.24 (m, 2, $\text{H}_2\text{C}=\text{CC}$), 4.70 (br s, 2, (C_2) $\text{C}=\text{CH}_2$), 3.97 (d, 2, $J = 5.7$ Hz, $=\text{CCH}_2\text{O}$), 3.43 (t, 2, $J = 6.7$ Hz, OCH_2C), 2.0 (m, 2, $J = 8.1$ Hz, allylic CH_2), 1.81-1.67 (m, 5, CH_3 and CH_2); IR (neat) $=\text{CH}_2$ 3080 cm^{-1} , $=\text{C}(\text{H})$ 3020 cm^{-1} , $\text{C}=\text{C}$ 1655 cm^{-1} , CO 1110 cm^{-1} . Anal. Calcd for $\text{C}_9\text{H}_{16}\text{O}$: C, 77.09; H, 11.50. Found: C, 76.94; H, 11.32. Fraction 2 (0.234 g of colorless liquid, 92% pure by capillary GC) was further purified by preparative-scale GC at 160 $^\circ\text{C}$: ^1H NMR (270 MHz in CDCl_3) δ 4.70 (br s, 2, $=\text{CH}_2$), 3.94-3.73 (m, 3, OCH), 3.34 (m, 1, OCH), 2.23-1.96 (m, 4, allylic and homoallylic CH_2), 1.72 (s, 3, CH_3), 1.66-1.45 (m, 3, ring CH); IR (neat) $=\text{CH}_2$ 3080 cm^{-1} , $\text{C}=\text{C}$ 1655 cm^{-1} , CO 1055 and 1090 cm^{-1} . Anal. Calcd for $\text{C}_9\text{H}_{16}\text{O}$: C, 77.09; H, 11.50. Found: C, 77.11; H, 11.42.

(3) **6-Iodo-1-hexene.** 1-Hexen-6-ol was converted to the tosylate by conventional methods³² and was used in the following step without purification. The tosylate (4.3 g, 16.9 mmol) was heated at reflux in acetone for twenty-four h with sodium iodide (7.62 g, 50.8 mmol) and sodium bicarbonate (2.27 g, 27.1 mmol). After cooling, the acetone solution was filtered through Celite and concentrated on the rotary evaporator to an orange paste. This material was washed with 50 mL of diethyl ether. The recovered ether layer was washed with 2 \times 50 mL

(31) Manning, T. D. R.; Kropp, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 889.
(32) Hilgetz, G.; Martini, A., Ed. "Preparative Organic Chemistry"; Wiley-Interscience: New York, 1972; p 229.

Table V. DARK Reactions, Limiting Complex 1 Conditions^a

time, min	[methallylbenzene] _{av} ^b , M	time, min	[methallylbenzene] _{av} ^b , M
85	1.38×10^{-3}	150	2.73×10^{-3}
100	1.47×10^{-3}	170	3.27×10^{-3}
110	1.70×10^{-3}	200	4.45×10^{-3}
120	2.26×10^{-3}	230	5.66×10^{-3}
130	2.50×10^{-3}	255	7.73×10^{-3}
140	2.58×10^{-3}	400	1.57×10^{-2}

^a For time 85, 110, 140, 150, 170, 200, 230, and 255 min first-order analysis: slope = $2.04 (\pm 0.23) \times 10^{-5} \text{ s}^{-1}$; intercept = 3.31 ± 0.02 ; correlation = 0.963. ^b Relative to 0.02 M mesitylene; average concentration of methallylbenzene for two data points at each time interval.

Table VI. DARK Reaction, Limiting Iodobenzene Conditions^a

time, min	[methallylbenzene] _{av} , M	time, min	[methallylbenzene] _{av} , M
150	5.18×10^{-3}	272	6.30×10^{-3}
180	5.81×10^{-3}	300	8.70×10^{-3}
210	6.42×10^{-3}	330	9.40×10^{-3}
240	7.11×10^{-3}		

^a First-order analysis (for all except $t = 272$ min): slope = $3.91 \times 10^{-5} \text{ s}^{-1}$; intercept = -4.025 ; and correlation = 0.995.

of water, 2×50 mL of 5% sodium thiosulfate, and 2×25 mL of saturated NaCl solution, dried over anhydrous Na_2SO_4 followed by 4A molecular sieves, and concentrated by rotary evaporation, to give 2.9 g of colorless liquid (82% yield), density 1.33 g/mL. This material was vacuum distilled (at 10 mmHg) at 60–62 °C before use in the cross-coupling reaction.

The products of reaction between complex 1 (0.832 g, 2.23 mmol) and 6-iodo-1-hexene (0.796 g, 3.79 mmol) were isolated in the same manner as described above. (Some nickel black was formed during the 48 h reaction period.) Capillary GC (uncorrected for differences in response factors) indicated that the coupled products were present in a 98:2 linear-to-cyclic ratio. The linear material was purified by preparative-scale GC at 140 °C: ¹H NMR (360 MHz in CDCl_3) δ 5.812 (m, 1, C=CHC), 4.968 (m, 2, $\text{H}_2\text{C}=\text{CC}$), 4.674 (br s, 2, (C)₂C=CH₂), 2.08–1.97 (m, 4, allylic CH₂'s), 1.708 (s, 3, CH₃), 1.50–1.25 (m, 6, CH₂'s); IR (neat) =CH₂ 3080 cm^{-1} , C=C 1655 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{18}$: C, 86.87; H, 13.12. Found: C, 86.76; H, 13.37.

Kinetics Experiments. (A) Isolation Method. (1) DARK Reactions. A 50-mL Airlessware flask containing a stir bar and fitted with a septum was purged of air. Complex 1 (0.250 g, 0.670 mmol) was transferred to this vessel in a glovebag and the flask degassed. This flask was kept under a positive pressure of argon until the reaction was complete. DMF containing 0.02 M mesitylene as internal standard was degassed before 33.5 mL were transferred by syringe to the reaction flask. The reaction flask was then completely covered with foil and submerged in a 0 °C (± 0.5 °C) constant-temperature bath. After thermal equilibrium was achieved (usually 30–45 min later) the iodobenzene was added all at once by syringe (time = 0). Aliquots were withdrawn periodically and quenched in a 1 mL hexane/1 mL 3 M sodium chloride in 2 N hydrochloric acid mixture at -22 °C (dry ice in carbon tetrachloride). (Two or three data points were taken at each time interval for better accuracy.) The hexane layer was immediately analyzed by quantitative GC (column A or B) for the presence of methylallylbenzene. No detectable isomerization of product occurred under the reaction or quench conditions. The results of a typical dark kinetic run appear in Tables V and VI. The data were analyzed by using the KINADD program, obtained from Professor Jack R. Norton, for second, first, and zeroth-order kinetics. The first-order analysis had the best correlation, but it was still not acceptable. Thus k_{obsd} may only be used for the purpose of comparison.

(2) LIGHT Reactions. These reactions were set up identically with the DARK reaction method, except that the reaction vessel was not covered with foil. A 275-W tungsten lamp was positioned 13 in. above the surface of the solution. In most cases, the lamp was turned on for 5 min at the point of addition of iodobenzene. After this irradiation period, the flask was completely covered with foil such that the ensuing reaction took place in the dark. A typical example of the results of these experiments appears in Table VII.

(3) Added NiBr₂/DARK Reactions. Anhydrous nickel(II) bromide (6.56 g, 30.0 mmol) was weighed into a 100-mL Airlessware flask and degassed. DMF (75 mL) containing 0.04 M mesitylene was transferred by syringe to the Airlessware flask. A reflux condenser was attached

Table VII. LIGHT Reaction, Limiting Complex 1 Conditions^a

time, min	[methallylbenzene] _{av} , M	time, min	[methallylbenzene] _{av} , M
8	5.80×10^{-4}	38.1	2.09×10^{-3}
11	7.30×10^{-4}	44.1	2.62×10^{-3}
13	8.10×10^{-4}	50	3.01×10^{-3}
16	8.30×10^{-4}	65.2	4.15×10^{-3}
21	9.20×10^{-4}	75	6.30×10^{-3}
24	1.10×10^{-3}	100.3	1.13×10^{-2}
30	1.60×10^{-3}	110	1.38×10^{-2}
32	1.68×10^{-3}	150	2.01×10^{-2}
35	1.81×10^{-3}	180	2.16×10^{-2}

^a First-order analysis (for time 8–50 min): slope = $4.61 (\pm 0.26) \times 10^{-5} \text{ s}^{-1}$; intercept = $3.78 (\pm 0.004)$; and correlation = 0.982.

Table VIII. Added NiBr₂, DARK Reaction, Limiting Complex 1 Conditions^a

time (min)	[methallylbenzene] _{av} , M	time (min)	[methallylbenzene] _{av} , M
10.7	2.09×10^{-3}	50	8.12×10^{-3}
20	3.88×10^{-3}	60	1.04×10^{-2}
34	5.52×10^{-3}	77	1.48×10^{-2}
40	6.46×10^{-3}	92.5	1.67×10^{-2}
45	7.29×10^{-3}		

^a First-order analysis (for $t = 20$ –77 min): slope = $1.26 \times 10^{-4} \text{ s}^{-1}$; intercept = 3.27; and correlation = 0.971.

Table IX. Initiation by Sodium Naphthalene

time, min	[methallylbenzene] _{av} , M
30	$<1 \times 10^{-3}$
60	$<1 \times 10^{-3}$
90	$<1 \times 10^{-3}$
120	$<1 \times 10^{-3}$
150	$<1 \times 10^{-3}$
At 155 min 0.5 mL of solution G Was Added	
160	2.2×10^{-3}
180	2.6×10^{-3}
195	2.8×10^{-3}
210	2.8×10^{-3}
240	3.0×10^{-3}
300	3.1×10^{-3}
330	3.4×10^{-3}

under a flow of nitrogen and the NiBr₂ solution heated for 12 h at 80 °C in an oil bath under an atmosphere of nitrogen. The solution was cooled to room temperature and filtered through a coarse frit under an atmosphere of argon. This stock solution (solution F) was then used as the solvent for kinetic runs with a large excess of nickel bromide (0.40 M). These experiments were performed as described in Kinetics, part A.1, except that the (allyl)nickel complex was dissolved and equilibrated in solution F before iodobenzene was added. A representative example of the results of these experiments appears in Table VIII.

(B) Initiation Experiments. (1) Sodium Naphthalene as Initiator. Sublimed naphthalene (0.100 g, 0.780 mmol) was placed in a 50-mL Airlessware flask, stopped with a serum cap, submerged in liquid nitrogen, and degassed. Sodium (0.190 g, 8.3 mmol) was freshly cut into 2-mm cubes under deaerated petroleum ether and placed in the reaction flask under a stream of nitrogen. Freshly distilled THF (45 mL) was transferred by cannula to the flask containing the sodium metal and naphthalene. This mixture (solution G) immediately turned dark green.

No detectable amount of methallylbenzene was produced from a solution containing 0.02 M complex 1 (0.241 g, 0.646 mmol in 65 mL) and 0.02 M iodobenzene (0.264 g, 1.29 mmol in 65 mL of DMF) after 150 min. Addition of 0.5 mL of solution G (ca. 1.3 mol % sodium naphthalene based on complex 1) to this reaction mixture produced detectable amounts of product within 5 min.

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