ment on the mechanism for the formation of the cyclopropanes **4a** and **4b** nor on the cyclopropanation reactions of simple olefins, since the very electron-rich diene **3** would be expected to favor the formation of the zwitterionic intermediate **8** compared to less activated olefins.

The Diels–Alder reactions of α,β-unsaturated carbene complexes are known and occur with 1,3-dienes via a [4 + 2] cycloaddition at the unsaturated carbon–carbon bond of the carbene carbon substituent.[11] Thus on the basis of the reactions observed for complexes **1** and **2**, one would anticipate the possibility that both [2 + 1] and [4 + 2] cycloadditions could occur for the reaction of the diene **14** and the complex **13**; however, to date only Diels–Alder products have been observed for the reactions of α,β-unsaturated complexes and 1,3-dienes.[11] The reaction of the tungsten complex **13b** gives the Diels–Alder adduct **18** in 34% yield;[12a] whereas, the chromium complex **13a**[13] reacts to give two products, the cyclopropane **15** and the seven-membered ring silyl enol ether **17**. The stereochemical assignment of **17** was made considering that it has been determined that *cis*-divinylcyclopropanes undergo Cope rearrangement via a boat transition state.[14] Since *cis*-divinylcyclopropanes undergo Cope rearrangement much faster than their corresponding trans isomers, it can be deduced that the ratio of the *trans*-cyclopropane product **15** and the Cope product **17** from the reaction of the chromium cyclohexenyl carbene complex **17a** and diene **14** is a reflection of the stereoselectivity of the cyclopropanation reaction. The *trans*-divinylcyclopropane **15** will undergo the Cope rearrangement to give **17** at 90°C, and since this rearrangement is essentially quantitative, this tandem cyclopropanation/Cope rearrangement could be utilized for an efficient preparation of highly functionalized fused seven-membered rings.[4]

From the point of view of the synthetic methodological development of transition-metal organometallics, the two reactions indicated in Scheme II represent an ideal situation. The reaction of the carbene complex **13** with diene **14** can be fine tuned to give either the tandem cyclopropanation/Cope product **17** or the Diels–Alder product **18** by judicious choice of the metal in the complex. These reactions are remarkably chemospecific in their reactions with the 1,3-diene **14** as the chromium complex **13a** gave no detectable amounts of the Diels–Alder product, and the tungsten complex **13b** gave less than 0.5% of the cyclopropane **15**.[12a] The rate of the Diels–Alder reaction of the tungsten complex **13b** with diene **14** is also remarkable when compared to the reaction of its closest carbon analogue, the cyclohexenyl ester **13c**, which occurs with **2** in 30 h at 190 °C.[15] Further studies will be needed to determine how the nature of the metal can so dramatically affect the product distribution in these reactions.

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Supplementary Material Available: Spectral and physical data for compounds **2b**, **4a,b**, **5a–f**, **5a′–f′**, **7**, **15**, **17**, and **18** (4 pages). Ordering information is given on any current masthead page.

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Bimetallic Catalysis. A New Method for the Activation of Chloroarenes toward Palladium-Catalyzed Coupling with Olefins

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Palladium-catalyzed olefin arylation, developed primarily by Heck, is a well-established method for the coupling of activated olefins with aromatic halides (Scheme I).[1] The reaction is general for a broad range of substituents both on the arene and the olefin and is useful for the preparation of a wide array of elaborated arenes from relatively simple starting materials.

A serious limitation to this method is its failure with aryl chlorides. A method for the activation of chloroarenes toward olefin arylation is desirable because of the ready availability and relative inexpense of these materials. For example, bromobenzene undergoes palladium-catalyzed coupling with ethyl acrylate to give ethyl cinnamate in 78% yield[2] but performing the reaction with chlorobenzene lowers the yield to 4%.[3] Only in the presence of styrene or stoichiometric amounts of preformed **1** (X = Cl) has successful coupling of olefins with chlorobenzene been observed.[4,5] Chloroarenes substituted with electron-withdrawing groups undergo olefin coupling but rarely in yields above 30%. An indirect method based on palladium-catalyzed CO extrusion from aroyl halides has been reported.[6] We wish to report a new method of coupling chloroarenes and olefins in excellent yield by means of a novel bimetallic nickel/palladium catalyst system. To our knowledge, this is the first demonstration of chloroarenes participating in the Heck arylation reaction in a synthetically useful fashion.

In a typical experiment, the chloroarene (10 mmol) is treated with NaI (11 mmol) and $NiBr_2$ (2 mmol) in DMF at 140 °C for 4–5 h. Gas chromatographic and mass spectral analysis at this point indicates that approximately 5% of the starting chloroarene has been converted to the corresponding iodoarene. The mixture is cooled and treated with the olefin (11 mmol), $Pd_2(dba)_3$ (0.05 mmol), $P(o\text{-tol})_3$ (4 mmol), and Et_3N (11 mmol). The mixture is heated overnight at 140 °C (usually 16–18 h). The salts are precipitated from the cooled reaction mixture upon addition of Et_2O. Filtration and removal of DMF by washing of the organic fraction with small amounts of saturated NaCl followed by

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Scheme I

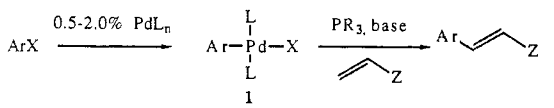
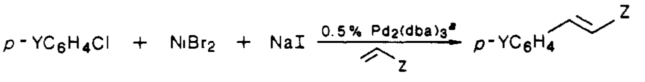


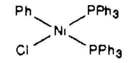
Table I. Coupling of Chloroarenes



entry	Y	Z	coupling prod., isoltd yield (%)
1	H	COOEt	64
2	COOMe	COOEt	25
3	COMe	COOEt	75
4	OMe	COOEt	75
5	Me	COOEt	73
6	CN	COOEt	85
7	H	CN	50
8	NO_2	COOEt	0

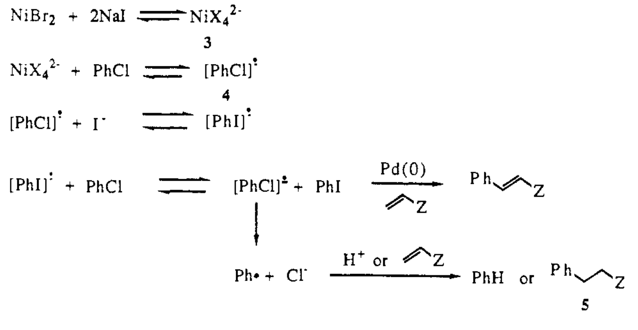
[a] dba = dibenzylideneacetone.

Table II. Nickel Sources Investigated

source	convsn/selectivity (%)[b]
Ni(II) sources[a]	
$NiBr_2$/NaI	65/>90
$NiBr_2$	35/74
$NiBr_2$/LiCl	0/0
$NiCl_2$	0/0
$NiCl_2$/NaI	50/>90
$Ni(acac)_2$/NaI	0/0
$Ni(PPh_3)Br_2$/NaI	<10/<10
 2	45/5
Ni(0) sources[a]	
$Ni(PPh_3)_4$/NaI	<10/<10
$Ni(cod)_2$/NaI	20/80
$NiBr_2$/Zn	0/0
$Ni(CO)_2(PPh_3)_2$[c]	<10/<10[d]
$Ni(CO)_2[P(OPh)_3]_2$[c]	<10/<10[d]

[a] Reactions performed under conditions described in text. [b] % conversion = (mol PhCl at start−mol PhCl at end)/mol PhCl at start × 100; % selectivity ; mol product/(mol PhCl at start−mol PhCl at end) × 100. [c] $Pd(OAc)_2$ used as palladium source. [d] Catalyst decomposed.

Scheme II. Proposed Mechanism of Exchange/Heck Sequence



chromatographic purification gives the desired product. The reaction is best performed in two stages; combining the components simultaneously results in a lower yield. Appropriate control reactions verify the necessity of having both nickel and palladium catalysts present in the mixture. The results for a number of chloroarenes are given in Table I.

The reaction is tolerant of both electron-donating and electron-withdrawing substituents on the arene and gives arylated olefins in a single step from readily available starting materials (entries 2–6). Only the E isomer is observed by ^{1}H NMR. Chlorobenzene undergoes coupling with ethyl acrylate to give ethyl cinnamate in 64% yield (entry 1), a significant improvement over the highest reported value for this reaction.[3] Cinnamonitrile is prepared by substituting acrylonitrile for ethyl acrylate (entry 7). The product formed from the coupling of *p*-chloroanisole and ethyl acrylate is of interest as the cytotoxic principal of the Chinese herb *Kaempferia galanga* L[7] (entry 4). The principal side reactions of the process (occurring in less than 5% total yield) are dehalogenation of the arene and reduction of the double bond of the coupled product.

The success of the reaction apparently depends on the nickel-catalyzed conversion of a small amount of the chloroarene to the corresponding iodoarene in situ. The subsequent Heck reaction consumes the iodoarene formed and drives the unfavorable exchange equilibrium toward product. The reaction is most sensitive to the nickel catalyst used, as evidenced by the small number of catalyst systems that promote coupling. The effects of a number of different nickel species are summarized in Table II.

The mechanism of halide exchange has been suggested to proceed via a Ni(0) species formed in situ;[8] however, we find that preformed Ni(0) species are uniformly inferior to Ni(II) complexes in promoting the coupling. Notably, complex **2**, the adduct formed upon oxidative addition of a nickel(0) species to chlorobenzene,[9] gives a very low selectivity for the Heck coupling product. The activity of the optimum catalyst, $NiBr_2$, is completely quenched in the presence of Zn metal, conditions reported to generate Ni(0) in solution.[8] The same authors observe iodide/bromide exchange in high yield in the absence of a reducing agent, conditions not conducive to the formation of Ni(0). We find that only nickel(II) complexes activate chlorobenzene toward Heck coupling under these conditions. The ligands on the nickel complex are critical; an excess of I^- must be present for a high yield coupling. For example, $NiCl_2$ alone does not afford ethyl cinnamate, but use of a $NiCl_2$/NaI mixture gives ethyl cinnamate in yield approaching that of the optimized $NiBr_2$/NaI system. Conversely, formation of product is completely suppressed when $NiBr_2$ is used in the presence of excess LiCl.

While extensive mechanistic studies have not been performed, our results are consistent with an electron-transfer mechanism for the halide exchange portion of the reaction. A possible mechanism is shown in Scheme II.

Under the conditions of the reaction, $NiBr_2$ is converted to tetrahedral polyhalo nickelate salt **3**.[10] The electron rich **3** initiates an $S_{RN}1$-like sequence by transferring an electron to PhCl giving radical anion **4**, which is activated toward chloride displacement by I^-.[11] Free iodobenzene is generated by electron transfer to a molecule of PhCl. Since the reduction potential of PhI is much lower than that of PhCl, the equilibrium would lie far to the left; however, the small equilibrium concentration of PhI is consumed under Heck conditions, and the reaction is eventually forced to completion. Reduction products (e.g., **5**) are observed as a result of trapping of the anionic intermediates by $Et_3NH^+Cl^-$ or excess olefin in solution. Supporting this hypothesis is the suppression of the reaction by the addition of 5% *p*-dinitrobenzene, a known radical scavenger, and the failure of *p*-nitrochlorobenzene to undergo coupling (Table I, entry 8).[12] The exact mechanism for

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transfer of an electron to the arene is unknown but may be facilitated by a bridging iodide as suggested by Kumada in his Ni-catalyzed synthesis of biphenyls.[13] Kochi has suggested an electron-transfer mechanism for halide exchange of arenes in nonpolar solvents.[14]

The mechanism suggests that NiX_4^{2-} is a reducing agent for chloroarenes. Accordingly, we have performed some preliminary electrochemical measurements on the $NiBr_2$ system. All measurements were performed in DMF at a Pt disk-working electrode against a silver wire reference. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium tetrafluoroborate, and the concentration of the substrate was 0.005 M. Cyclic voltammetry at 100 mV/s sweep rate indicates an oxidation wave for solutions of $NiBr_2$ and NaI that does not appear in the cyclic voltammogram of either component separately. While not unequivocal, this observation is consistent with the formation of a better reducing agent in solution upon interaction of $NiBr_2$ and NaI. The nature and reducing ability of this species is unknown. Mechanistic study and application of this new method to the synthesis of other systems is underway.

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The Cage Effect and Apparent Activation Parameters for Bond Homolysis

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A number of recent[1-5] results demonstrate that transition metal carbon bond homolyses occur in solution at only slightly elevated temperatures. Up until now, these important observations have been interpreted[1-6] in terms of models[1] that do not include the effects of the cage pair intermediate which is unique to solution phase studies (Scheme I, Figure 1). We wish to point out that, as has been demonstrated with organic peroxides,[6-9] the cage effect must be considered in M–L bond homolyses in solution. We provide here a set of equations that will help clarify the connection between observed activation parameters ($\Delta H^{\ddagger}_{\mathrm{obsd}}$ and $\Delta S^{\ddagger}_{\mathrm{obsd}}$) and those for the homolytic elementary step in solution ($\Delta H^{\ddagger}_1(\mathrm{s})$, $\Delta S^{\ddagger}_1(\mathrm{s})$). These equations, while straightforward, have not been previously emphasized in the cage literature. They are especially significant for M–L systems, many of which cannot be studied in the gas phase where bond dissociation is not complicated by the cage effect. The formalism provided here is therefore of considerable current interest.

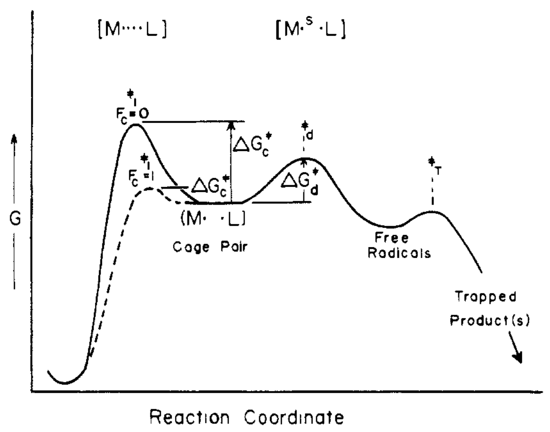

Figure 1.

Scheme I shows the phenomenological version of our cage effect model,[6] cast in terms of a metal–carbon (M–L) bond homolysis. The free-energy diagram, corresponding to this scheme, is shown in Figure 1 where the two limiting cases ($k_d \gg k_c$, solid line and $k_c \gg k_d$, dashed line) are indicated. The k_{-1} of Scheme I is the rate constant for recombination of *free radicals* to form the cage pair. The rate constant designated k_c is for cage pair combination and is expected to be greater than k_{-1} ($k_c \neq k_{-1}$). The k_d step in Scheme I is meant to describe the diffusive disappearance of the cage pair and is also *not*, in general, expected to be equal to k_{-1}.[10a]

Scheme I defines k_1 as the rate constant for the formation of the *cage pair in solution.* The k_T process of Scheme I designates the reaction of one or both of the *free radicals* (M•, L•) with a

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(10) (a) The value of k_{-1} and $\Delta H^{\ddagger}_{-1}$ in the gas phase must also be kept distinct from $\Delta H^{\ddagger}_{-1}$, $\Delta H^{\ddagger}_{d}$, and $\Delta H^{\ddagger}_{c}$ in solution. For simplicity, recombination is the only *chemical* cage reaction that we have included in Scheme I. Disproportionations, etc. could be included[6] and in fact are probable for M–L systems with β–hydrogens.[2f] (b) The suggestion,[1] widely employed[2-5] prior to the availability of eq 2 and 3 herein, that bond dissociation energies can be obtained by simply subtracting the activation enthalpy for a diffusion-controlled reaction in the solvent in which $\Delta H^{\ddagger}_{\mathrm{obsd}}$ was measured ($\Delta H^{\ddagger}_{-1} \sim 2$ kcal/mol for acetone or toluene) requires the implicit assumptions that $F_c \sim 1$ and that solvation effects are not important. Most literature estimates of F_c are not this large in fluid solvents such as those used for the $\Delta H^{\ddagger}_{\mathrm{obsd}}$ determinations. However, most quantitative values for F_c come from cage pairs with intervening small molecules. Higher F_c values are possible in M–L systems where no small molecule is formed in the homolytic event. A high value of F_c means that the rate determining transition state is $\ddagger_d$ (Figure 1); $\ddagger_d$ is well removed from $\ddagger_1$ and is subject to medium effects in addition to M•, L• structural effects. Schemes[1] that do not recognize the cage pair intermediate will not be able to separate these effects. (c) The activation entropy associated with eq 1, defined $\ln(k_{\mathrm{obsd}}/T)$ as T goes to infinity is $\Delta S^{\ddagger}_{\infty} = \Delta S^{\ddagger}_1(\mathrm{s}) - R{\cdot}\ln\{1 + \exp[(\Delta S^{\ddagger}_c - \Delta S^{\ddagger}_d)/R]\}$. This definition does not apply except at $T \rightarrow \infty$. (d) This approximation rests on *purely numerical* results and is quite distinct from the *analytic expression* for $\Delta H^{\ddagger}_{\mathrm{obsd}}$ (eq 2). It is accurate outside of the $0.1 < F_c < 0.9$ interval and is otherwise good to about ±2 eu. $\Delta S^{\ddagger}_{\mathrm{obsd}}$ does not have as good a definition as usual unless F_c is a constant over the temperature range used for the k_{obsd} measurements.

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