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Catalysis by Rhodium and Iridium Complexes in the Nucleophilic Addition of Allylic Stannanes to Carbonyl Compounds

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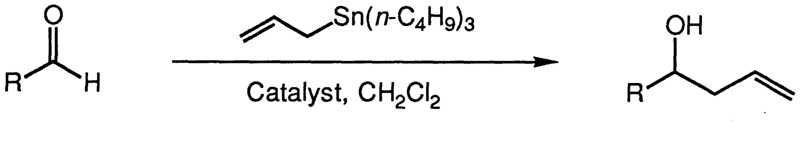
The catalysis of the nucleophilic addition of an allylic stannane to aromatic aldehydes by cationic rhodium and iridium complexes is described. The scope, generality, and several mechanistic speculations concerning this process are discussed. Initial attempts at utilizing optically active catalysts for the enantioselective addition of allyltributyltin to benzaldehyde are also outlined.

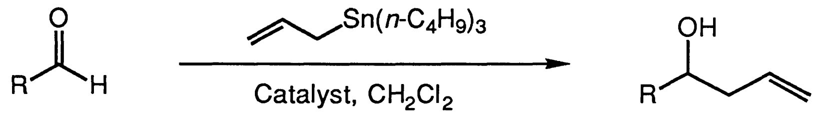
Lewis acids are an ubiquitous presence in organic synthesis, mediating an enormous number of transformations ranging from simple acetal formation to complex polyene cyclizations. While most commonly employed Lewis acids have been derived from main group and early transition series elements, many late transition metal complexes display considerable Lewis acidic character which can be exploited in a number of useful synthetic reactions.(1-4) Recent results in this area include the use of several Lewis acidic transition metal complexes as catalysts for the Diels-Alder reaction between acrolein and butadiene,(1) the ruthenium catalyzed reaction between Danishefsky's diene and benzaldehyde,(2) as well as reports of transition metal catalyzed condensations between silyl ketene acetals and aldehydes.(3) The seminal work of Gladysz(4a) on chiral rhenium complexes of aldehydes and ketones has amply demonstrated the potential of transition metal based Lewis acids in asymmetric synthesis, as well as providing considerable mechanistic insight into the nature of the interactions of ketones and aldehydes with transition metal complexes.(4) Here we describe the use of transition metal complexes as catalysts for the addition of allylic stannanes to aromatic aldehydes. The reaction between carbonyl compounds and allylstannane derivatives has seen widespread use in organic synthesis, as these processes generally proceed in good yields and with high stereoselectivity.(5) Addition of allylic stannanes in the absence of catalysts is observed at elevated temperatures(6) and pressures;(7) however, addition at lower temperatures must be facilitated by the presence of strong Lewis acids such as $BF_3 \cdot Et_2O$,(8a) $AlCl_3$,(8b) $TiCl_4$,(8c,d) and silicon based Lewis acids.(8e) In connection with our interests in the development of transition metal mediated methods for the construction of carbon-carbon bonds, we have found that several cationic complexes of rhodium and iridium effectively catalyze the addition of allylic stannanes to aromatic aldehydes under exceedingly mild conditions.



(1)

A number of complexes have been examined for catalytic activity, with the most effective being the cationic complexes of rhodium and iridium shown in Table 1.9) Several results from these investigations proved surprising. For example, Hersh had previously found $[CpFe(CO)_2 \cdot THF] \bullet BF_4$ (THF = tetrahydrofuran, Cp = C_5H_5) to be a very effective catalyst for the aforementioned Diels-Alder cycloaddition,1) but this complex did not catalyze the addition of allylstannane to aldehydes. In the present work, a cationic complex does seem to be required, as the use of two commonly encountered neutral organometallic complexes, Wilkinson's catalyst ($Rh(PPh_3)_3Cl$) and $Pd(PPh_3)_4$, results in no addition. In all cases extremely pure catalyst is utilized to rule out the possibility of catalysis by impurities. Control reactions demonstrate that the reaction is effected by the transition metal catalyst and not by decomposition of the counterion, in this case the hexafluorophosphate, perchlorate, and tetrafluoroborate anions. Thermal addition of the allylstannane has also been experimentally ruled out (Entry 13).

Table 1. Results of the Catalyzed Addition of Allyltributyltin to Various Aldehydes



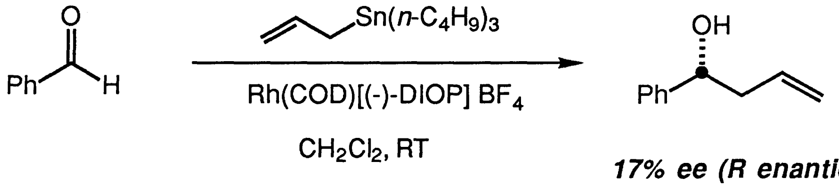
Entry	R	Catalyst a) (mol %)	Ratio RCHO : R_3SnR_3	Solvent	Temp °C	Time h	Yield %b)
1	C_6H_5	$Ir(CO)(PPh_3)_2ClO_4$ (5%)	1:1	CH_2Cl_2	25	30	83
2	C_6H_5	$Ir(CO)(PPh_3)_2ClO_4$ (3%)	1:1	CH_2Cl_2	25	28	48
3	C_6H_5	$Ir(CO)(PPh_3)_2ClO_4$ (3%)	1:1	CH_2Cl_2	45	10	97
4	C_6H_5	$Rh(CO)(PPh_3)_2ClO_4$ (1%)	1:1	Toluene	25	26	35
5	C_6H_5	$Rh(CO)(PPh_3)_2ClO_4$ (1%)	1:1	Toluene	110	26	55
6	C_6H_5	$Rh(CO)(PPh_3)_2ClO_4$ (1%)	1:1	CH_2Cl_2	25	26	60
7	C_6H_5	$Rh(CO)(PPh_3)_2ClO_4$ (1%)	1:1	CH_2Cl_2	45	36	31
8	C_6H_5	$Rh(CO)(PPh_3)_2ClO_4$ (1%)	1:2	CH_2Cl_2	25	26	92
9	C_6H_5	$Rh(CO)(PPh_3)_2ClO_4$ (1%)	2:1	CH_2Cl_2	25	26	93
10	p-MeO-C_6H_4	$Rh(CO)(PPh_3)_2ClO_4$ (1%)	1:1	CH_2Cl_2	25	48	55
11	3,4,5-$(MeO)_3$-C_6H_2	$Rh(CO)(PPh_3)_2ClO_4$ (1%)	1:1	CH_2Cl_2	25	15	87
12	C_6H_5	$Rh(COD)[(-)\text{-}(DIOP)]BF_4$ (1%)	1:1	CH_2Cl_2	45	31	90 c)
13	C_6H_5	None	1:1	CH_2Cl_2	25	48	0

a) The preparation of these complexes are given in Ref. 9; COD = 1,5-cyclooctadiene, DIOP = 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (available from Aldrich Chemical Co.). b) GC yields are given; isolated yields are typically ca. 5% lower. c) Enantiomeric excess is 17%, with the (+)-(R) enantiomer being preferentially formed.13)

Good yields are obtained for the addition using an excess (1.5-2.0 fold) of either the carbonyl compound or the allylic stannane with as little as 1 mol% of catalyst in methylene chloride at room temperature (Entries 8 and 9).10) A significant solvent effect is observed, as the reaction proceeds smoothly in methylene chloride, while in toluene heating is required for only moderate conversion. While allylic silanes typically undergo addition to carbonyl compounds under the influence of Lewis acid catalysis,11) the transition metal complexes described in Table I do not catalyze the addition of allyltrimethylsilane to benzaldehyde.

These reaction conditions have proven very selective for aromatic aldehydes. The yields with aliphatic aldehydes are negligible even under forcing conditions; judicious choice of ligands may overcome this problem. Ketones and α,β-unsaturated aldehydes have also been found to be unreactive. Electron withdrawing groups on the aromatic ring impede the reaction, while electron donating groups do not have a deleterious effect on addition. This is demonstrated by Entry 11, as 3,4,5-trimethoxybenzaldehyde requires only fifteen hours at room temperature for complete reaction. The aliphatic aldehydes seem to be better ligands for the metal complex, in this case $Rh(COD)(PPh_3)_2PF_6$, than the aromatic aldehydes; this binding may contribute to their lack of reactivity. Evidence for this comes from the observation that hexanal inhibits the reaction of benzaldehyde with allyltributyltin in the presence of $Rh(COD)(PPh_3)_2PF_6$.

In recent years exciting advances have been made in the use of chiral Lewis acids for the enantioselective formation of carbon-carbon bonds via carbonyl addition reactions.12) The ease with which transition metal complexes can be prepared in optically pure form makes these compounds attractive as catalysts for enantioselective synthesis. To determine the effectiveness of optically active rhodium-based Lewis acids in catalyzing the asymmetric addition of allylic stannanes to aldehydes, we have examined an optically pure complex possessing the chiral bidentate phosphine ligand, (-)-DIOP. The result is summarized in Table 1 (Entry 12) and Equation 2. Recovered products show only a small degree of asymmetric induction (17% ee of the R antipode) using this catalyst system.13) This level of asymmetric induction is comparable to those obtained by Reetz in rhodium-catalyzed condensations between ketene acetals and benzaldehyde.3b) Efforts to optimize the enantioselectivity of these additions and thoroughly understand both the origin and sense of the observed asymmetric induction will be reported in due course.



(2)

17% ee (R enantiomer)

Although the mechanism of the Lewis acid mediated reaction between allylic stannanes and carbonyl compounds is still a matter of some debate,14) a proposal concerning the mechanism of the present reaction can be advanced. The initial step of this sequence could involve activation of the aldehyde by complexation to the transition metal complex in a σ-sense,4b) either to an empty coordination site (displacing solvent) or by displacement of another ligand. Carbon-carbon bond formation can then occur by reaction of this activated species with the allyl stannane, via a six centered transition state, affording the O-stannylated adduct. The carbinol product is then isolated after standard workup (silica gel chromatography). Attempts to more thoroughly elucidate the mechanism of these additions are currently underway in our laboratories.

These studies have demonstrated the utility of transition metal based complexes as catalysts for the allylation of aromatic carbonyl compounds proceeding under extremely mild conditions. Other aspects of this chemistry, including the diastereoselectivity of crotyl stannane addition, will be the subject of future reports. Further utilization of these transition metal complexes for a variety of transformations, including the opening of oxiranes with trimethylsilyl cyanide and azide, is also being investigated.

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