δ 4.94, 5.05, and 6.22 for free butadiene), suggesting a very asymmetric mode of binding to the dimetal center.

The butadiene ligand in I is labile. If the reaction flask (after complete development of the blue-purple color but before crystal growth) is placed under vacuum for a few seconds, the blue-purple color becomes blacker, and if crystals are grown at this point, a significant number of bright yellow crystals of $W_2(OCH_2CMe_3)_6$ and orange crystals of $W_2(OCH_2CMe_3)_6(py)_2$ form along with the blue-black needles of I. Furthermore, if pure I is dissolved in $C_6D_6$ under a nitrogen atmosphere in an NMR tube fitted with a septum cap, a black solution results, and $^1H$ NMR resonances for free butadiene and $W_2(OCH_2CMe_3)_6$ can be seen along with signals attributable to I. On the basis of the relative intensities of these signals, ignoring that the free butadiene may not be completely dissolved in the $C_6D_6$ solution, the complex appears to be roughly 90% dissociated in solution.

An ORTEP drawing of the central $W_2O_6N(C_4H_6)$ moiety of the $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(C_4H_6)$ molecule is shown in Figure 1.[8] The core structure can be viewed in terms of a confacial bioctahedron. The octahedral geometry is clearly appropriate for W(1). For W(2) the $\eta^4$-$C_4H_6$ ligand would have to occupy cis sites. An alternative geometric description for W(2) might be based on a four-legged stool capped by the $\eta^4$-$C_4H_6$ ligand. The bridging carbon atom, C(10), is slightly closer to W(2) than to W(1) (cf. W(2)–C(10) = 2.32 (1) Å vs W(1)–C(10) = 2.43 (1) Å. However, the significance of the W(1)–C(10) bond is evident from its trans influence, which produces a notably long W(1)–O(5) bond in relation to the other terminal W–O alkoxide bonds. Also of note are the metric parameters associated with the W(2)–$\eta^4$-$C_4$ moiety. The C(10)–C(11) distance appears longer (1.457 (15) Å) compared to the two other C–C distances (1.40 (1) Å (av)). Collectively the structural data are consistent with the existence of a W–W double bond, $(W{=}W)^{8+}$, wherein the butadiene is counted as the sum of a bridging alkyl and a π-allyl ligand. The $^{13}C$ NMR data are also interpretable in this way. Specifically, the high-field carbon resonance of the $C_4H_6$ ligand occurs at δ 44.8 and shows coupling to two inequivalent hydrogen atoms ($J_{^{13}C\text{-}^1H}$ = 149 and 124 Hz) as well as coupling to $^{183}W$ ($J_{^{183}W\text{-}^{13}C} \approx 34$ Hz, $I$ = 25%), indicative of the bridging carbon C(10). The other carbon resonances are further downfield and show larger values of $^1J_{^{13}C\text{-}^1H}$ and smaller values of $J_{^{183}W\text{-}^{13}C}$: δ 66.2 (t, $J_{^{13}C\text{-}^1H}$ = 157 Hz, $J_{^{183}W\text{-}^{13}C} \approx 24$ Hz, $I$ = 14%); δ 102.9 (d, $J_{^{13}C\text{-}^1H}$ = 164 Hz); δ 111.8 (d, $J_{^{13}C\text{-}^1H}$ = 174 Hz).[9]

Greater insight into the bonding in I might be gained from MO calculations, and this together with studies of the reactivity of I are planned.

**Acknowledgment.** We thank the Department of Energy, Office of Basic Sciences, Chemical Division, for support.

**Supplementary Material Available:** Listings of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances and angles, and least-squares planes and stereoviews and VERSORT drawings giving the atom-numbering scheme for I (10 pages); a listing of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

(8) Crystals of I suitable for X-ray analysis were grown from the reaction of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and 1,3-butadiene (1 atm) in toluene at −20 °C. Crystal data at −173 °C: $a$ = 13.006 (2) Å, $b$ = 17.583 (2) Å, $c$ = 10.351 (2) Å, α = 98.61 (1)°, β = 104.13 (1)°, γ = 80.60 (1)°, $Z$ = 2, $d_{calcd}$ = 1.511 g cm$^{-3}$, and space group $P\bar{1}$. Of the 10 405 reflections collected (Mo Kα, 6° ≤ 2θ ≤ 45°) 8858 were unique and the 5514 having $F > 3\sigma(F)$ were used in the refinement. The tungsten, oxygen, carbon, and nitrogen atoms were refined with anisotropic thermal parameters. Several of the hydrogen atoms were located, including those on the bridging carbon atom, C(10). The remainder were included in calculated positions. It should be noted that there are short (2.5–2.6 Å) interatomic distances involving W(1) and the H atoms on C(10). The final residuals are $R(F)$ = 0.0418 and $R_w(F)$ = 0.0430.

(9) NMR data reported herein were obtained from toluene-$d_8$ solutions at 22 °C on a Varian 300 spectrometer.

# Enantioselective Allylation of Grignard Reagents with Nickel–Diphosphine Catalysts

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*Summary:* A highly enantioselective (up to 94% ee) alkylation of cyclic allyl phenyl ethers with Grignard reagents catalyzed by nickel complexes of $C_2$-symmetric chiral diphosphine ligands is described; for the ligands related to (+)-(*R*,*R*)-cyclopentane-1,2-diylbis(diphenylphosphine) the enantioselectivity of the reaction appears to be influenced much more by steric than by electronic factors, which, however, strongly affect the chemoselectivity of the process.

The enantioselective allylation reactions of organometallic derivatives of the main-group elements (hard nucleophiles) such as Grignard reagents have been much less investigated than those of stabilized nucleophiles (soft nucleophiles).[1,2] Synthetic, stereochemical, and mecha-

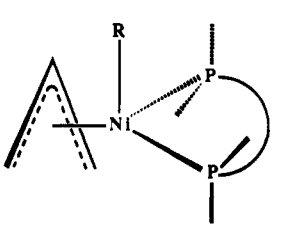


**Figure 1.**

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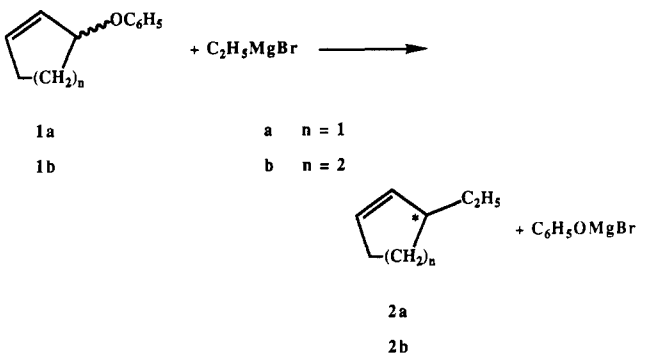
**Table I. Cross-Coupling Reactions of Cyclopent-1-en-3-yl Phenyl Ether (1a) and of Cyclohex-1-en-3-yl Phenyl Ether (1b) with Ethylmagnesium Bromide[a]**

| | 1a | | | 1b | | |
|---|---|---|---|---|---|---|
| catalyst precursor | conversn, % | yield, % | enantioselectivity *S*/*R* | conversn, % | yield, % | enantioselectivity *S*/*R* |
| **3a** | ~100 | 92 | 91.4/8.6 | ~100 | 99 | 87.3/12.7 |
| **3b** | ~100 | 40[b] | 91.6/8.4 | 7[c] | 7 | 84.7/15.3 |
| **3c** | 92 | 8[b] | 70.1/29.9 | 51 | 23 | 50.8/49.2 |
| **4a** | ~100 | 90 | 96.8/3.2 | 93 | 84 | 91.7/8.3 |
| **4b** | ~100 | 91 | 90.3/9.7 | 88 | 71 | 82.9/17.1 |
| **4c** | 99 | 67 | 8.9/91.1 | 31 | 11 | 17.6/82.4 |
| **5** | 99 | 5[b] | 49.0/51.0 | 82[c] | 27 | 50.0/50.0 |

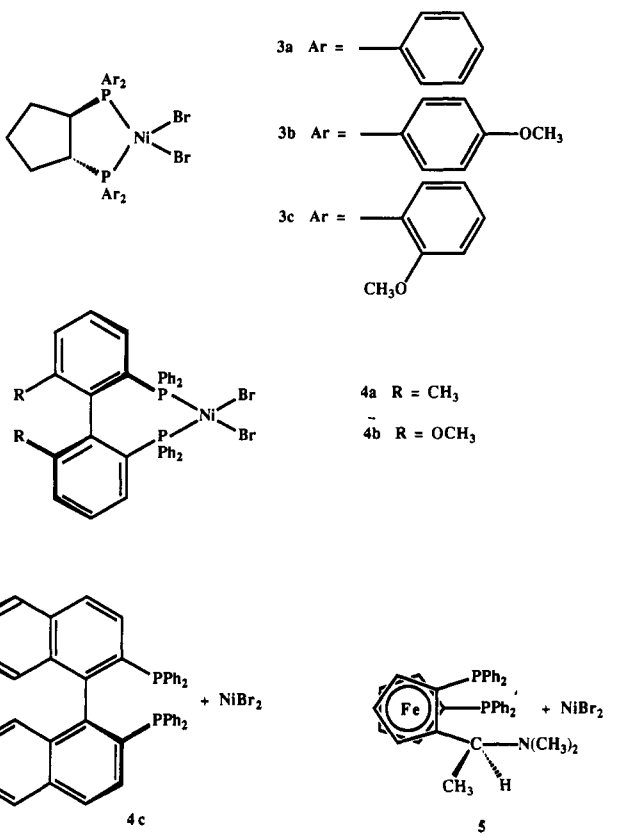
[a] Reaction conditions: room temperature, 24 h (unless otherwise stated), 4 mmol ether, 5 mmol Grignard reagent, 0.02 mmol of catalyst precursor in 10 mL of diethyl ether. [b] Most of the substrate is rearranged to *o*-(cyclopent-2-en-1-yl)phenol. [c] After 96 h.

**Scheme I**




nistic studies have shown that the former reaction is effectively catalyzed by nickel–diphosphine complexes[3] and have inferred that attack of the nucleophile at the coordinated allyl moiety is mediated by the metal[4] (Figure 1) and that reductive elimination of the coupling product takes place at the level of the $\eta^3$ intermediate.[5] The structure of the invoked intermediate suggests that the asymmetric bias by the chiral ligand should be more effective than in the case in which the attack of the nucleophile is external. Furthermore, the use of ligands having $C_2$ symmetry should also be beneficial due to the reduced number of possible intermediates,[6] particularly when the rigidity of the carbon skeleton joining the two phosphorus atoms of the ligand is able to bring about a conformationally rigid array of the phenyl substituents.[7,8]

**Chart I**




For allylic intermediates having symmetric allyl moieties (e.g., of the cyclic type) asymmetric induction should be determined by diastereotopic selection[9] of the attacking group on either allylic terminus and, therefore, possibly influenced by the electronic properties of the ligand. However, no information on this aspect is available in the literature.

We report herein that, in fact, the use of rigid $C_2$-symmetric chiral diphosphine ligands brings about high enantioselectivity (optical yield up to ~94%) in the alkylation of cyclic phenyl ethers (Scheme I) and that the asymmetric induction for this reaction seems to be more sensitive to steric than to electronic factors. The chiral catalyst precursors used were the nickel dibromide complexes of (+)-(*R*,*R*)-cyclopentane-1,2-diylbis(diphenylphosphine),[10] (+)-*trans*-cyclopentane-1,2-diylbis(bis(*p*-

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methoxyphenyl)phosphine), and (+)-*trans*-cyclopentane-1,2-diylbis(bis(*o*-methoxyphenyl)phosphine)[11] (**3a–c**, respectively) as well as of the atropoisomeric (*R*)-(6,6′-dimethylbiphenyl-2,2′-diyl)bis(diphenylphosphine) (Biphemp)[12] and of (*R*)-(6,6′-dimethoxybiphenyl-2,2′-diyl)-bis(diphenylphosphine) (MeO-Biphep)[13] (**4a,b**, respectively; Chart I). The results are summarized in Table I together with those obtained with (*S*)-Binap/$NiBr_2$[14] (**4c**) and (*S,R*)-BPFFA/$NiBr_2$[15] (**5**) as the catalyst precursor. The enantioselectivity of the reaction has been determined through gas chromatography using a 50-m enantiomer differentiating capillary column[16] (Lipodex C) and is expressed in Table I by the measured molar ratio between the two enantiomers.

Catalyst **3b** is much less reactive than **3a**; due to this lower reactivity in the case of **1a** most of the substrate is rearranged to *o*-(cyclopent-2-en-1-yl)phenol. The enantioselectivities displayed by the two catalytic systems are equal when **1a** is the substrate and quite similar for **1b**. Also, catalyst **3c** is much less active than **3a**; in the case of **1b** extensive elimination takes place at the expense of alkylation. Furthermore, **3c** causes a rather low enantioselectivity, which is very close to zero for **1b**, in sharp contrast to the case for **3b**. Catalysts **4a,b** show very similar reactivities, the extent of rearrangement for **1a** and the extent of elimination for both substrates being rather low. **4a**, however, is significantly more enantioselective than **4b**. Catalyst **4c**, which contains the atropoisomeric ligand Binap (structurally related to the Biphemp ligand), is substantially less enantioselective than **4a**. Furthermore, the catalyst precursor **5**, which contains a chiral phosphine successfully used in other coupling reactions,[17] in addition to being of very low reactivity, gives practically no enantioselectivity in the reactions examined. It seems worthwhile to observe that the enantiomeric excess reached in the formation of 3-ethylcyclopent-1-ene with **4a** as the catalyst precursor is the largest ever observed in enantioselective catalytic reactions leading to the formation of purely aliphatic hydrocarbons.

The present results show some discrepancies as far as the effect of the substitution on the chemo- and enantioselectivity of the reaction is concerned. In fact, if we consider the series of catalysts **3a–c**, we can deduce that their effectiveness is reduced by increasing the basicity of the ligand. A similar modification (even if not exactly the same) on going from **4a** to **4b** seems to have almost no effect with respect to activity and chemoselectivity. This substitution does, however, appreciably influence the enantioselectivity; in contrast, **3a,b** show no enantioselectivity differences. The very low enantioselectivity observed for **3c** with respect to that for **3a,b** is in keeping with a larger effect of steric factors with respect to electronic factors in the sterid discrimination phenomena which take place in this allylation reaction. Due to the possibility of interaction of the *o*-methoxy group with the metal in the catalytic species derived from **3c**, a change in mechanism cannot be completely excluded. The homochirality of the products obtained with the catalysts having ligands with a center of chirality (**3a,b**) and those having ligands with an axis of chirality (**4a,b**) is probably a consequence of the homochiral λ conformation of the chelate rings, shown in the crystal structure determination of complexes containing these ligands.[10,12,13] A homochiral conformation of the chelate ring is expected to impose a homochiral helicity to the two aryl substituents on each phosphorus atom[18] and therefore to bring about prevalence of the same enantiomeric product. The results obtained with **4c** are also in keeping with this interpretation.[12] The lower enantioselectivity displayed by this ligand with respect to that of **4a** could be due to the differences in the conformation of the diphenylphosphino substituents, which were already recognized for complexes of the two ligands.[12] The fact that the enantioselectivity in the alkylation of **1a** is always larger than that observed in the alkylation of **1b** is probably a consequence of a more rigid allyl moiety for **1a** than for **1b** in the intermediate of Figure 1.

The reported results show that it is possible to prepare cyclic olefins with very high enantiomeric excesses. The synthesis of new optically active polymers which might have interesting properties therefore appears possible.[19]

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