formed complexes unambiguously indicated the allyl groups to be bound to Ni solely in an η^3 -fashion. The ¹H spectra of 4c exhibited only one resonance for the syn and anti protons of the allylic terminal, suggesting syn-anti proton exchange via a short-lived η^1 -allylnickel complex 5 rapid on the NMR time scale.^{13b} The four allylic hydrogens of 4b also appeared as only



one resonance,13b presumably attributable to both rapid syn-anti proton exchange and rapid site exchange of the two allylic termini.^{13c} The latter process is most probably associated with the well-known intramolecular rearrangement of d⁸, 5-coordinated complexes.¹⁵ The occurrence of this rearrangement in 4 manifested itself also in the coalescence of the two ³¹P resonances of 4b and 4c at the higher temperatures.^{13c} This coalescence cannot be attributable to intermolecular phosphine exchange nor to occurrence of a monodentate dppen ligand, since the spin couplings between some allyl ligand hydrogens and two equivalent ³¹P nuclei were observed in the higher temperature ¹H NMR spectra.

On raising the temperature of the solution containing 4 to above -20 °C, rapid, nearly quantitative formation of the pentafluoroallylbenzenes occurred. The kinetics of this process for 4a and 4b were followed by ¹H NMR spectroscopy at -19 to 10 °C to show clean first-order dependence of the rate on the amount of the complex, with k_1^{16} being unvaried on changing the amount of added diphosphine (1-2 equiv) and PPh₃ (0-4 equiv). Of particular note is the great difference between the activation energy (ΔH^*) for the reductive elimination from 18-electron complex 4b $(59 \pm 4 \text{ kJ/mol})^{17}$ and that from 16-electron complex 1b (122) \pm 10 kJ/mol).¹⁷ The ratio of the rate constants at -10 °C for 4b versus 1b (9 \times 10⁻⁹ h⁻¹, extrapolated) amounts to 10⁸.

A possibility that the short-lived species 5 is responsible for the enhanced reactivity of 4 appears less likely¹⁸ for the following reasons. Provided that the relative reactivity of 16-electron η^3 -allyl and 16-electron η^1 -allyl forms described in the palladium complexes (2 > 3) also applies in the case of the nickel complexes 1 and 5, the order of the reactivity is deduced to be $4 \gg 1 > 5$. The considerably low reactivity of 5 is also consistent with the slow rate of the reductive elimination of a related complex, Ni- $(CH_3)(C_6F_5)(dppen)^{14,19}$ ($\Delta H^{\ddagger} = 98 \pm 2 \text{ kJ/mol}$), since the competitive experiments employing η^1 -allyl(methyl)metal com-plexes of Pt^{IV} and Au^{III} suggested²⁰ the reactivity of the η^1 -allyl

(17) ΔS^* (J/K mol) is as follows: 4b, -88 ± 35 (-19 °C); 1b, 3 ± 40 (101 °C). The large negative value in the former case might be attributed, in part, to freezing of fluxional movements in 4 at the transition state for the C-C

coupling. (18) Participation into the rapid C-C coupling of alternative four-coordinated η^1 -allyl species having a structure considerably distorted from a regular square-planar geometry, though no precedence of this type of organonickel complexes has been known, remains to receive further experimental and theoretical scrutiny.

(19) Prepared from *trans*-Ni(CH₃)(C₆F₅)(PPh₃)₂ and dppen in tetra-hydrofuran.^{7b} Rate constant (h⁻¹) in benzene is 5.4 (90 °C), 2.4 (82 °C), and Notion and the second state of added PPh₃ (0-5 equiv) and dppen (3 equiv). $\Delta S^* = -32 \pm 15 \text{ J/K mol.}$ (20) (a) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E.; Lavington, S.

W. J. Chem. Soc., Dalton Trans. 1974, 1613-1618. (b) Ozaki, S.; Komiya, S. Abstracts Papers 56th Annual Meeting Chem. Soc. Jpn., Tokyo, 1988; Abstr. no. 31VB26. We are indebted to Professor Komiya for informing us of this and related unpublished results. group with respect to the reductive elimination to be comparable to that of the methyl. The coupling from 18-electron η^1 -allylnickel, Ni(η^1 -allyl)(Ar)(PR₃)₃ appears also unlikely in view of the rate from 4 being independent of the added phosphine. Efforts are under way to gain insight into structures of 18-electron η^3 -allylnickel complexes and their relevance to the low barrier exit^{6b} to the C-C coupling step.

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Optically Active 2-Ethenyl-1,3-dioxolanones as 3-Carbon Synthons. Allylnickel Derivatives as **Homoenolate Equivalents**

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The development of reversed polarity synthons¹ and new methods for organic stereocontrol² are important concerns of current synthetic organic research. We report herein (1) a new, allylnickel approach to homoenolate equivalent chemistry³ and (2) the coupling of this methodology with a new enantioselective aldol equivalent reaction⁴ as part of a new approach to 3-carbon synthon stereocontrol.

As detailed elsewhere,⁵ optically active 2-ethenyl-1,3-dioxolan-4-ones are available in a single step by condensation of acrolein with optically active (R)- or (S)-2-hydroxy acids (eq 1, $R = Me, Ph, c-C_6H_{11}).$

$$\sum_{0}^{R} \sum_{0H}^{DH} + \sum_{0}^{H} \sum_{H^{+} \times C_{6}H_{6}}^{-H_{2}0} \qquad R \underbrace{}_{0}^{C} \sum_{0}^{H} (1)$$

In other work, we have shown that these compounds undergo Lewis acid⁶ and palladium⁷-catalyzed conjugate addition reactions with organic nucleophiles. We now report that the metal-centered nucleophile, bis(1,5-cyclooctadiene)nickel(0),⁸ reacts with

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(5) A procedure similar to that employed in the preparation of the 5,5-pentamethylene analogue by Soulier et al.^{5a} was followed. In all cases, the 2-ethenyl-1,3-dioxolanone products are isolated as 2:1 cis/trans mixtures suitable for stereoselective applications. (a) Farines, M.; Soulier, J. Bull. Soc. Chim. Fr. 1970, 332. (b) Friebe, T. L.; Krysan, D. J.; Mackenzie, P. B., manuscript in preparation

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Table I. Halocarbon Coupling Reactions with Compound 2

entry	halocarbon	product	yield ^a (%)	
1	bromobenzene	3a	77 (96)	
2	1-bromoethene	3b	79 (97)	
3	(E)-1-bromo-2-phenylethene	3c ^b	77 (96)	
4	(Z)-1-bromo-2-phenylethene	3d ^c	75 (90)	
5	1-iodopropane	3e	82 (94)	
6	2-iodopropane	3f	72 (93)	

a Isolated yield of purified product, isolated crude yield in parentheses. ^b Product >95% (E)-styryl derivative. ^c Product 83:17 Z/Emixture of styryl double bond isomers.

(5R)-5-cyclohexyl-2-ethenyl-1,3-dioxolan-4-one to yield the allylnickel complex 1 (eq 2), which upon in situ treatment with



chlorotrimethylsilane gives the corresponding silylated derivative 2.9 ¹H NMR spectroscopy indicates that compound 2 exists in solution as a mixture of two diastereomers (8:1 ratio in C_6D_6). The major diastereomer is assigned the syn allyl stereochemistry based on the observation of a 9.6 Hz C(1)H-C(2)H allyl proton coupling constant;¹⁰ the chirality at $C(1)^{11}$ of the major diastereomer and the stereochemistry of the minor diastereomer have not been determined.

In the presence of light and a coordinating solvent, compound 2 undergoes efficient homoenolate coupling reactions with halocarbons to give the corresponding (E)-enol ethers (eq 3).¹² The



(9) Preparation of 1 and in situ conversion to 2: (All manipulations were carried out under a nitrogen atmosphere with purified, deoxygenated solvents.) Bis(1,5-cyclooctadiene)nickel(0) (15.0 g, 0.0545 mol, 1.00 equiv) was suspended in tetrahydrofuran (210 mL) and treated with a degassed solution of (5R)-5-cyclohexyl-2-ethenyl-1,3-dioxolan-4-one (12.8 g, 0.0655 mol, 1.20 equiv, 2:1 cis/trans) in tetrahydrofuran (30 mL). The mixture was stirred until all of the bis(1,5-cyclooctadiene)nickel(0) had dissolved (10 min) following which time a rust-colored precipitate began to form. After 3 h, the supernatant was removed via cannula, and the remaining solid was washed with tetrahydrofuran (2 \times 60 mL) and with dichloromethane (2 \times 40 mL) to give compound 1 as a rust-colored microcrystalline solid. Suspension of the solid in dichloromethane (90 mL) and treatment with chlorotrimethylsilane a burgundy red solution. This was stirred for 30 min after which the volatiles were removed under vacuum (0.1 Torr) to give a red oil. Crystallization from diethyl ether (50 mL) at -25 °C gave dark red crystals of 2 (two crops, 15.4 g, 77.8% overall yield from bis(1,5-cyclooctadiene)nickel(0)). Anal. (C_{28} - $H_{50}Cl_2Ni_2O_6Si_2$) C, H, Cl.

(10) For a discussion of the relationship of allyl proton coupling constants to syn/anti stereochemistry, see: Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel. Volume 1*; Academic Press: New York, 1974. (11) (a) C(1) refers to the oxygen-substituted allyl carbon and may possess

either syn-1S or syn-1R stereochemistry. Although the solution stereochemistry has not been assigned, the solid-state structure of compound **2** has been determined by X-ray crystallography.^{11b} Only one diastereomer is observed. evincing the syn-1S configuration. Experiments to relate the solid state and solution structures are in progress. (b) Sabat, M.; Krysan, D. J.; Mackenzie, P. B., manuscript in preparation.

(12) Typical procedure: Compound 2 (3.50 g, 0.00963 mol, 1.00 equiv) was dissolved in benzene (35 mL) and treated with dimethylformamide (7.46 mL) and 1-iodopropane (4.70 mL, 0.0482 mol, 5.00 equiv). Upon irradiation with a sunlamp (GE 275W Model RSW) for 2.5 h at 10 °C, the initially burgundy red solution became emerald green and deposited a blue-green powder. The mixture was subsequently stirred 3 h then transferred to a larger vessel via cannula and diluted with pentane (140 mL) to complete precipitation of the nickel halide. After 4 h of stirring, the supernatant was separated from the nickel halide precipitate via filtration through a filter paper tipped cannula. The near colorless filtrate was evaporated under vacuum (0.1 Torr) to give **3a** as a pale yellow oil (2.84 g, 94.4%, E/Z = 9:1). Vacuum distillation (bp 70–75 °C, 0.002 Torr) gave analytically pure **3e** (2.47 g, 82%). Anal. (C17H32O3Si) C, H.

reactions are highly regioselective (>95%) and stereoselective $(E/Z = 9:1 \text{ before enrichment})^{.13}$ Treatment of the enol ether products with aqueous acid yields the corresponding aldehydes with loss of the optically active auxiliary.14

Successful reactions are observed with a broad range of halocarbons, including bromobenzene, bromoalkene, and primary and secondary iodoalkanes (Table I).¹⁵ Tertiary alkyl and allylic halides also couple; however, the yields are depressed in these cases (ca. 30% for 2-iodo-2-methylpropane and 3-chloro-1-propene). The reactions of isomerically pure (E)- and (Z)-2-bromo-1phenylethenes (entries 3 and 4) show that the reactions proceed with high but not complete retention of bromoalkene double bond configuration. These results closely parallel those of Corey et al.¹⁶ and Hegedus et al.¹⁷ in their pioneering studies of the coupling reactions of simple allylnickel halide complexes with halocarbons.¹⁸ On the basis of this analogy, we assume a similar Ni(I)/Ni(III) radical chain mechanism¹⁹ to be operative in these reactions.

In addition to being of interest as a mild and versatile new homoenolate equivalent methodology, the allylnickel chemistry is of interest as an entry to enantioselective enol functionalization chemistry. As exemplified below, the optically active enol ether products of homoenolate coupling undergo novel aldol equivalent reactions with acetals (eq 4).²⁰



The observation of synthetically useful levels of diastereoselectivity in these reactions suggests that similarly successful reactions will also be possible with other electrophiles. We note further that the optically active dioxolanone products of these reactions are themselves potential starting materials for diastereoselective acetal carbon substitution reactions.²¹ Considered together, these reactions constitute a promising new approach to 3-carbon synthon stereocontrol.

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Supplementary Material Available: Spectroscopic and analytical data for all new compounds (3 pages). Ordering information is given on any current masthead page.

(13) The end ethers are subject to enrichment to higher E/Z ratios by fractional crystallization (e.g., for 3a, E/Z > 99:1 after two crystallizations from pentane) or by fractional distillation (e.g., for 3e, E/Z = 21:1 after

distillation through a 10-cm Vigreux column). (14) 1 N HCl/THF 1:1, 8 h, 25 °C, Et₂O/H₂O extraction, 95%. (15) Satisfactory ¹H and ¹³C NMR spectra and elemental analyses have been obtained for all products. The optical purity of 3e has been established as >95% by aldol equivalent condensation with benzaldehyde dimethyl acetal (cf. eq 4) and subsequent derivatization to (2R)-2-benzylhexanoic acid.²⁰

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