Hz) and $(OC)_5WP(C_6H_5)_2CH_2P^+(C_6H_5)_2CH_3[I^-]$ ($^2J_{PP}$ = 8.1 Hz). For the ligand $P(OCH_2)_3P$, it has been observed that J_{PP} becomes more positive with increasing s character and effective nuclear charge.[4] If these patterns are followed in our systems, it would be predicted that $^3J_{PP}$ for $(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)$ is positive and becomes more so upon quaternization, while $^2J_{PP}$ for $(OC)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$ is −106.2 Hz and becomes ±8.1 Hz upon quaternization. These predictions are based upon trends which have been observed for a relatively small number of systems and their validity will be established only by the determination of more signs of J_{PP}.[12]

Acknowledgment. Financial support from the Council of Faculty Research, Eastern Illinois University, is acknowledged.

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Synthesis with Zerovalent Nickel. Coupling of Alkenyl Halides with Bis(1,5-cyclooctadiene)nickel(0)

Sir:

Bis(1,5-cyclooctadiene)nickel(0)[1] is a powerful zerovalent nickel catalyst for diene oligomerization[2] and a reactive species in oxidative addition of allyl,[3] benzyl,[4] and aryl halides.[5] The study of the coupling of aryl halides with bis(1,5-cyclooctadiene)nickel [$Ni(COD)_2$] showed clearly that the nickel reagent reacts rapidly and selectively with certain carbon–halogen bonds in the presence of a wide variety of other functional groups.[5] Herein we report that alkenyl halides react in a parallel way with $Ni(COD)_2$, producing symmetrical 1,3-dienes directly. The mild reaction conditions and, in certain cases, the high efficiency and high stereospecificity of the process point to potential synthetic applications in inter- and intramolecular coupling of alkenyl halides.

The experimental procedure is illustrated for the conversion of *trans*-2-bromostyrene to *trans,trans*-1,4-diphenyl-1,3-butadiene. $Ni(COD)_2$ (563 mg; 2.08 mmol) was transferred to a three-necked flask which had been alternately evacuated and filled with argon three times, and 15 ml of oxygen-free dimethylformamide was added. With the mixture frozen at −78°, 683 mg (3.74 mmol) of *trans*-2-bromostyrene[6] was added all at once *via* syringe. The mixture was allowed to warm to 25° over 1 hr and then stirred at 25° for 10 hr followed by 35° for 2 hr. The mixture (homogeneous green) was poured into ether and washed with water several times. Quantitative ^1H nmr analysis and quantitative glpc analysis of the residue from the ether solution indicated the presence of *trans,trans*-1,4-diphenyl-1,3-butadiene in a yield of 70 ± 2%. Repeated crystallization from methyl alcohol gave colorless crystals (mp 149.5–151°, lit.[7] mp 153°) in 46% yield.

In the absence of electron-withdrawing groups, *i.e.*, with simple alkenyl halides, the yields of coupling products are only moderate, 34–60%, and a mixture of geometric isomers results, with an apparent tendency toward the more stable isomer (Table I). On the other hand, 2-halo- and 3-haloacrylates react very rapidly (−20 to 0°) with $Ni(COD)_2$ to produce symmetrical unsaturated diesters in high yield and with complete retention of configuration (Table II). The most important reason for the only moderate yields of the simple 1,3-dienes is likely to be catalytic oligomerization of the initially formed 1,3-diene by unreacted $Ni(COD)_2$ or a related intermediate nickel species;[2] in fact, longer reaction times (>24 hr/25°) lead to lower yields of coupling products.

The products reported in Tables I and II are known compounds with the exception of dibenzyl *trans,trans*-muconate (Table II, entry 7) which had mp 108–109° and showed spectral data in complete accord with the structure. For confirmation, the diester was hydrolyzed in aqueous base to afford *trans,trans*-muconic acid (mp 301°, lit.[8] mp 301°).

The isomeric 2,4-hexadienes (Table I) were collected separately by preparative glpc and identified by comparison of ir absorption maxima with those reported by Bartlett;[9] the isomers also showed the same order of elution observed by Whitesides, under the same glpc conditions.[10]

The coupling product from 2-bromo- and 2-chloroacrylates (Table II, entries 1–4), 2,3-dicarbomethoxy-1,3-butadiene, is easily polymerized and could not be isolated efficiently; the yields were determined using quantitative ^1H nmr analysis, by integration of the characteristic peaks due to the vinyl hydrogens in the product (δ 5.82 and 6.29) relative to a precise amount of an internal standard. Base hydrolysis of the crude mixture from the coupling reaction afforded 2,3-dicarboxy-1,3-butadiene, identical in ir absorption maxima with literature values;[11] mp 192–192.5°, lit.[11] 182–185°.

The ^1H nmr spectral data for the geometric isomers of dimethyl muconate clearly distinguish the isomers;[12] both the yields and identification of the products were done by analytical ^1H nmr spectroscopy for entries 5–7 in Table II. The task was simple because the reactions are stereospecific within the limits of ^1H nmr detection, estimated to be *ca.* 2%.

The reactions of the haloacrylate esters exemplify the mildness of the nickel-promoted coupling method.[13]

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Table I. Coupling of Alkenyl Halides with Bis(1,5-cyclooctadiene)nickel(0) at 25°

$$\mathrm{2RCH{=}CHX + Ni(COD)_2 \longrightarrow RCH{=}CHCH{=}CHR + NiX_2 + 2COD}$$

Alkenyl halide	Solvent, ligand[a]	Duration, hr	Products (% of total coupling product)	Yield,[b] conversion (%)
1. trans, R = Ph; X = Br	DMF, none	10/25° 2/35°	trans,trans (100)	70, 100
2. cis, R = CH_3; X = Br	Ether, Ph_3P	12	t,t (19); c,t (81); c,c (0)	53, 100
3. trans, R = CH_3; X = Br	Ether, $(n\text{-}Bu)_3P$	5	t,t, (94); c,t (6); c,c (0)	58, 90
4. trans, R = CH_3; X = Br	Ether, Ph_3P	12	t,t (84); c,t (16); c,c (0)	51, 100
5. trans, R = CH_3; X = Br	DMF, none	22	t,t (72); c,t (28); c,c (0)	48, 100

[a] Approximately 2.0 mol [per mole of $Ni(COD)_2$] of an additional ligand was present where indicated. [b] The yields refer to the combined yield of all isomers and are based on quantitative glpc analyses using an internal standard with commercial samples of the products for calibration.

Table II. Coupling of Haloacrylate Esters with Bis(1,5-cyclooctadiene)nickel(0)

Alkenyl halide	Solvent, ligand[a]	Duration, hr	Product[b]	Yield,[c] conversion (%)
1. $CH_2{=}CBrCO_2CH_3$	Ether, none	17	$CH_3OCOC({=}CH_2)C({=}CH_2)CO_2CH_3$	12, 85
2. $CH_2{=}CBrCO_2CH_3$	Ether, Ph_3P	4.5	Same as (1)	89, 100
3. $CH_2{=}CClCO_2CH_3$	Ether, Ph_3P	4.5	Same as (1)	67, 75
4. $CH_2{=}CClCO_2CH_3$	Ether, Ph_3P	9.0	Same as (1)	69, 100
5. *cis*-$BrCH{=}CHCO_2CH_3$	Ether, Ph_3P	15	$CH_3OCOCH{=}CHCH{=}CHCO_2CH_3$ (cis,cis)	99, 100
6. *trans*-$BrCH{=}CHCO_2CH_3$	Ether, $(n\text{-}Bu)_3P$	5.0	$CH_3OCOCH{=}CHCH{=}CHCO_2CH_3$ (trans,trans)	92 (73[d]), 100
7. *trans*-$BrCH{=}CHCO_2CH_2Ph$	DMF, none	18	$PhCH_2OCOCH{=}CHCH{=}CHCO_2CH_2Ph$ (trans,trans)	90 (84[d]), 100

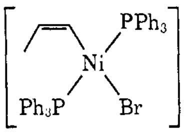
[a] Approximately 2.0 mol [per mole of $Ni(COD)_2$] of an additional ligand was present where indicated. [b] See the discussion for confirmation of product structure and methods of determining yields. [c] The yields are from quantitative ¹H nmr analysis. [d] This yield is based on isolated material with appropriate spectral properties.

The carboalkoxy groups accelerate the rate of coupling and provide no important side reactions even in the preparation of 2,3-dicarbomethoxy-1,3-butadiene, a very sensitive product which polymerizes rapidly in the absence of inhibitors. The order of halogen reactivity is iodo > bromo > chloro, but even 2-chloroacrylates are reactive enough to couple smoothly at 25°.

In general, a donor ligand is necessary to promote smooth coupling, although even weak donors such as dimethylformamide are effective when used as the solvent. Acetonitrile, ether, and *n*-pentane as solvents allow only very slow reaction of alkenyl halides with $Ni(COD)_2$ at 25°, and at elevated temperatures the nickel reagent decomposes to nickel metal without promoting coupling. Ether is a useful solvent in the presence of 2 mol of triphenylphosphine (or tri-*n*-butylphosphine) per mole of $Ni(COD)_2$ (Tables I and II).

Synthetic applications of the intermolecular coupling reaction are limited to symmetrical products, but great potential exists for the intramolecular coupling (cyclization) of alkenyl halides in the synthesis of complex molecules where mild conditions and selectivity are demanded by an array of sensitive functional groups.[14] A very simple example of intramolecular coupling is the reaction of *cis,cis*-1,6-diiodo-1,5-hexadiene[15] with $Ni(COD)_2$ in dimethylformamide to produce 1,3-cyclohexadiene in 67% yield (quantitative glpc analysis). Under the same conditions, *trans,trans*-1,6-dibromo-1,5-hexadiene[16] was completely converted to nonvolatile products.

A reasonable mechanism for the nickel-promoted coupling of alkenyl halides would involve initial oxidative addition to give an alkenylnickel(II) halide (*e.g.*, **1**



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from *cis*-1-bromopropene), an intermediate parallel with those in copper- and silver-promoted couplings.[10] However, the mixture of isomers obtained in certain of the coupling reactions (Table I) is in surprising contrast with the high stereospecificity observed using copper and silver.[10] Clearly, the isomerization of the double bond could occur during formation of **1** or during subsequent steps leading to the coupling product. In an attempt to generate **1** by an alternate and stereospecific route and to examine the configurations of the resulting dienes, *cis*-propenyllithium[10] was mixed with bis(triphenylphosphine)nickel(II) dibromide[17] in ether at 0°. The mixture of 2,4-hexadienes produced after 4.0 hr at 25° consisted of cis,cis (68%), cis,trans (26%), and trans,trans (6%). The direct coupling of *cis*-bromopropene under parallel conditions (entry 2, Table I) is much less stereospecific; the mixture of products is consistent with partial inversion of configuration during oxidative addition.

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Further work is under way to delineate the mechanism of the intermolecular coupling reaction and to more fully investigate nickel-promoted cyclization reactions.

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Studies of Cation Hydration

Sir:

Cation-water interactions have been of interest to chemists for many years but only relatively recently have accurate experimental data[1] been available on the energetics of such processes. There has been considerable interest in predicting the structure of ion hydrates using theoretical molecular orbital techniques, and a large number of semiempirical[2] and *ab initio*[3] calculations have been reported in the literature.

We have been carrying out high-accuracy *ab initio* molecular orbital studies on cation hydrates and now have a number of results which may be of general interest.

In Table I, we have calculated the energy of complex formation and minimum energy M-O distance for Li^+, Be^{2+}, Na^+, Mg^{2+}, Al^{3+}, K^+, and Ca^{2+} monohydrate.[4] These complexes have a C_{2v} structure, with the metal along the line bisecting the oxygen lone pairs. A simple classical ion-dipole model would predict this geometry but would not give any information about the minimum energy M–O distance or the ΔE of complex formation. Our calculations on Li^+, Na^+, and K^+ hydrate are in very good agreement with experiment and with similar SCF studies,[3a] so we have some confidence in our prediction of the energetics and structure for the other cations.

Table I. Cation–Water Interactions

M	$-\Delta E_{\text{exptl}}$, kcal/mol	$-\Delta E_{\text{calcd}}$, kcal/mol	R, Å
Li^+	34	37	1.85
Be^{2+}		140	1.50
Na^+	24	27	2.20
Mg^{2+}		80	1.95
Al^{3+}		180	1.75
K^+	18	18	2.65
Ca^{2+}		53	2.40

Our long-term interests are in larger ion–water clusters which might approximate ions in liquid water. The many-body interaction ideas discussed by Hankins, *et al.*,[5] in their studies of water dimer and trimer are very useful in this regard. These ideas are summarized in eq 1. In a collection of n particles at positions x_1,

$$E(x_1,x_2,\ldots,x_n) = \sum_{i=1}^{n} E(x_i) + \sum_{i>j=1}^{n} E^{(2)}(x_i,x_j) + \sum_{i>j>k=1}^{n} E^{(3)}(x_i,x_j,x_k) + \sum_{i>j>k>l} E^{(4)}(x_i,x_j,x_k,x_l) + \ldots \qquad (1)$$

$x_2, \ldots, x_n$, the total energy can be represented in terms of the energies of the individual particles, $E^{(1)}$, interacting pairs of particles $E^{(2)}$, triplets $E^{(3)}$, etc. If we can show by our *ab initio* calculations that terms such as $E^{(4)}$ are small for geometries of interest, we can determine the energies of essentially infinite clusters of molecules using the results of three-body potential surface studies which determine the various $E^{(1)}$, $E^{(2)}$, and $E^{(3)}$ terms. We have carried out SCF calculations on Be^{2+} and three water molecules, using a slightly smaller basis set[6] than in the cation–single water studies, to determine the magnitude of the $E^{(2)}$, $E^{(3)}$, and $E^{(4)}$ terms for a typical configuration.[7] All Be–O distances were 1.5 Å (that found in the single $Be-H_2O$ complex); two waters were placed along the x and $-x$ axes, with hydrogens in the xy plane, the third was along the z axis, with hydrogens in the xz plane. The results of carrying out SCF calculations on one, two, three, and four molecule combinations are presented in Table II. As one can see, the size of the three water interaction and four-body interaction is quite small compared to the other terms and gives one confidence that large ion hydrate clusters can be studied by only carrying out computations on one, two, and three molecule clusters. For example, the relative energy of tetrahedral and octahedral coordination of an ion hydrate can be determined by calculating the following potential surfaces as a function of R(M–O): (1) the ion–single water surface; (2) the ion, one water along the x axis, the other along the $-x$; (3) the ion, one water along the x axis, the other along the y axis; and finally (4) the ion, one water along the x axis and the other approaching at a tetrahedral angle from the x axis. Such studies are now under way in our laboratory.

A final subject of interest is the effect of an ion on the hydrogen bonding ability of a water molecule nearby. We have begun this study using Li^+ as our representative cation, placing one water in the optimum geometry for

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(4) The basis sets used in these calculations were as follows: for water, Dunning's optimum contraction [*J. Chem. Phys.*, **53**, 2833 (1970)] of Huzinaga's 9s/5p → 4s/2p augmented by a set of d polarization functions on oxygen and a set of p functions on hydrogens (see ref 5 for the exponents); for Li and Be, a 9s/3p set contracted to 4s/2p (see P. A. Kollman, *et al.*, *J. Amer. Chem. Soc.*, in press, for details); for Na, Mg, and Al, Huzinaga's [*J. Chem. Phys.*, **50**, 1371 (1969)] 11s/7p contracted to 6s/4p was used; and for K^+ and Ca^{2+} Wachter's 14s/9p → 8s/6p [*ibid.*, **52**, 1033 (1970)] basis was used.

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(6) No d functions on oxygen or p on hydrogens were included in the $Be-3H_2O$ calculations.

(7) Obviously, the two-, three-, and four-body energies are geometry dependent. Our Be–O distance is shorter than the one expected for the higher hydrates, so the three- and four-body terms are larger in magnitude than they would be at the minimum energy configuration. Thus, our calculations give "upper bounds" for the magnitude of these higher order energy terms.