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Synthesis and carbon-carbon bond-forming reactions of tungsten, molybdenum, and rhenium enolates

Clayton H. Heathcock*, Jeffrey J. Doney, and Robert G. Bergman*

Department of Chemistry, University of California
Berkeley, California 974200

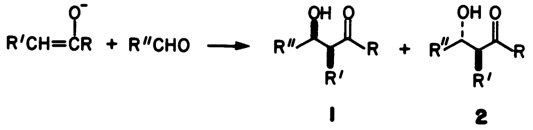
Abstract - Alkylation of sodium cyclopentadienyl(tricarbonyl)metallates of tungsten and molybdenum with α-chloro ketones and α-chloro esters gives stable tungsten and molybdenum enolates (**23a–23d**). Similar alkylation of sodium pentacarbonylrhenate provides rhenium enolates **24**. Compounds **23** lose carbon monoxide and rearrange to η^3-oxaallyl complexes **25** upon irradiation. Compounds **25** react with benzaldehyde to give transition metal aldolates (**26**), which may be converted into the silylated aldol (**27**) and the corresponding metal chloride (**28**) upon reaction with trimethylsilyl chloride. Rhenium enolate **27** undergoes thermal aldol reaction with benzaldehyde and suffers exchange of one carbonyl ligand upon being heated with triphenylphosphine. The resulting cis monophosphine complex (**30**) and compound **27** itself both react with triphenylphosphine in refluxing acetonitrile to give complex **31**, in which the enolate moiety has been transferred from rhenium to the nitrile function. Several schemes for establishing catalytic cycles based on the foregoing reactions are suggested.

Since the first report of the aldol addition reaction in 1838 (ref. 1), enolate ions have occupied a position of singular importance in organic chemistry. A large fraction of the most general synthetic methods involve these important intermediates. Nevertheless, until about 30 years ago, there was little direct study of enolate ions *per se*, since most reactions in which they are involved were carried out under protic conditions where enolates are formed only as transient intermediates. Obvious exceptions are the enolates derived from β-dicarbonyl compounds, which may be prepared in alcoholic, or even in aqueous solutions.

The situation began to change in 1949 and 1950 when Frostick and Hauser introduced diisopropylaminomagnesium bromide as a catalyst for the Claisen condensation (ref. 2) and Hamell and Levine reported the first use of lithium diisopropylamide (LDA) for the same purpose (ref. 3). These strong bases have the useful property of being soluble in aprotic solvents such as ether and THF, and allow the stoichiometric production of enolate salts. The first report of a stoichiometrically formed enolate salt came from Dunnavant and Hauser, who prepared the enolate of ethyl acetate with lithium amide in ammonia and demonstrated that it reacts with aldehydes and ketones to give β-hydroxy esters in low yield (ref. 4). The utility of such preformed enolate salts was graphically demonstrated by M. W. Rathke in an important paper published in 1970 (ref. 5). Rathke showed that the sodium enolate is unstable even at -78 °C, but that the lithium enolate, prepared with lithium bis(trimethylsilyl)amide in THF, is stable indefinitely at -78 °C, and that solutions of ethyl lithioacetate react smoothly with aldehydes and ketones to give the corresponding aldols in high yield.

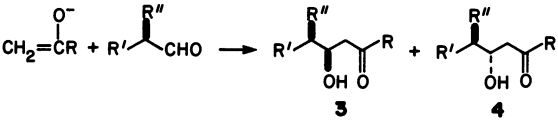
In the last decade, we have seen an intense investigation of the preparation, structures, and chemical reactivity of preformed metal enolates. The reader is referred to several recent review articles for a more complete coverage of the field (ref. 6-11). A large part of this interest has revolved about the increasing importance of stereocontrol in organic synthesis. In this regard, there has been a great deal of success in understanding and using stereoselective aldol addition (ref. 8, 9 & 11) and alkylation (ref. 10) reactions.

In the context of the aldol reaction, two fundamentally different kinds of stereoselectivity are possible and have been investigated. In reactions between prochiral enolates and prochiral aldehydes, two new stereocenters may be created by way of two diastereomeric transition states (eq 1). The reslting isomers (1 and 2) are referred to as syn and anti, respectively (ref. 12). This type of stereoselectivity has been referred to as "simple diastereoselection" (ref. 13).



(1)

A second kind of stereoselectivity is possible in reactions occurring between a chiral aldehyde and an achiral enolate (eq 2), or vice versa (eq 3). In this case, the two stereoisomeric products (3/4 or 5/6) also result from diastereomeric transition states, but the origin of the stereochemical preference for one transition state over the other is related to the intrinsic "diastereofacial preference" (ref. 13) of the chiral reactant.



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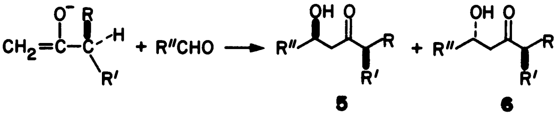
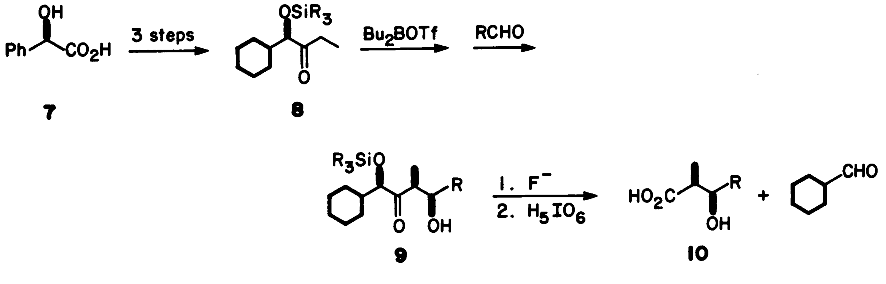


(3)

In aldol reactions of the type symbolized by eq 3, there is the possibility of realizing asymmetric induction in formation of the new carbinol stereocenter if the chiral assembly depicted by "CHRR'" is possible of being converted into other, more useful functionality. In such an application, "CHRR'" is referred to as a "chiral auxilary." Most chiral auxiliaries are natural products such as amino acids, hydroxy acids, terpenes, or carbohydrates.

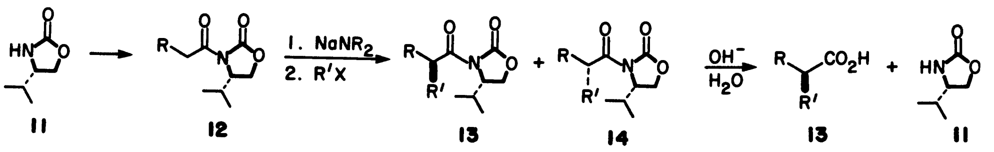
From a practical viewpoint, the first level of asymmetric induction is that in which the chiral auxiliary is stoichiometrically consumed in the overall process. An example of this kind of "first order" asymmetric induction is the method of Masamune (ref. 14), in which mandelic acid (7) is converted by a three-step procedure into the enantiomerically homogeneous α-silyloxy ketone 8 (eq 4) (ref. 15). The boron enolate of the latter substance shows excellent diastereofacial preference in reactions with aldehydes, giving aldols 9 in high purity (ref. 16 & 17). Desilylation of 9 and periodic acid cleavage of the resulting α-hydroxy ketone provides the corresponding β-hydroxy acid (10) and cyclohexanecarboxaldehyde.



(4)

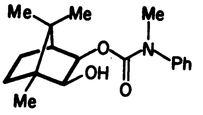
In the foregoing process, the chiral auxiliary is mandelic acid and at least one mole of this material is expended for each mole of hydroxy acid prepared. Because of the relatively high cost of the enantiomeric mandelic acids (>$1.50 per gram), this process is relatively uneconomical.

A more efficient process is one in which the chiral auxiliary, although still used stoichiometrically, can be recovered and reused. Notable examples of such "second order" asymmetric induction processes are the contributions of Evans (ref. 18) and Helmchen (ref. 19). In the Evans procecedure (eq 5), a carboxylic acid is converted into a chiral imide (6) by reaction with the valine-derived auxiliary 11. Imide 12 is alkylated, giving diastereomeric



(5)

imides 13 and 14 in ratios ranging from 6:1 to >100:1. Chromatographic purification (if necessary) and hydrolysis of the major diastereomer results in overall enantioselective synthesis of acid 13. The Helmchen strategy is similar, except that chiral auxiliary 14, derived from the readily-available terpene camphor, is employed.



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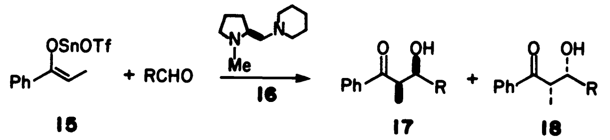
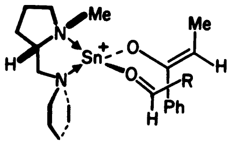
Both the Evans and the Helmchen strategies may also be used in aldol reactions. An important feature of these processes is the fact that the chiral auxiliaries (11 or 14) are obtained from relatively inexpensive natural products (valine and camphor, respectively) and may, in principle, be fully recovered and recycled. However, in practice, yields are never quantitative, and the overall efficiency of auxiliary recovery is rarely greater than 50%.

The most efficient kind of asymmetric induction is one in which the chiral auxiliary is used catalytically (note that this is not necessarily the same as using the metal moiety--which may be less valuable than the auxiliary--in a catalytic manner). Outstanding examples of such processes are the Monsanto procedure for enantioselective catalytic hydrogenation of dehydro amino acids (ref. 20) and the Sharpless procedure for epoxidation of unsaturated alcohols (ref. 21); in each of these processes, both the metal and ligand are employed catalytically. Thus far, there has been no report of catalytic asymmetric induction in alkylation or aldol reactions of enolates (ref. 22). The best progress that has been made in this direction is in the use of chiral auxiliaries such as diamine 16 in the reactions of Sn(II) enolates with aldehydes (eq 6); enantiomer ratios in the range 3:1 to >20:1 have been achieved (ref. 23).



(6)

The source of the asymmetric induction in the foregoing process is presumably a conformational preference in the coordinated Sn(II) enolate (e.g., 19). However, even in this process, it is still necessary to employ the auxiliary stoichiometrically. In order to realize catalytic asymmetric induction, one of the two following conditions must be satisfied:



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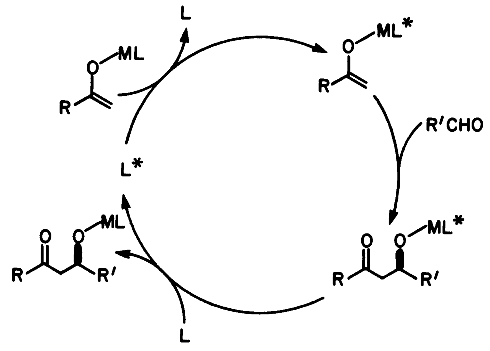
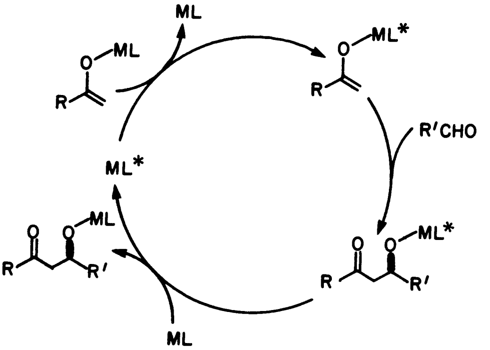
Condition 1: Suppose the enolate ion is intimately associated with a given metal cation that is also associated with various ligands and that nucleophilic reactions of the enolate are faster than cation exchange. If ligand exchange is fast relative to nucleophilic reactions of the enolate, one may imagine the nucleophilic reaction occurring while the enolate is associated with an added chiral auxiliary. Catalytic asymmetric induction can result if the enolate is more reactive when it is associated with the chiral auxiliary than when it is not. A hypothetical catalytic cycle based on these conditions is outlined in Scheme 1.

Scheme 1



Condition 2: Suppose that the enolate ion reacts in intimate association with a metal ion, but that cation exchange is faster than nucleophilic reactions of the enolate. In this case, one may imagine that two cations may be in solution, one associated only with achiral ligands, and one bearing a chiral ligand. Catalytic asymmetric induction may be realized if the enolate is more reactive when associated with the chiral cation than when it is associated with the achiral cation. Scheme 2 illustrates a catalytic cycle based on these conditions.

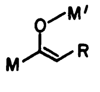
Scheme 2



Thus far, neither of these hypothetical situations has been demonstrated experimentally. Indeed, it seems improbable that the necessary conditions _can_ be met with main group metal enolates for several reasons. For enolates of cations such as lithium, sodium, and magnesium, exchange of the enolate with various cations is undoubtedly too rapid for condition 1 to be met and ligand exchange on the metal cation is probably too fast for condition 2 to be satisfied. With other metals (boron, silicon, tin, and most early transition metals; e.g., titanium, zirconium), either ligand exchange on the metal or exchange of the enolate with various cations is probably too slow. Furthermore, even if a suitable main group metal could be found, it would still be necessary to discover a chiral auxiliary which, when associated with the metal ion, would significantly enhance the nucleophilic reactivity of an associated enolate ion.

It is noteworthy that the two most important catalytic asymmetric reactions (Monsanto hydrogenation and Sharpless oxidation) employ transition metal templates associated with chiral ligands. For these reasons, we have iniated an investigation of the reactions of transition metal enolates with the ultimate goal of developing a system that will allow such catalytic asymmetric induction in carbon-carbon bond-forming reactions of enolates.

Until recently little information was available on transition metal enolates, but interest is clearly growing. Two types of enolates have been prepared and studied. One is illustrated by structure **20**, in which a transition metal acyl complex is formally deprotonated. This gives a species which actually contains two metals: that from the transition series replacing one of the σ-bound atoms at the center carbon of the enolate, and a main-group metal associated with the enolate π-system. Several studies--one of the earliest from one of our groups (ref. 24), and more extensive contributions from the laboratories of Liebeskind (ref. 25) and Davies (ref. 26) demonstrated that these species undergo typical reactions with electrophiles at the main-group coordinated π-system, with the transition metal moiety acting essentially as a chiral substituent. Substantial stereoselectivity has been observed in some systems by employing the transition metal group in this way. However, little utilization of the transition metal-carbon bond in direct chemical transformations has been investigated.



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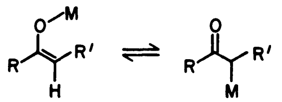


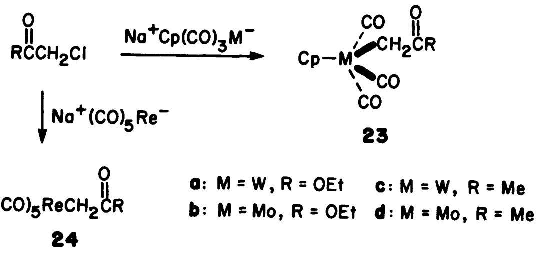
21 **22**

Much less is known about systems such as **21**, which contain only a transition metal, and which have this metal associated directly with the enolate π-system. The best-studied systems have been prepared using so-called "early" transition metals (i.e., situated to the left of Group VI in the periodic table), such as titanium and zirconium (ref. 26). Several have been reported to undergo aldol reactions. As might be expected from early-metal systems, those which have been directly characterized appear to have exclusively oxygen-bound structures. Only a few later transition metal, carbon-bound structures (**22**) have been reported. These have been referred to in the literature as "substituted methyl," "acylmethyl," and "oxoallyl" complexes, and surprisingly little is known about their chemistry (ref. 27). In particular, reactions with organic electrophiles such as aldehydes and nitriles have not been reported.

Before turning our attention to the interesting question of catalytic asymmetric induction, it has been necessary for us to develop reliable syntheses of a variety of transition metal enolate systems, and to delineate the scope of their reactivity in carbon-carbon bond-forming reactions. As will be shown, we have found that such enolate systems may be readilly prepared on multigram scale, isolated as stable, monomeric species, and fully characterized by conventional (spectroscopic, analytical and x-ray) techniques. Despite this tractability they are reactive and do, in fact, possess nucleophilic properties. Thus far, we have documented a photochemical aldol reaction in the tungsten and molybdenum series and a thermal reaction with acetonitrile in the rhenium series.

Treatment of the carbonylmetallate salts (ref. 29) Na[Cp(CO)$_3$M] (M = Mo, W) or Na[(CO)$_5$Re] with α-chloro carbonyl compounds leads in all the cases illustrated in Scheme 3 to the enolates **23a–23d** and **24**. These materials were isolated by crystallization from hexane and characterized fully by IR, ^{1}H and ^{13}C NMR and elemental analysis.

Scheme 3



In addition, crystals of the ethoxycarbonyl(methylene)tungsten complex **23a** suitable for X-ray analysis were obtained. Solution of the structure confirmed the carbon-bound enolate formulation, as illustrated in the ORTEP diagram shown in Figure 1. It is important to note that the reactions summarized in Scheme 3 are practical; compound **23a**, for example, has been prepared on a 15 g scale.

The tungsten enolate **23a** is air-stable and thermally robust. Even in the presence of benzaldehyde, it remains unchanged after heating for 52 h at

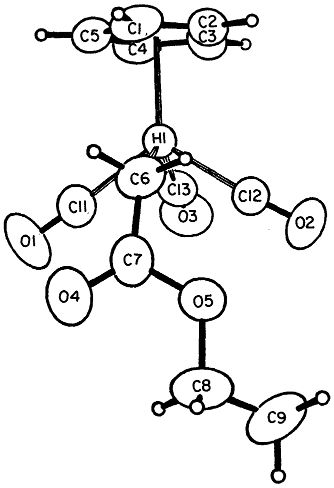
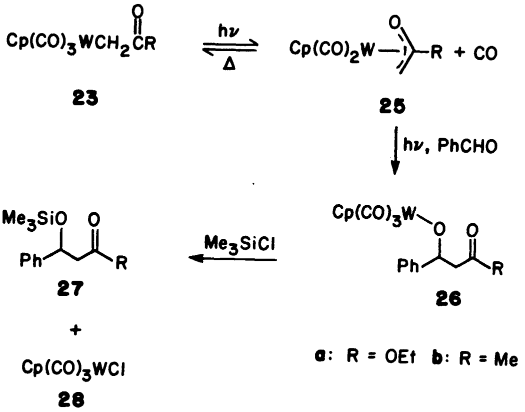


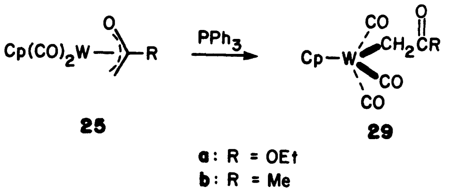
Fig. 1. ORTEP plot of the x-ray structure of compound **23a**.

110 °C in C_6D_6. However, it is sensitive to light, and if left in a clear bottle exposed to normal laboratory illumination for several days, the initially yellow crystals slowly acquire the red color characteristic of the tungsten dimer $[Cp(CO)_3W]_2$. Irradiation of a benzene or THF solution of **23a** that also contains benzaldehyde leads to a metal salt of the aldol addition product **26a** (75-77% yield by ^{1}H NMR internal standard) along with 11% ethyl acetate. Aqueous workup provides the pure aldol in 38% isolated yield (isolation procedure not yet optimized). If trimethylsilyl chloride is added after irradiation, or if the irradiation is carried out in the presence of trimethylsilyl chloride, and the reaction mixture is then heated at 60 °C or irradiated for an additional 2 h, **26a** is quantitatively converted into the silylated aldol **27a** and cyclopentadienyltricarbonyltungsten chloride (**28**).

Scheme 4



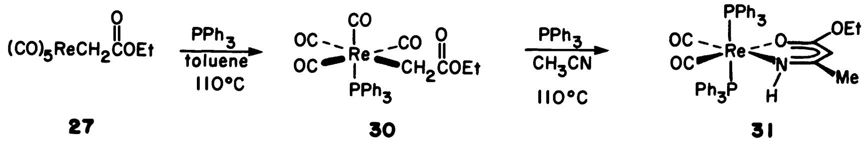
Irradiating **23** in the absence of aldehyde results in loss of one equivalent of CO (quantified by Toepler pumping the evolved gas), and generation of the η^3-oxaallyl derivative **25** (85% yield by ^{1}H NMR internal standard). Compound **25** is air- and heat-sensitive, and efforts to isolate it in pure form have not yet been successful. However, solutions of **25** are stable for hours at room temperature or days at -40 °C. Compound **25** regenerates **23** on treatment with CO; it is converted to the new cis phosphine-substituted η^1-enolate **29** on treatment with triphenylphosphine (89% isolated yield, eq 7).



(7)

Reaction of two equivalents of benzaldehyde with **25** in benzene-d_6 over a period of four days in the absence of light yields a 2:1 mixture of the aldol addition product **26a** and ethyl acetate. Intermediate **25a** reacts with benzaldehyde more rapidly if a benzene-d_6 solution of the two reactants is irradiated in a sealed tube under the foregoing conditions; complete reaction is observed in 6 h (0.01 M **25a**, 0.01 M benzaldehyde, Hanovia 450-watt low pressure lamp, uranium glass filter). These observations suggest that in the photochemical reaction with benzaldehyde, irradiation produces the oxaallyl complex, and that this reacts thermally to give aldol addition product and ketone or ester (Scheme 4). Similar observations have been made with each of the four tungsten and molybdenum enolates illustrated in Scheme 4.

The rhenium enolate **27** undergoes aldol reactions thermally, although with less efficiency than the photochemical processes observed with the tungsten and molybdenum systems. In addition, we have uncovered an unusual reaction of this system with acetonitrile. Reaction of **27** with phosphines leads stereospecifically to the cis-substituted complex **30**. When either compound **27** or **30** is heated at 110 °C for 2 days with excess PPh_3 in acetonitrile, a sharp-melting, crystalline material precipitates and has been isolated in 44% yield (eq 8). Determination of the structure of this material by X-ray diffraction showed it to be **31**, a rhenium complex of the condensation product of the enolate moiety with acetonitrile (Figure 2).



In summary, our preliminary studies have shown that carbon-bound transition metal enolates can be prepared in a straightforward and general way; they may be isolated and characterized by conventional techniques and are capable of undergoing aldol addition reactions with benzaldehyde. Our experiments in the rhenium series demonstrate that carbon-carbon bond forming reactions with much less reactive electrophiles, such as nitriles, are also possible. The preliminary investigations provide a strong indication that oxaallyl complexes are intermediates in the tungsten and molybdenum aldol reactions, but many additional mechanistic questions remain to be answered about these processes.

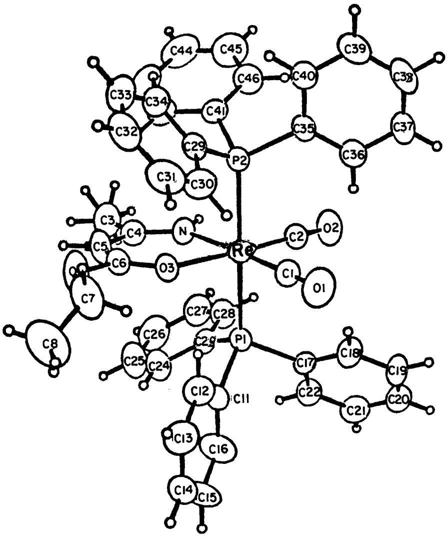
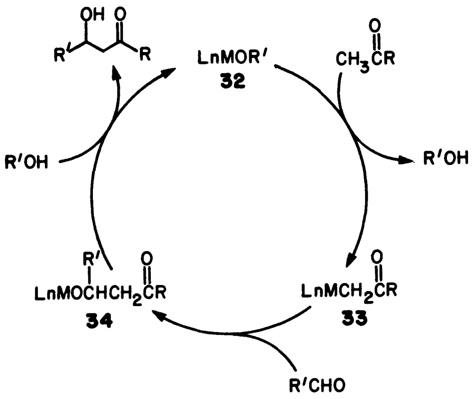


Fig. 2. ORTEP plot of the x-ray structure of compound 31.

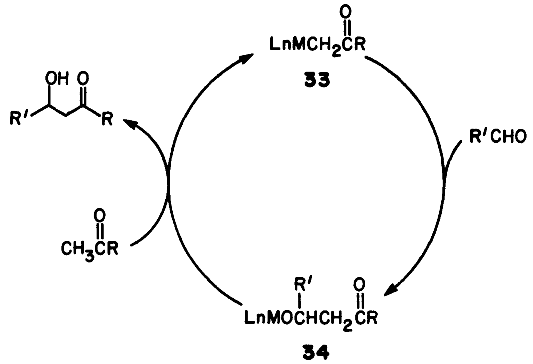
Our future line of research in this project will be to more fully delineate the scope and mechanisms of the reactions of transition metal enolates with organic electrophiles. One of the most interesting phases of our future work will be efforts to establish catalytic cycles, for eventual application in asymmetric carbon-carbon bond-forming processes. Of the two types of catalytic cycle suggested earlier, the second, in which a catalytic amount of metal, equipped with fixed chiral ligands, seems most accessible. One such hypothetical cycle could result if we are able to form transition metal enolates by the acid-base reaction of a metal alkoxide (32) with a ketone or ester (Scheme 5).

Scheme 5



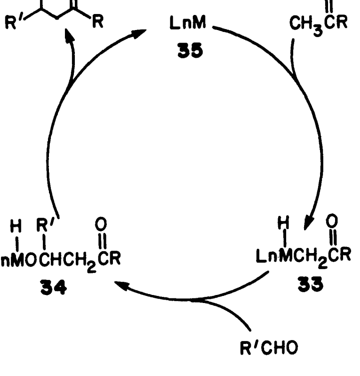
After the aldol reaction (33 --> **34**), the alcohol molecule produced in the first step of the cycle might exchange with the metal aldolate to give the aldol product, regenerating 32. Of course, since **34** is an alkoxy metal complex, an independent OR' might not be needed in this cycle. Scheme 6 shows a more efficient variant of this process in which the ketone or ester reacts directly with aldol complex **34** to regenerate the reactive intermediate 33 and deliver the aldol.

Scheme 6



Another possible variant of this cycle, involving C-H activation (ref. 30) as the enolate-forming step, is shown in Scheme 7. Preliminary results on C-H activation selectivities indicate it is realistic to expect Ir and Rh complexes with appropriate substitution to favor attack at α-carbonyl hydrogens of methyl ketones, at least (ref. 31). In this reaction, the initial insertion product 33 would undergo the aldol reaction to give **34**, which would suffer reductive elimination to give the aldol and active catalyst, 35.

Scheme 7



If we are able to establish viable catalytic cycles in transition metal enolate aldol reactions, the logical extension will be to equip the metal with one of the readilly available chiral phosphine ligands [e.g., DIOP, DIPAMP, CHIRAPHOS, or BINAP (ref. 32-35)] and search for asymmetric induction.

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REFERENCES AND NOTES

1. R. Kane, Ann. Physik Chem. [2], **44**, 475 (1838); J. Prakt. Chem. **15**, 129 (1838).

2. F. C. Frostick, Jr. and C. R. Hauser, J. Am. Chem. Soc., **71**, 1350 (1949).

3. J. M. Hamell and R. Levine, J. Org. Chem., **15**, 162 (1950).

4. W. R. Dunnavant and C. R. Hauser, J. Org. Chem., **25**, 503 (1960).

5. M. W. Rathke, J. Am. Chem. Soc., **92**, 3222 (1970).

6. L. M. Jackman and B. C. Lange, Tetrahedron, **33**, 2737 (1977).

7. T. Mukaiyama, Org. React., 28, 203 (1982).

8. D. A. Evans, J. V. Nelson, and T. R. Taber, in Topics in Stereochemistry; E. L. Eliel, N. L. Allinger, and S. Whilen, Eds; Wiley, New York, 1982; Volume 13, Chapter 1.

9. C. H. Heathcock, in Comprehensive Carbanion Chemistry; E. Buncel and T. Durst, Eds; Elsevier, Amsterdam; 1984, Part B, Chapter 4.

10. D. A. Evans, in Asymmetric Synthesis; J. D. Morrison, Ed; Academic Press, New York, 1984; Volume 3, Chapter 1.

11. C. H. Heathcock, in Asymmetric Synthesis; J. D. Morrison, Ed; Academic Press, New York, 1984; Volume 3, Chapter 2.

12. For a definition of the syn/anti convention, see: S. Masamune, Sk. A. Ali, D. L. Snitman, and D. S. Garvey, Angew. Chem. Int. Ed. Engl., **19**, 557 (1980).

13. C. H. Heathcock, C. T. White, J. J. Morrison, and D. VanDerveer, J. Org. Chem., **46**, 2290 (1981).

14. S. Masamune, W. Choy, F. A. J. Kerdesky, and B. Imperiali, J. Am. Chem. Soc., **103**, 1566 (1981).

15. The technique of employing the enolate of an α-silyloxy ketone as a surrogate for other other carbonyl enolates was first introduced and developed at Berkeley. See inter alia: (a) C. T. Buse and C. H. Heathcock, J. Am. Chem. Soc., **99**, 2337 (1977); (b) C. H. Heathcock, C. T. Buse, W. A. Kleschick, M. C. Pirrung, J. E. Sohn, and J. Lampe, J. Org. Chem., **45**, 1066 (1980); (c) C. T. White and C. H. Heathcock, J. Org. Chem., **46**, 191 (1981).

16. The t-butyl analog of silyloxy ketone **8** has also been studied: (a) C. H. Heathcock, M. C. Pirrung, C. T. Buse, J. P. Hagen, S. D. Young, and J. E. Sohn, J. Am. Chem. Soc., **101**, 7077 (1979); (b) C. H. Heathcock, M. C. Pirrung, J. Lampe, C. T. Buse, and S. D. Young, J. Org. Chem., **46**, 2290 (1981).

17. It is interesting that the lithium enolate of the t-butyl analog shows opposite diastereofacial preference in its reactions with aldedhydes; a mechanistic rationale has been advanced for this lithium-boron dichotomy: C. H. Heathcock, in Asymmetric Reactions and Processes in Chemistry; E. L. Eliel and S. Otsuka, Eds.; American Chemical Society: Washington, D.C., 1982.

18. D. A. Evans, M. D. Ennis, and D. J. Mathre, J. Am. Chem. Soc., **104**, 1737 (1982).

19. R. Schmierer, G. Grotemeier, G. Helmchen, and A. Selim, Angew. Chem. Int. Ed. Eng., **20**, 207 (1981).

20. (a) W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, 1445 (1968); (b) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Adv. Chem. Ser., No. 132*, 274, (1974).

21. K. B. Sharpless and T. R. Verhoeven, *Aldrichimica Acta*, **12**, 63 (1979).

22. For a discussion of work in this area, see ref. 11, pages 200-206.

23. N. Iwasawa and T. Mukaiyama, *Chem. Lett.*, 1441 (1982).

24. K. H. Theopold, P. N. Becker, and R. G. Bergman, *J. Am. Chem. Soc.*, **104**, 5250 (1982).

25. (a) L. S. Liebeskind, M. E. Welker, and V. Goedken, *J. Am. Chem. Soc.*, **106**, 441 (1984); (b) L. S. Liebeskind and M. E. Welker, *Organometallics*, 2, 194 (1983).

26. (a) S. G. Davies, I. M. Dordor, J. C. Walker, and P. Warner, *Tetrahedron Lett.*, **25**, 2709 (1984); (b) G. J. Baird, S. G. Davies, R. H. Jones, K. Prout, and P. Warner, *J. C. S. Chem. Commun.* 745, (1984); (c) P. J. Curtis and S. G. Davies, *J. C. S. Chem. Commun.* 747 (1984); (d) S. G. Davies and J. I. Seeman, *Tetrahedron Lett.*, **25**, 1845 (1984); (e) N. Aktogu, H. Felkin, G. J. Baird, S. G. Davies, and O. Watts, *J. Organomet. Chem.*, **262**, 49 (1984).

27. (a) D. A. Evans and L. R. McGee, *Tetrahedron Lett.*, **21**, 3975 (1980); (b) Y. Yamamoto and K. Maruyama, K. *Tetrahedron Lett.*, **21**, 4607 (1980); (c) M. T. Reetz and R. Peter, *Tetrahedron Lett.*, **21**, 4691 (1980); (d) R. H. Grubbs and J. R. Stille, *J. Amer. Chem. Soc.*, **105**, 1664 (1983); (e) S. C. H. Ho, D. A. Strauss, J. Armantrout, W. P. Schaefer, and R. H. Grubbs, *ibid* **106**, 2210 (1984); (f) M. D. Curtis, S. Thanedar, and W. M. Butler, *Organometallics*, **3**, 1855 (1984); (g) J. M. Manriquez, P. J. Fagan, T. J. Marks, C. S. Day, and V. W. Day, *J. Amer. Chem. Soc.* **100**, 7114 (1978). For an example of a late transition metal enolate which has also been assigned the O-bound structure, see (h) Y. Ito, M. Nakatsuka, N. Kise, and T. Saegusa, *Tetrahedron Lett.* **21**, 2873 (1980).

28. (a) R. B. King, M. B. Bisnette, and A. Fronzaylia, *J. Organomet. Chem.*, **5**, 341 (1966); (b) J. Engelbrecht, T. Greiser, and E. Weiss, *J. Organomet. Chem.*, **204**, 79 (1981); (c) V. Galamb and G. Palyi, *J. Organomet. Chem.*, **209**, 183 (1981); (d) Y. Yamamoto and K. Maruyama, *J. Am. Chem. Soc.* **104**, 2323 (1982); (e) D. Milstein, *Acc. Chem. Res.*, **17**, 221 (1984); (f) W. G. Hatton and J. A. Gladysz, *J. Am. Chem. Soc.*, **105**, 1657 (1983); (g) G. V. Nizova, M. V. Serdobov, A. T. Nititaev, and G. B. Shul'pin, *J. Organomet. Chem.* **275**, 139 (1984); (h) R. Bertani, C. B. Castellani, and B. Crociani, *ibid* **269**, C15 (1984); (i) J. K. P. Ariyaratne, A. M. Bierrum, M. L. H. Green, M. Ishaq, C. K. Prout, and M. G. Swanwick, *J. Chem. Soc. (A)*, 1309 (1969); (j) C. D. Hoff, F. Ungvary, R. B. King, and L. Marko, *J. Am. Chem. Soc.*, **107**, 666 (1985). Transition metal enolates are also presumably involved as short-lived intermediates in several reported reactions of α-halocarbonyl compounds with low valent complexes; see, e.g., (k) H. Alper and D. Des Roches, *J. Org. Chem.*, **41**, 806 (1976); (l) E. Yoshisato and S. Tsutsumi, *J. Amer. Chem. Soc.*, **90**, 4448 (1968); *Chem. Commun.* 33, (1968).

29. (a) J. E. Ellis, *J. Organomet. Chem.*, **86**, 1 (1975); (b) H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966); (c) R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).

30. (a) A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, **105**, 3929 (1983); (b) R. G. Bergman, *Science*, **223**, 902 (1984).

31. R. A. Periana, P. O. Stoutland, and R. G. Bergman, unpublished results.

32. H. B. Kagan and J. C. Frian, in *Topics in Stereochemistry*; N. L. Allinger, and E. L. Eliel, Eds; Wiley, New York; 1977, Volume 10.

33. W. S. Knowles, M. J. Sabacky, B. D. Vineyard, and C. J. Winkauff, *J. Am. Chem. Soc.*, **97**, 2567 (1975).

34. M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6262 (1977).

35. A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souch, and R. Noyori, *J. Am. Chem. Soc.*, **102**, 7932 (1980).