

lar models show that in IVa the metal ion centers can approach more closely than they do in IIa. We suggest that in IVa electron transfer is by an "outer-sphere" mechanism, in the sense that transfer does not make use of the bridging group, whereas in IIa the bridging group is implicated. This suggestion is supported by the fact that for IVa the rate is very sensitive to $[H^+]$ whereas, for IIa (and for IIIa), it is not. An important path for the polarographic reduction of acetatopentamminecobalt(III) involves H^+ ;¹⁴ redox reactions at a mercury electrode in many respects have the characteristics of outer-sphere electron transfer processes in homogeneous systems.¹⁵ In any case, the utility of the approach to the study of both inner and outer-sphere electron transfer appears to be demonstrated even in the limited series described.

Chloride ion enhances the rates for IIa, IIIa, and IVa, and more for IVa than it does for IIa or IIIa. The $Ru^{II}-OH_2$ position is labile enough so that a path for the overall reaction can involve $Ru^{II}-Cl$ as reactant. The higher sensitivity of IVa compared to IIa and IIIa to chloride ion may indicate that an additional component contributes to the effect in IVa, the chloride ion in this case affecting the rate even short of entering the coordination sphere of $Ru(II)$.

It should be pointed out that the effect of the product $Ru(III)$ reacting with the Co^{III} -ligand- Ru^{II} species can be exploited in increasing the half-life for intramolecular electron transfer. By adding the $Ru(III)$ product in known amount and by determining the equilibrium constant for reaction I, the half-life in the presence of the product can be used to calculate the intrinsic rate. An effort to take advantage of the reaction in question in compound I failed because of complications arising from sulfate complexation. The effect, however, is easy to observe qualitatively in any of the systems.

Enough has been done on the chemistry of $Co(III)$ and $Ru(II)$ to make it certain that bridging groups in great diversity can be used in extending the studies. For $Co(III)$, besides carboxyl as the lead-in group, nitrile, imine, and saturated nitrogen can be used; for Ru , in addition to the last three, also donor sulfur. Thus, a systematic study of rates of intramolecular transfer as a function of the separation of the metal atoms and of the electronic properties of the bridging groups is possible using the approach applied in the four systems studied.

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Stephan S. Isied, Henry Taube*

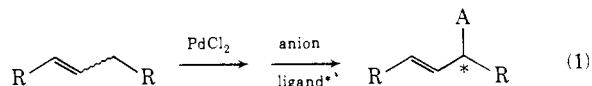
Department of Chemistry, Stanford University
Stanford, California 94305

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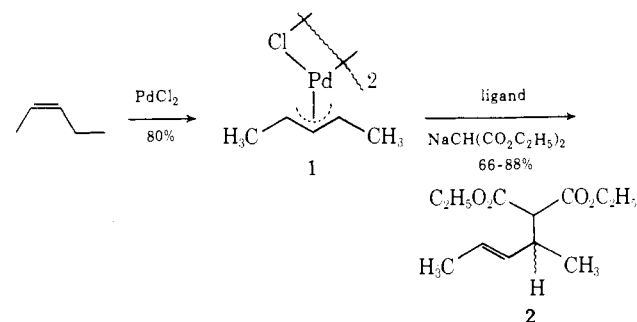
New Synthetic Reactions. Asymmetric Induction in Allylic Alkylations

Sir:

The development of direct methods for asymmetric creation of a new carbon-carbon bond continues to present a major challenge.^{1,2} The application of organometallics in such cases has had mixed results.³⁻⁵ In most cases, reasonable optical inductions (up to 33%) are observed only when exceedingly low temperatures and certain optically active solvents are employed.³ A unique feature of the allylic alkylation procedure is its potential in chiral synthesis. We wish to report that alkylation of a π -allylpalladium complex to form a sp^3 - sp^3 carbon-carbon bond⁶ leads to surprisingly high optical yields without resorting to chiral solvents and at temperatures from -40 to $+25^\circ$ (eq 1, where the asterisk indicates chiral center).



A simple system of relatively high symmetry was examined to provide a vigorous test of the potential for optical induction inherent in the method. The alkylation involved reaction of *syn,syn*-1,3-dimethyl- π -allylpalladium chloride dimer (1) (prepared by treatment of *cis*-2-pentene with palladium chloride, sodium chloride, cupric chloride, and sodium acetate in acetic acid⁷) and diethyl sodiomalonate. Experimentally, the ligand and π -allylpalladium species are mixed in THF at the stated temperature after which a solution of diethyl sodiomalonate in THF is added. A wide range of



ligands including triphenylphosphine, trimethyl phosphite, 1,2-bis(diphenylphosphino)ethane, and *N,N,N',N'*-tetramethylethylenediamine (but not *N,N,N',N'*-tetramethyl-2,3-dimethoxy-1,4-butanediamine³) promoted alkylation in isolated yields ranging from 66 to 88%. Use of the optically active ligands (+)-2-

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(7) In addition, an approximately 10% relative yield of *syn*-1-ethyl- π -allylpalladium chloride dimer is formed in this reaction.

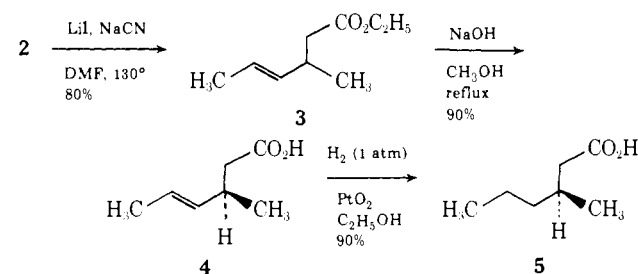
Table I

Ligand	P(N)/Pd ^e	Conditions, °C	Time, hr	Rotation of product, deg				Opt yield, %
				2 (c, CHCl ₃)	3 (c, CHCl ₃)	4 (c, CHCl ₃)	5 (c, benzene)	
(+)-DIOP	4/1	0, then 25	1, then 2	-3.64 (22.0)		-4.47 (5.88)	-0.34 (2.94)	12.2 ± 0.8 ^a (13.4 ± 2.8) ^b
(+)-DIOP	4/1	-40, (H ₂ O) 25	9.5, 16	-6.42 (3.16)				22.4 ± 2.2 ^c
(+)-DIOP	4/1	-78, (H ₂ O) 25	72, 1	-5.15 (6.08)				17.9 ± 1.8 ^c
(+)-ACMP	2/1	25	0.5	-4.11 (1.36)				17.9 ± 1.8 ^{c,d}
(+)-ACMP	2/1	-40, (H ₂ O) 25	9, 16	-5.38 (25.0)	-4.74 (9.50)	-7.10 (4.29)		24.4 ± 1.6 ^{a,d}
(+)-ACMP	2/1	-78, (H ₂ O) 25	72, 4	-5.15 (2.35)				22.4 ± 2.8 ^{c,d}
(-)-Sparteine	4/1	25	2	-5.81 (3.13)				20.2 ± 2.1 ^c
(-)-DMIP	4/1	0, 25	1, 3	-0.59 (2.54)				2.0 ± 0.3 ^c

^a Based on maximum rotation range for 4 of 39.6–34.5°. ^{11a} ^b Based on maximum rotation for 5 of 2.5°. ^{11b} ^c Based on maximum rotation range for 2 of 26.1–31.9° calculated from range of 4. ^d Corrected for 80% optical purity of (+)-ACMP. ^e The ratio of the number of phosphorus (or nitrogen) atoms of the ligand to the number of palladium atoms of the complex.

3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(+)-DIOP],⁸ (+)-*o*-anisylcyclohexylmethylphosphine [(+)-ACMP],⁹ dimethylisopropylphosphine [(–)DMIP],^{4,10} and (–)-sparteine produced the allylic alkylation product 2 optically active. Table I summarizes the data.

To determine the optical purity and absolute configuration of the product, correlation with *trans*-3-methyl-4-hexenoic acid and 3-methylhexanoic acid of known absolute configuration¹¹ was carried out. Treatment of 2 with lithium iodide and sodium cyanide in hot dimethylformamide¹² effected decarboethoxylation to 3. Hydrolysis produced the unsaturated acid 4 (identical in all respects with an authentic sample^{11a}) for which a maximum rotation of 34.5–39.6° has been reported.^{11a} Hydrogenation of 4 gave the saturated acid 5 for which a maximum rotation of 2.5° has been



reported.^{11b} It has been further established that dextrorotatory 4 has the *R* configuration. Based upon these data, allylic alkylation produced the *S* isomer with optical yields ranging from 2 to 24% (see Table I). The data indicate that the proximity of the asymmetry to the complexing atom in the ligand rather than steric

bulk plays the dominant role. Thus, sparteine and ACMP give higher optical yields than DIOP and DMIP with the last ligand giving the lowest. As generally observed, decreasing the temperature increases the optical induction although going to –78° has a deleterious effect. Such a result suggests that at this low temperature carbon–carbon bond formation may not be occurring (but carbon–palladium bond formation may have occurred¹³). Formation of the final product then takes place during the subsequent warm-up after aqueous quenching.

The optical yields obtained in this case are among the highest known for such carbon–carbon bond formation with the exception of the oligomerization reaction of Wilke and coworkers.⁴ Such an achievement illustrates another unique feature of the allylic alkylation method.

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(14) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient.

Barry M. Trost,*¹⁴ Thomas J. Dietsche

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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Radical Reduction with Naphthalenide Ion and Evidence for Carbanion Oxidation by Halides

Sir:

The reaction of sodium naphthalenide with organic halides has been shown to produce organic radicals plus halide ions *via* electron transfer from the radical