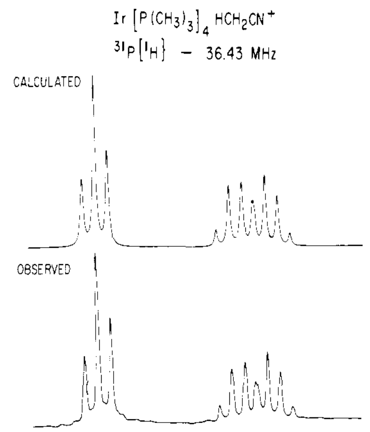

Figure 1. The $^{31}P\{^1H\}$ 36.43-MHz spectrum of $Ir[P(CH_3)_3]_4(H)(CH_2CN)^+Cl^-$ in acetonitrile at 30 °C. The calculated spectrum is constructed with δ_A 53.8 ppm, δ_B 59.6 ppm, δ_C 61.1 ppm, $J_{AB} = J_{AC} = J_{BC} = 19$ Hz.

prepared by addition of the bidentate phosphine to a benzene solution of $Ir_2Cl_2(C_8H_{14})_4$.[4] Stable red acetonitrile solutions of **1** showed ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra consistent with a four-coordinate structure.[5] Pressurization of this solution with 1 atm of CO_2 yielded a colorless solution in hours; this color change was reversed by evacuation at 80 °C. The CO_2 addition and evacuation cycle are repeatable.

^{31}P NMR spectra of **1** were recorded in the presence of either broad band proton decoupling radiation ($^{31}P\{^1H\}$) or CW aliphatic proton decoupling irradiation ($^{31}P\{CW^1H\}$). The latter type of decoupling allowed the identification of hydride containing species through the phosphorus-hydride spin-spin coupling. The ^{31}P NMR spectrum of **1** in CH_3CN showed a singlet (δ −56.6 ppm) under both decoupling conditions. After pressurizing with CO_2, the now colorless solution displayed a singlet (δ −26.9 ppm) in the $^{31}P\{^1H\}$ spectrum and a doublet in the $^{31}P\{CW^1H\}$ spectrum. The same experiments performed in CD_3CN showed only singlets.[6] These results indicate that all phosphorus nuclei in **2** (vide infra) are equivalent on the NMR time scale and are coupled to a single hydridic proton which arises from the acetonitrile solvent. ^1H NMR spectra showed a hydride quintet at δ −22.2 ppm ($J_{P-H} = 13$ Hz) in CH_3CN and no hydride resonance in CD_3CN.[7] The NMR spectra of **2** indicate it to be trans or fluxional cis; work on similar species[8,9] suggests that a trans structure is the likely choice.

Addition of HCl then BF_3/CH_3OH to the colorless solution of **1** and CO_2 in acetonitrile afforded methyl cyanoacetate, identified mass spectrometrically. The above data are consistent with the scheme:

$$[Ir(depe)_2]Cl + CH_3CN \xrightleftharpoons{K_1'} [Ir(H)(CH_2CN)(depe)_2]Cl$$

1

$$[Ir(depe)_2]Cl + CH_3CN + CO_2 \xrightleftharpoons{K_2'} [Ir(H)(O_2CCH_2CN)(depe)_2]Cl$$

$$K_2' \gg K_1' \qquad \mathbf{2}$$

The corresponding rhodium complex, $[Rh(depe)_2]Cl$, does not react with acetonitrile even in the presence of CO_2. $[Rh(Me_2PC_2H_4PMe_2)_2]Cl$ does not metalate acetonitrile or nitromethane detectably. However, CO_2 addition reversibly results in carboxylation of nitromethane, analogous to the chemistry of $[Ir(depe)_2]Cl + CH_3CN + CO_2$.

Acetonitrile is also readily metalated (and carboxylated) by $[Ir(PMe_3)_4]Cl$ (**3**). This species is much more reactive than **1** as is illustrated by its reactions with acetonitrile and CO_2. The reaction of **3** with acetonitrile at room temperature is quite rapid ($\tau_{1/2} \simeq 10$ min) and the K_1 is sufficiently large that only *cis*-$[Ir(H)(CH_2CN)(PMe_3)_4]Cl$ (**4**) (Figure 1) is observable via $^{31}P\{^1H\}$ NMR. Addition of CO_2 at room temperature to an equilibrated solution of **3** in acetonitrile (e.g., **4**) affords no observable reaction; however, immediate addition of CO_2 to a solution of **3** in acetonitrile (i.e., **3**) yields $[Ir(H)(O_2CCH_2CN)(PMe_3)_4]Cl$ (**5**). These results indicate that **4** is not the species whose reaction with CO_2 yields **5.** In this case at least, the carboxylation is not CO_2 insertion into the metal-carbon bond formed in eq 1.[10]

The metalation and carboxylation reactions have been observed with a range of ML_4^+ complexes and activated hydrocarbons. As illustrated above, Rh complexes are less reactive than the corresponding Ir species, and bulkier ligands attenuate reactivity. The observed correlation of extent of reaction with metal basicity (Ir > Rh) and C–H bond acidity suggests electrophilic attack at the metal. Work is in progress to elucidate the mechanisms of the metalation and carboxylation reactions.

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(4) T. Herskovitz, to be submitted for publication.
(5) (a) The NMR data do not exclude a small amount of a cationic five-coordinate species involving solvent coordination, $ML_4S^+Cl^-$. (b) E. L. Muetterties and P. L. Watson, *J. Am. Chem. Soc.*, **98,** 4665 (1976), have reported $\{Co[P(OCH_3)_3]_4NCCH_3\}^+$; A. D. English and F. A. Van-Catledge, unpublished results.
(6) The singlets in the ^{31}P spectra of the sample pressurized with CO_2 in CD_3CN are slightly broadened due to phosphorus deuterium coupling.
(7) ^{31}P spectra at 36.43 MHz were recorded in FT mode using 10-mm tubes on a Bruker HFX-90 with Digilab FTS-3 data system; negative chemical shifts are downfield from external 85% H_3PO_4. ^1H spectra were recorded at 220 MHz in CW mode, using 5-mm tubes on a Varian HR 220; positive chemical shifts are downfield from internal tetramethylsilane.
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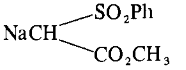
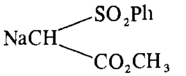
A. D. English, T. Herskovitz*
Contribution No. 2449
Central Research and Development Department
Experimental Station
E. I. du Pont de Nemours and Company, Inc.
Wilmington, Delaware 19898
Received October 27, 1976

Asymmetric Induction in Catalytic Allylic Alkylation

Sir:

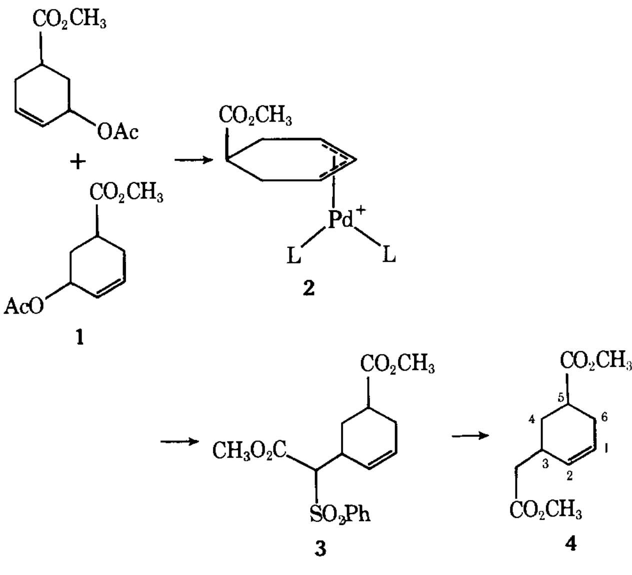
Catalytic processes for forming C–H bonds with creation of chirality have progressed almost to the limit in some cases.[1] Such reactions have been much less successful in forming C–C bonds.[2] The most successful is in an olefin oligomerization system developed by Wilke.[2b] We wish to report that optical yields in the range of 35–45% can be obtained in a catalytic allylic alkylation without resorting to impractically low temperatures.

Table I. Catalytic Asymmetric Alkylation of 5

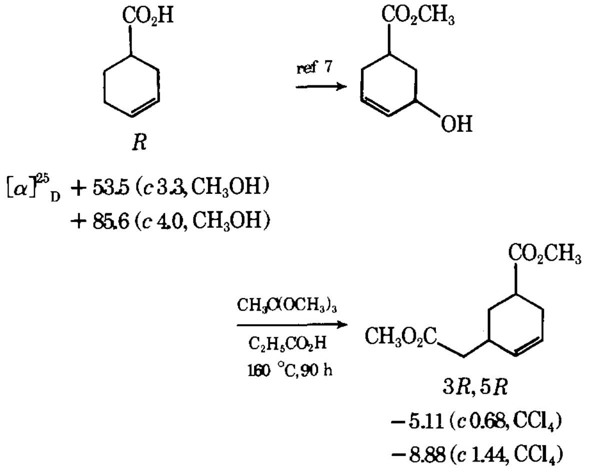
Entry	Ligand[a]	Nucleophile	Solvent[b]	Chemical yields: Alkylation	Chemical yields: Decarbomethoxylation or desulfonylation	Rotation of 7 (C, CCl_4)	Optical yield
1	(+) DIOP[c]	$NaCH(CO_2CH_3)_2$	DME	57	94	+0.833 (3.85)	21
2	(+) DIOP[c]	$NaCH(CO_2CH_3)_2$	THF	98	60	−1.5 (1.0)	37
3	(+) DIOP[c,f]	$NaCH(CO_2CH_3)_2$	DME	82	74	+1.55 (2.75)	38
4	(−) DIPAMP[d]	$NaCH(CO_2CH_3)_2$	DME	62	87	−0.65 (1.2)	16
5	(+) CAMPHOS[e]	$NaCH(CO_2CH_3)_2$	DME	99	80	−1.50 (1.2)	37
6	(+) CAMPHOS[e]	 $NaCH(SO_2Ph)(CO_2CH_3)$	DME	76	78	−1.60 (2.25)	39
7	(+) DIOP[c]	 $NaCH(SO_2Ph)(CO_2CH_3)$	DME	84	87	−1.86 (2.25)	46

[a] Reaction utilized tetrakis(triphenylphosphine)palladium and the indicated ligand. [b] Reaction performed at the reflux temperature of the indicated solvent. [c] 2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.[1d] [d] 1,2-Bis(*O*-anisylphenylphosphino)ethane.[1a] [e] 1,2,2-Trimethyl-*cis*-1,3-bis(diphenylphosphino)methylcyclopentane.[11] [f] This reaction performed with catalyst generated from (+)DIOP and palladium(0) in the absence of any achiral phosphine.

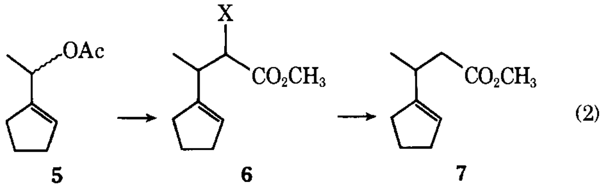
cis-3-Acetoxy-5-carbomethoxycyclohexene (**1**)[3] provides an interesting system to explore since the products from such a compound can serve as an intermediate in alkaloid synthesis.[4] While this compound is chiral, the presumed intermediate **2** in allylic alkylations catalyzed by palladium in the absence of chiral ligands is achiral. Treatment of racemic **1** with 0.75 mol % of tetrakis(triphenylphosphine)palladium and 10 mol % of (+)-DIOP[1d] in refluxing DME with the sodium salt of methyl phenylsulfonylacetate led to the alkylation product **3** (77% yield) which was directly desulfonylated with 6% sodium amalgam in methanol containing disodium hydrogen phosphate[5] to **4**, $[\alpha]^{25}_D$ −2.16° (*c* 1.5, CCl_4).



In order to determine the optical yield and absolute configuration of **4**, it was prepared independently from cyclohex-3-enecarboxylic acid of known optical purity (56 and 91%) and absolute configuration (eq 1).[6,7] With these data, **4** obtained from the allylic alkylation consists of 62% *R,R* and 38% *S,S* isomers. While several reasonable models can be put forth to rationalize the relatively high asymmetric induction and the absolute configuration, this speculation will be postponed for a full account.



(1)



(2)

An alternative system gave somewhat improved optical yields. Alkylation of racemic **5** by the sodium salt of dimethyl malonate gave **6**, X = CO_2CH_3, which was directly decarbomethoxylated with lithium iodide and sodium cyanide in hot DMF[8] to give **7**. Use of the chiral shift reagent, tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium,[9] separates the methyl ester signals into two at δ 13.61 and 13.55 which allows determination of the optical purity. Use of different chiral phosphines in conjunction with tetrakis(triphenylphosphine)palladium led to optical yields in the region of 20–37% as summarized in Table I. Several features should be noted. Lowering the reaction temperature approximately 10° (entry 2 vs. entry 1) approximately doubled the optical yield. Preparation of a (+) DIOP complex of palladium and use of this reagent as the catalyst (i.e., alkylation in the absence of achiral phosphines) also approximately doubles the optical yield (entry 1 vs. entry 3).

Enhanced optical yields are obtained when a bulkier nucleophile is employed as with the sodium salt of methyl phenylsulfonylacetate. In this case the initial alkylation product **6**, X = $PhSO_2$, is directly desulfonylated as previously reported. An optical yield of 46% utilizing (+) DIOP was obtained. While CAMPHOS[11] gave a slightly lower optical yield in this case, with malonate anion CAMPHOS approximately double the optical yield relative to DIOP under identical conditions.

Optical yields of this magnitude for carbon–carbon bond forming reactions at normal temperatures (70–80 °C) in a catalytic process are among the highest seen and suggest this approach as an exciting solution to asymmetric induction in carbon–carbon bond forming reactions. The higher optical yields in the case of allylic acetate **5** may arise in part due to the fact that the intermediate π-allylpalladium complexes with chiral phosphines are diastereomeric. Most strikingly, the present observations demand a racemization of **5** or an interconversion of diastereomers of the intermediate π-allyl complexes accompanying the conversion of **5** to **7** and thus may be contrasted to our earlier work.[3] While several rationales can be envisioned and detailed discussion will be reserved for a future publication, it appears that the slower rates of alkylation due to the presence of excess phosphine relative to palladium allows a palladium catalyzed acetate ion induced racemization of the starting allylic acetate to compete with alkylation.

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Barry M. Trost,* Paul E. Strege
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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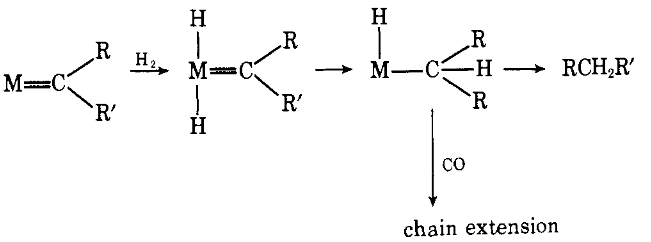
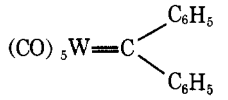
Reaction of Molecular Hydrogen with Transition Metal Carbene Complexes: Reductive Cleavage of the Carbene Ligand

Sir:

The current shortage of petroleum has focused renewed attention on alternative methods of producing organic fuels. The reduction of coal-derived carbon monoxide/hydrogen mixtures by heterogeneous transition metal catalysts in the Fischer–Tropsch process is one such alternative.[1-3] However, little is known about the mechanism of these reductions. We have previously reported the synthesis and properties of several transition metal formyl complexes,[4] which may well serve as models for the first intermediate in the reduction of CO by H_2. Our continued interest in this area has led us to study the reaction of molecular hydrogen with metal carbene complexes, a process which may be related to the chain-termination step of the Fischer–Tropsch synthesis[5] (Scheme I). Here we report that the tungsten and chromium carbene complexes **1–4** react with molecular hydrogen to give organic products derived from reductive cleavage of the carbene ligand.

Scheme I





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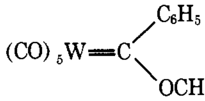

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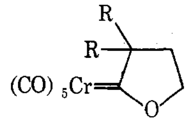

3, R = H
4, R = CH_3

The diphenylcarbene complex, **1**,[6] which does not possess stabilizing heteroatom substituents bonded to the carbene carbon, was chosen as one of the best available models for the alkyl-hydrido type of metal carbene complexes postulated as intermediates in the Fischer-Tropsch reaction. When **1** is dissolved in decalin and reacted at 100 °C for 20 h with 69 atm of H_2, a 41% yield of diphenylmethane is obtained,[7] along with small amounts of tetraphenylethylene and tetraphenylethane. $W(CO)_6$ (58% by IR analysis) is the only identified tungsten containing product, and TLC analysis indicates that **1** is totally consumed during the reaction. Hydrogenation of **1** in benzene-d_6 gives Ph_2CH_2 (100% d_0), which indicates that solvent does not participate in product formation.[8] The temperatures employed in the reduction reactions of all the carbene complexes (**1–4**) are generally in excess of those required for thermal decomposition and for ^{13}CO exchange.[9-11] A prior dissociation of CO may well be required for these reductions.

Phenylmethoxycarbene complex **2**,[12] reacts with H_2 to give significantly higher yields of organic product than its nonheteroatom stabilized counterpart, **1**. Thus, a solution of **2** in decalin reacts with 1.8 atm of H_2 at 140 °C for 5 h to give benzyl methyl ether (92%), toluene (3%), bibenzyl (1%), *trans*-stilbene (1%), and *E*- and *Z*-α,α'-dimethoxystilbene (3%).[7] The higher temperature required for this reaction parallels the higher temperatures required for the thermal decomposition and the ^{13}CO exchange of **2** compared with **1**.

The reaction of H_2 with **3** and **4** was studied primarily to determine if the carbene ligand could be cleaved reductively from these cyclic complexes in a synthetically useful manner. Since **3** and related compounds have been shown to be easily elaborated[13-15] and useful in organic synthesis,[16,17] a reductive cleavage of the carbene ligand could be a synthetically important procedure. We have found that cleavage does occur in good yields. For example, reaction of **3**[18] with 69 atm of H_2 in decalin at 170 °C gives tetrahydrofuran (THF) in 95%