Fe–Fe distances and the dihedral angles between the two triangular wings of the cluster are nearly identical in I and II. Compared to Fe_4C clusters containing an underivatized carbido carbon, the wingtips of the cluster in I and II are opened up to give a greater dihedral angle and longer Fe–C distances for the wingtip Fe atoms. In both I and II, the carbon p orbitals, which in the underivatized Fe_4C clusters were used only for bonding with the cluster Fe atoms, are now used for bonding within the organic group as well as for cluster bonding. Steric constraints on the orientations of the carbomethoxy group in I and on the acetyl group in II were examined in a semiquantitative fashion by using simple interactive molecular graphics routines. In I, the observed axial orientation of the organic group that optimizes bonding interactions is found also to minimize steric repulsions. In II the observed off-axis tilt of the acetyl group is shown similarly to reflect steric constraints. The molecular orbital calculations suggest that bonding interactions are not disrupted by this reorientation of the organic group in the Fe(1)Fe(4)C(14) (approximate) plane. The interactive molecular graphics routines were also used to generate a model for the structure of II based on the molecular structure of the $Fe_4(CO)_{12}C$ core in I. The reasonable correspondence between the observed and "predicted" orientations of the acetyl group demonstrates the possible utility of these simple methods in predicting certain cluster conformations.

Acknowledgment. The authors acknowledge with gratitude a stimulating correspondence with Professor D. F. Shriver on the subject of molecular graphics and its limitations and for access to a preprint of ref 31.

Registry No. I, 72872-04-9; II, 99922-06-2; $Et_4N[HFe_4C(CO)_{12}]$, 79723-27-6; $(Et_4N)_2[Fe_4C(CO)_{12}]$, 83270-11-5; $(Et_4N)_2[Fe_6C(CO)_{16}]$, 11087-55-1; $FeCl_3$, 7705-08-0.

Supplementary Material Available: Tables of anisotropic thermal parameters for I and II (4 pages); tables of structure factors for I and II (30 pages). Ordering information is given on any current masthead page.

Preparation and Reactions of an Alkylzinc Enolate

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The preparation, characterization, and reactivity of ethylzinc enolate **3** are reported. Enolate **3** is less reactive than the corresponding lithium enolate but undergoes many of the same reactions. The unprecedented protonation of **3** by secondary amines is reported. The metal exchange reaction used to prepare **3** is not a general method for the preparation of other alkylzinc enolates.

Recent interest in the stereochemistry of the aldol addition reaction[1] has resulted in significant interest in the specific generation and characterization of metal enolates.[2,3] Those involving zinc have received less attention, although they would appear to offer additional coordination sites for the incorporation of auxiliary ligands for stereocontrol. The most general methods for the direct generation of zinc enolates are metal exchange between lithium enolates and zinc chloride[4] and reduction of α-bromo carbonyl compounds, as in the Reformatsky reaction.[5] In addition to these methods for preparing halozinc enolates, there are a few reports on the synthesis of alkylzinc enolates. Dialkylzinc reagents are useful polymerization catalysts; however, addition of diethylzinc to chalcone affords a stable ethylzinc enolate which has been characterized (eq 1).[6] The direct synthesis of *n*-butyl(dimethyl malonato)zinc by deprotonation of dimethyl malonate with di-*n*-butylzinc has been demonstrated (eq 2).[7] This approach is probably not applicable to the synthesis of nonactivated ketone enolates due to the low basicity of dialkylzinc reagents.[8] Boersma and co-workers[4b] have reported that the exchange reaction between ethylzinc methoxide and enol acetates affords ethylzinc enolates that decompose by polymerization or by reaction

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(1) For reviews of the aldol reaction, see: (a) Mukaiyama, T. *Organic Reactions*; Wiley: New York, 1982; Vol. 28, p 203. (b) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, p 111. (c) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1.

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(3) For crystallographic structural studies of transition-metal enolates, see: (a) Heathcock, C. H.; Doney, J. J.; Bergman, R. G. *Pure Appl. Chem.* **1985**, *57*, 1789 and ref 26 and 27 therein. (b) Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 3724. (c) Grassi, A.; Longo, P.; Musco, A.; Porzio, W.; Scrivanti, A. *J. Organomet. Chem.* **1985**, *289*, 439. (d) Planalp, R. P.; Andersen, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 7774. (e) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *Ibid.* **1983**, *105*, 2068. (f) Czauderna, B.; Jogun, K. H.; Stezowski, J. J.; Foehlisch, B. *Ibid.* **1976**, *89*, 6696. (g) Mercury enolate: Potenza, J. A.; Zyontz, L.; San Filippo, J.; Lancette, R. A. *Acta. Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2624.

(4) See the seminal paper by House: (a) House, H. O.; Crumine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *J. Am. Soc. Chem.* **1973**, *95*, 3310. See the recent work by Boersma where self-condensation of chlorozinc enolates was observed: (b) Dekker, J.; Schouten, A.; Budzelaar, P. H. M.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1987**, *320*, 1.

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(7) Kawakami, Y.; Tsuruta, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 247.

(8) Inoue, S.; Imanaka, Y. *J. Organomet. Chem.* **1972**, *35*, 1.

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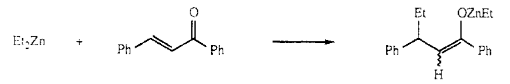
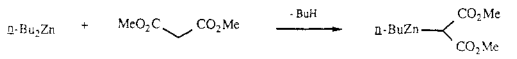
with the methyl acetate produced in the exchange reaction (eq 3). In a related approach, a metal exchange reaction between (−)-menthyl bromoacetate and di-*n*-propylzinc affords a zinc ester enolate which reacts with benzaldehyde (eq 4).[9] The intermediate alkylzinc enolate presumably formed in this latter method has not been studied.



(1)



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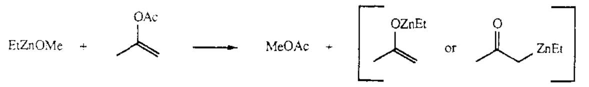

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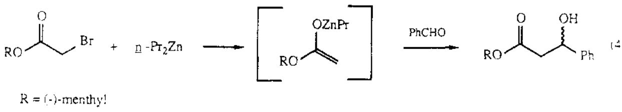
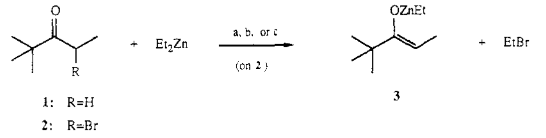


(4)

R = (-)-menthyl

In connection with a continuing study of stereoselective aldol reactions, we explored the preparation of alkylzinc enolates via metal exchange with a dialkylzinc reagent and their reaction with carbonyl compounds, in both the absence and presence of additional ligands. In this report we describe the synthesis, characterization, and reactivity of the novel ethylzinc enolate **3**, derived from 2,2-dimethyl-3-pentanone (**1**)[10] via bromo ketone **2**. This system was chosen for our initial investigation, since the corresponding lithium[11] and magnesium[12] enolates have been well-studied.

The requisite bromo ketone **2**[12] was synthesized by the reaction of **1** with bromine in carbon tetrachloride. Equimolar quantities of **2** and commercial diethylzinc were combined under nitrogen, and the reaction was followed by ^{1}H NMR spectroscopy (eq 5). Either C_6D_6 or tetrahydrofuran-d_8 (THF-d_8) were suitable solvents for the reaction; however, a substantial rate enhancement was observed in THF-d_8. The desired ethylzinc enolate **3** was isolated as a colorless oil in quantitative yield and >90% purity by removing the volatile material under vacuum (0.05 torr). Enolate **3** could not be crystallized and was not stable to chromatography; however, it was of sufficient purity to be used in subsequent reactions. The thermal stability of **3** is remarkable; no decomposition was observed in a glovebox after days at room temperature or weeks at −40 °C. However, **3** decomposes readily upon exposure to air or moisture. On a preparative scale (5 mmol), **3** was prepared in a glovebox under nitrogen by slow addition of diethylzinc (10% excess) to **2**. After 2 h the bromoethane was removed under vacuum to afford **3** in quantitative yield.



(5)

a. C_6D_6, 80 °C, 20-30 h b. THF-d_8, 67 °C, 3 h c. THF-d_8, 25 °C, 50 h

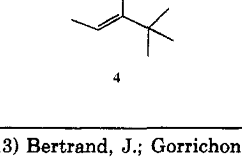
Table I. Comparison of NMR Spectral Data for 2,2-Dimethyl-3-pentanone Enolates

		chem shift, ppm				
M	solv	C_1[a]	C_2[b]	H_a[c]	J_{C-H}, Hz	ref
$ZnCH_2CH_3$	THF-d_8	165.5	93.0	4.41	155	
ZnBr	THF	164.7	96.6	...	...	13
MgBr	ether	162.4	95.5	4.54	154	15
Na	ether	172.3	78.2	3.84	152	15
Li	Benzene	169	84	...	...	16
HgBr	benzene	213	51	...	140	16

[a] Former carbonyl carbon. [b] Enolate vinylic carbon. [c] Enolate vinylic hydrogen.

Enolate **3** was characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The important data are summarized in Table I and compared with data for other enolates. Ethylzinc enolate **3** and the bromozinc enolate[13] have similar ^{13}C NMR characteristics. Although zinc ketone enolates are generally considered to exist with an oxygen- rather than a carbon-bound metal, there is still some controversy.[14] Two pieces of data in Table I strongly indicate that **3** contains an oxygen-bound metal. First, the ^{13}C chemical shift of C_1 in **3** is similar to that of the oxygen-bound magnesium, sodium, and lithium enolates[2] and not the presumably carbon-bound mercury enolate.[3g] Second, the coupling constant J_{C2-H_a} of **3** is nearly identical with that observed for the sodium and magnesium enolates[15] and different from the coupling constant of the mercury enolate.[16] The *Z* stereochemistry shown for **3** was confirmed by a nuclear Overhauser enhancement difference experiment. Irradiation of H_a enhanced the *tert*-butyl and vinyl methyl proton signals; irradiation of the vinyl methyl protons enhanced H_a only.

Enolate **3** was found to exist as a dimer by mass spectroscopy, $M_r(^{64}Zn)$ 412. The molecular weight in pentane solution was found to be 476 ± 17 (average of three trials) by isothermal distillation using the Singer method.[17] This value indicates that **3** also exists as a dimer in pentane solution. The discrepancy between the observed solution molecular weight and that expected for a dimer of **3** (M_r(calcd) 415) can be explained by the limited purity of **3**. The structure of this dimer is unknown, but it may be similar to the solvated dimer structure **4** determined for the corresponding bromomagnesium enolate by X-ray analysis.[2c] An alternative structure similar to that reported for the Reformatsky reagent derived from *tert*-butyl bromoacetate **5**[5d] seems less likely because the NMR data for **3** indicate an oxygen-bound metal.



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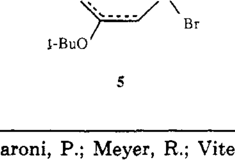

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[9] (a) Palmer, M. H.; Reid, J. A. *J. Chem. Soc.* **1962**, 1762. (b) Scott, L. T.; Cotton, W. D. *J. Am. Chem. Soc.* **1973**, *95*, 2708. (c) For use of an organocadmium reagent in a "Reformatsky" reaction, see: Cason, J.; Fessenden, R. J. *J. Org. Chem.* **1957**, *22*, 1326.

[10] Obtained from the reaction of trimethylacetamide with excess ethylmagnesium bromide: Whitmore, F. C.; Noll, C. I.; Mennier, V. C. *J. Am. Chem. Soc.* **1939**, *61*, 683.

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[15] Fellman, P.; Dubois, J.-E. *Tetrahedron Lett.* **1977**, *18*, 247.

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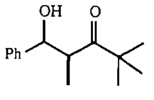
Table II. Aldol Reactions of Enolate 3 in the Presence of Diamine Ligands

entry	diamine	solv	temp, °C	yield,[a] %	ratio 6:7[b]	optical purity of 6,[c] % ee
1	none	THF	−78	93	98:2	...
2	none	pentane	25	76	95:5	...
3	8	THF	−78	66	17:83	20 (*S*,*S*)
4	8	ether	−78	74	16:84	26 (*R*,*R*)
5	8	toluene	−78	86	23:77	23 (*R*,*R*)
6	8	THF	25	66	40:60	...
7	TMEDA	THF	−78	90	78:22	...

[a] Yield after chromatography on silica gel. [b] The diastereomer ratio was determined by integration of the distinctive carbinol proton in the ^{1}H NMR spectrum of the crude product. [c] The enantiomer in excess is shown in parentheses. See ref 21.

The reactivity of 3 with various electrophiles was examined. The reaction of 3 with benzaldehyde was studied under various conditions, and the results are summarized in Table II. Benzaldehyde was added to a solution of 3 in an appropriate solvent at the specified temperature, and after 20 min the reaction was quenched with aqueous ammonium chloride. Standard workup afforded the known syn and anti aldols 6 and 7.[11,12] Condensation of 3 in THF at −78 °C gave 6 with high simple diastereoselection (entry 1). This syn selectivity is similar to that observed with the corresponding lithium enolate and indicates a kinetic preference for formation of the syn diastereomer.[12,18] Reaction of 3 in pentane at 25 °C also afforded 6 selectively (entry 2). Comparison with the corresponding lithium enolate indicates that the expected equilibration of the syn aldolate to the more stable anti aldolate in pentane is somewhat slower for 3 than for the lithium enolate.[18]



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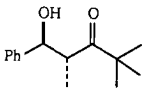
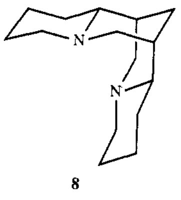


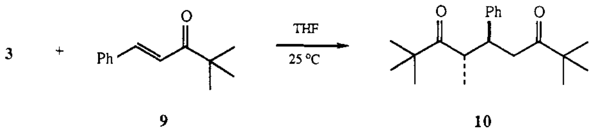
7

The work of Guette[19] using (−)-sparteine (8) as a chiral auxiliary in the Reformatsky reaction prompted us to look at the aldol condensation of 3 in the presence of 8. One mole of 8[20] was added to 3 at room temperature, the reaction mixture was cooled to −78 °C, and benzaldehyde was added. The results in Table II show that the presence of 8 had an unexpected effect upon the diastereoselectivity of the addition. A moderate anti selectivity was observed in THF, ether, and toluene (entries 3–5), while a smaller anti selectivity was observed at room temperature in THF (entry 6). This implicates a kinetic preference for formation of 7 rather than a facile equilibration of the initially formed syn aldolate to the more stable anti aldolate in the presence of 8.[18] When tetramethylethylenediamine (TMEDA) was used instead of 8 the reaction was syn selective but much less so than in the absence of a diamine (entry 7). The origin of the anti selectivity induced by 8 in these reactions is unclear. Table II also shows that 8 is not an effective chiral auxiliary in this aldol reaction.[21]



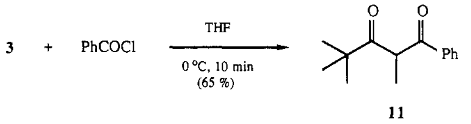
8

The reaction of 3 with other electrophiles was also investigated. Reaction of 3 with 2,2-dimethyl-5-phenyl-4-penten-3-one (9)[22] at −78 °C in ether was slow in contrast to the facile reaction of 9 with lithium enolates.[23] However, reaction of 9 with 1.5 mol of 3 in THF at 25 °C for 5 h afforded the anti Michael adduct 10[23c] in 76% yield, along with two minor, uncharacterized products (eq 6).



(6)

Treatment of 3 with benzoyl chloride gave the C-acylated product 11[24] exclusively in 65% yield (eq 7). Treatment of 3 with trimethylsilyl chloride gave *Z* enol silane 12[11,12] in 66% yield (eq 8). These reactions show that 3 is less reactive toward electrophiles than the corresponding lithium enolate. Each enolate affords the same reaction products in good yield, but the reactions of 3 can be carried out at room temperature.



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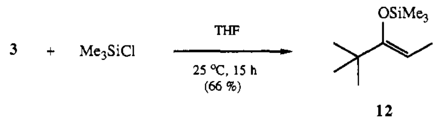

(8)

The protonation of 3 was investigated by adding a proton source to a solution of 3 in benzene and following the formation of 1 by ^{1}H NMR spectroscopy. Methanol caused complete conversion of 3 to 1 after 10 min at 25 °C. Diphenylamine (13) was treated with 3 at 25 °C in a sealed NMR tube; after 88 h the 3:1 ratio was 1.1:1 (eq 9). Longer reaction times did not alter this ratio. In order to show that an equilibrium had been established, the reaction shown in eq 9 was carried out in the reverse direction. Ethylzinc diphenylamide (14) was prepared by a literature procedure.[25] Reaction of equimolar quantities of 14 and 1 was followed by ^{1}H NMR spectroscopy, and after 69 h an invariant 3:1 ratio of 1:1 was attained. These

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[18] Heathcock, C. H.; Lampe, J. *J. Org. Chem.* **1983**, *48*, 4330.

[19] Guette, M.; Capillon, J.; Guette, J.-P. *Tetrahedron* **1973**, *29*, 3659.

[20] (−)-Sparteine was obtained as the hydrogen sulfate from Tokyo Kasei Chemical Co. and distilled from sodium hydroxide: bp 60–80 °C (0.02 torr); $[\alpha]_D$ −17.5°, (*c* 1.0 g/100 mL of ethanol).

[21] The enantiomeric excess of 6 was determined by using a Pirkle 1A chirally modified HPLC column. Diastereomers 6 and 7 had comparable optical purities. See: Pirkle, W. H.; Finn, J. M. *J. Org. Chem.* **1981**, *46*, 2935.

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[23] (a) Lithium amide enolate: Heathcock, C. H.; Henderson, M. A.; Oare, D. A.; Sanner, M. A. *J. Org. Chem.* **1985**, *50*, 3019. (b) Lithium ester enolate: Heathcock, C. H.; Oare, D. A. *J. Org. Chem.* **1985**, *50*, 3022. (c) Lithium ketone enolate: Oare, D. A.; Heathcock, C. H. *Tetrahedron Lett.*, in press.

[24] Maxwell, B. E. Ph.D. Thesis, University of California, Berkeley, 1985.

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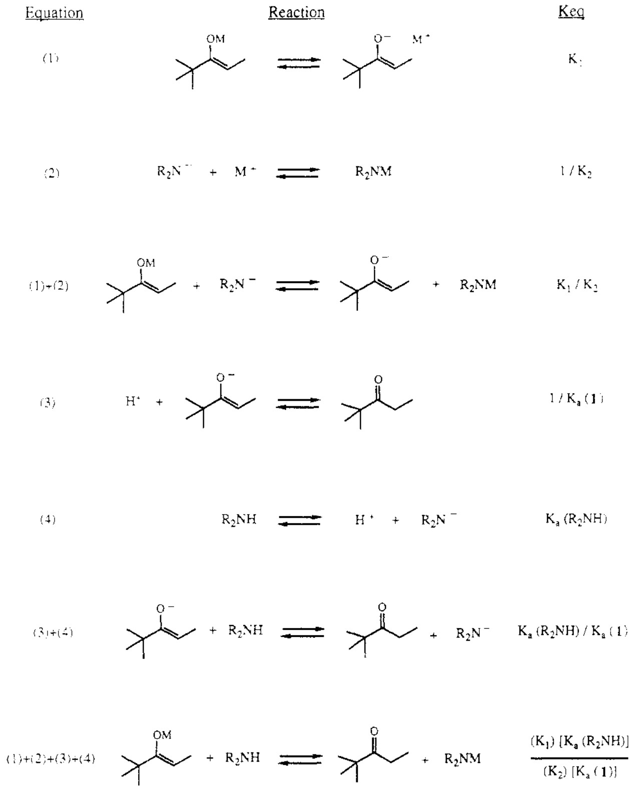
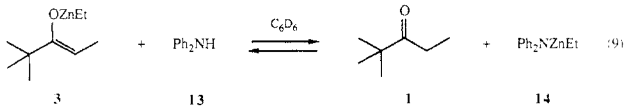
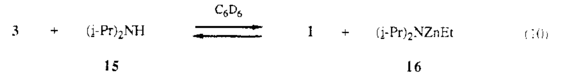
Scheme I. Relative Bond Heterolysis Constants for Eq 11



experiments establish that the reaction shown in eq 9 has an equilibrium constant near unity.

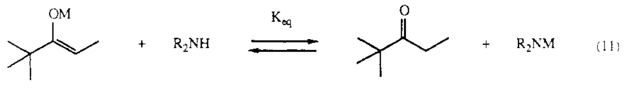


Partial protonation of **3** by the less acidic diisopropylamine (**15**) was also achieved, although heating was required to attain a reasonable reaction rate (eq 10). After 4 days at 45 °C the **3**:**1** ratio was 1.5:1; longer reaction times did not alter this ratio. In order to verify that equilibrium had been reached, ethylzinc diisopropylamide (**16**) was prepared by treatment of lithium diisopropylamide[26] with ethylzinc chloride.[27] Reaction of equimolar quantities of **16** and **1** at 45 °C for 29 h led to a **3**:**1** ratio which remained at 1.2:1. Therefore, the equilibrium constant for the reaction shown in eq 10 is also on the order of one.



$$3 + \underset{15}{(i\text{-Pr})_2NH} \xrightleftharpoons{C_6D_6} 1 + \underset{16}{(i\text{-Pr})_2NZnEt} \qquad (10)$$

The near thermoneutral character of the equilibria in eq 9 and 10 is in agreement with the recent report by Bryndza and co-workers[28] on the thermoneutral equilibria between organoruthenium and organoplatinum alkoxides and amides. However, the partial protonation of enolate **3** by secondary amines seems unusual because such equilibria generally favor the enolate for group I (1[39]) and II (2[39]) metals.[29] This discrepancy can be understood if the relative *heterolytic* bond dissociation constants are considered.[30] As shown in Scheme I, the equilibrium constant (K_{eq}) for reaction of a secondary amine with an enolate (eq 11) may be expressed as the product of the ratio of acid dissociation constants (K_a values) and the ratio of M–O and M–N heterolytic bond dissociation constants (K_1, K_2).

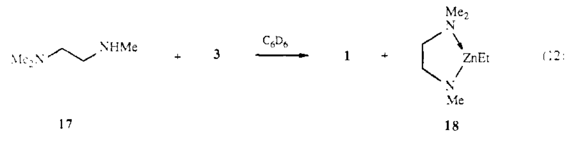


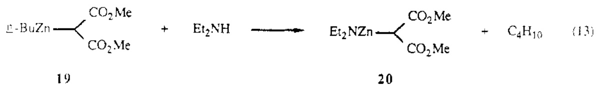
$$K_{eq} = (K_1/K_2)\,[K_a(R_2NH)/K_a(1)]$$

This formula is often used to estimate the K_{eq} of eq 11 for group I (1) and II (2) metal enolates.[29] In this case both the M–O and M–N bonds are ionic; i.e., K_1 and K_2 are both large and probably of a similar magnitude. Therefore, the ratio K_1/K_2 cancels and only the ratio of K_a's of the ketone and the amine is important. Using available acid dissociation constants for diphenylamine (pK_a = 22.4 in aqueous DMSO),[31] diisopropylamine (pK_a = 35.7 in THF),[32] and ketone **1** ($pK_a \simeq 21$),[33] we predict that for reactions between an alkali-metal enolate and diphenylamine or diisopropylamine, $K_{eq} \simeq 10^{-1}$ or 10^{-15}, respectively.

Such an analysis is not valid when M = ZnEt because Zn–O and Zn–N bonds are highly covalent. The ratio K_1/K_2, representing the relative extent of heterolysis of the Zn–O and Zn–N bonds, is now important. Since we have determined that for **3** K_{eq} is approximately one when R = Ph (eq 9) or R = *i*-Pr (eq 10), we can calculate the ratio K_1/K_2 in each case. Substitution of the appropriate values shows that $K_2 = 10^{-1}(K_1)$ and K_2 and $10^{-15}(K_1)$ for diphenylamine and diisopropylamine, respectively. In each case the Zn–N bond of the amide is more associated than the Zn–O bond of the enolate. Because the intrinsically more basic nitrogen anions are bound tightly via a covalent bond to zinc, they do not deprotonate **1** to the extent we expect. In addition, changing from diphenylamine to the more basic anion of diisopropylamine does not significantly change the K_{eq} of eq 11 because there is a concomitant decrease in the dissociation constant K_2 of the zinc amide.

An additional effect that should be considered in this case is the aggregation, both of the enolate and of the metal amide. Enolate **3** is probably dimeric in solution, and **14** is known to be dimeric in benzene.[25] An example in which chelation apparently shifts the equilibrium completely in favor of the zinc amide is the reaction of diamine **17** with **3** to give complete conversion to **1** after 40 min at 25 °C (eq 12). The reaction of **3** with amines to liberate **1** rather than ethane is to be contrasted with the reported reaction of **19** with diethylamine to afford zinc amide **20** (eq 13).[7]





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(26) Purchased as a white powder from Aldrich Chemical Co.

(27) Boersma, J.; Noltes, J. G. *Tetrahedron Lett.* **1966**, *1521.*

(28) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.

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(30) This analysis is essentially that applied by Bryndza and coworkers to the equilibria they observed between platinum and ruthenium alkoxides and amides; see ref 28.

(31) Stewart, P.; Douglass, P. *Can. J. Chem.* **1967**, *45*, 911.

(32) Fraser, R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232.

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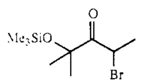
In order to investigate the reactivity of alkylzinc enolates further, we attempted the synthesis of some analogs of **3**. Bromo ketones **21–23** and the commercially available bromo esters **24** and **25** were studied. Compound **21** was synthesized by addition of the lithium enolate of 2-methyl-2-((trimethylsilyl)oxy)pentan-3-one[34] to bromine in THF at −78 °C.[35] Compounds **22**[36] and **23**[37] were synthesized according to the literature procedures. The reaction of diethylzinc with **21–25** was performed in both C_6D_6 and THF-d_8 by using the conditions employed for the synthesis of **3**; however, the results were disappointing. Either multiple products were formed (**22–25**), or the desired enolate was formed in low yield and unacceptable purity (**21**). In addition, synthesis of the methyl analogue of **3** was attempted by reacting dimethylzinc[38] with **2**. Reaction did not occur in C_6D_6, and in THF-d_8 the desired enolate was formed along with a number of byproducts.



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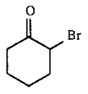

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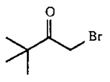

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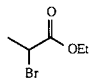

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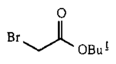

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In conclusion, the synthesis of ethylzinc enolate **3** from α-bromo ketone **2** and diethylzinc was accomplished in high yield. Enolate **3** is less reactive than the corresponding lithium enolate but undergoes many of the same reactions. However, the partial protonation of **3** by secondary amines has no precedent in alkali-metal enolate chemistry. The ramifications of this finding must be considered during the synthesis of any enolate of a relatively electronegative metal. The traditional method of enolate synthesis via deprotonation of a ketone with the appropriate metal amide is not expected to afford the enolate quantitatively. The thermal stability of alkylzinc enolates makes them useful for study of the structure and reactivity of zinc enolates, although the reaction of α-bromo carbonyl compounds with diethylzinc is not a general method for their preparation. We are presently pursuing alternative methods of preparing alkylzinc enolates to allow further investigation of their chemistry.

Experimental Section

General Data. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone immediately prior to use. Deuteriated solvents were dried over sodium/benzophenone, degassed under vacuum, and vacuum transferred into a dispensing container. NMR reactions were run on a 0.4-mmol scale in ca. 0.5 mL of solvent unless otherwise noted. The reagents were added to an NMR tube in a glovebox under nitrogen, and the tube was capped with a septum cap. For NMR reactions requiring a number of days the NMR tube was subsequently sealed under vacuum. All reactions involving organometallic reagents were conducted under a nitrogen atmosphere. IR spectra were recorded with a Perkin-Elmer Model 1420 ratio recording spectrometer. ^1H NMR spectra were obtained with the UCB 250, an FT instrument operating at 250 MHz. ^{13}C NMR spectra were obtained at 125 MHz with a Bruker AM-500 NMR spectrometer. In some cases distortionless enhancement by polarization transfer (DEPT) was used to assign the carbon resonances as CH_3, CH_2, CH, or C. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Significant ^1H NMR data are tabulated in order: number of protons, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), and coupling constant(s) in hertz. High-pressure liquid chromatography was performed with a Waters Model ALC/GPC-244 liquid chromatograph and a specified column. Gas chromatography was performed with a Varian Aerograph Model 920 instrument using a 4% Carbowax 20M on 60/80 mesh Chromosorb G column. Electron-impact mass spectra were recorded at the University of California, Berkeley (UCB) mass spectral facility on an Atlas MS-12, Consolidated 12-110B, or Finnegan 400 mass spectrometer. Elemental analyses were performed by the Micro-analytical Laboratory operated by the UCB College of Chemistry.

Standard Workup Procedure. After the reaction mixture had been quenched it was partitioned between H_2O and ether in a separatory funnel. The layers were separated and the aqueous layer was extracted with ether. The combined organic layers were washed with brine and dried ($MgSO_4$). The solvent was removed with a rotary evaporator to afford the organic products.

Ethylzinc Enolate 3. A. NMR Scale. To a dry NMR tube was added 1 mL of C_6D_6 in a glovebox under N_2. Bromo ketone **2**[12] (157 μL, 1 mmol) and diethylzinc (102 μL, 1 mmol) were added via syringe. The NMR tube was capped with a septum and removed from the glovebox. The septum cap was wrapped with Parafilm, and the reaction was followed by ^1H NMR spectroscopy. After 20–30 h at 75 °C the volatile material was removed under vacuum (0.06 torr, 2 h) to afford a quantitative crude yield of **3** (>90% pure by ^1H NMR spectroscopy) as a clear, colorless oil: IR (C_6H_6) 3030–2850, 1659, 1469, 1320, 1141, 1008 cm^{-1}; ^1H NMR (250 MHz, C_6D_6) δ 0.66 (q, 2, J = 8.1 Hz), 1.13 (s, 9), 1.37 (t, 3, J = 8.1 Hz), 1.68 (d, 3, J = 6.5 Hz), 4.60 (q, 1, J = 6.5 Hz); MS (^{64}Zn), m/z (relative intensity) 412 (0.09), 383 (0.46), 299 (6.11), 206 (15.03), 177 (10.47), 93 (base); exact mass calcd for $C_{18}H_{36}O_2{}^{64}Zn_2$ 412.1298, found 412.1300. Enolate **3** could also be prepared in THF-d_8. The reaction proceeded more rapidly in this solvent. After 49 h at room temperature the volatile material was removed to afford a colorless oil: ^1H NMR (250 MHz, THF-d_8) δ 0.18 (q, 2, J = 8.1 Hz), 1.10 (s, 9), 1.13 (t, 3, J = 8.1 Hz), 1.65 (d, 3, J = 6.6 Hz), 4.41 (q, 1, J = 6.6 Hz); ^{13}C NMR (125 MHz, THF-d_8) δ −0.244 (CH_2), 11.670 (CH_3), 12.428 (CH_3), 29.211 (CH_3), 37.403 (C), 92.977 (CH), 165.528 (C). The density of **3** was 1.1 g/mL.

B. Preparative Scale. To 785 μL (5.0 mmol) of **2** was slowly added 563 μL (5.5 mmol) of diethylzinc in a glovebox under N_2. The solution initially turned yellow but was colorless after 2 h at 25 °C. The volatile material was removed under vacuum to afford a quantitative crude yield of **3** which was >90% pure.

Aldol Reaction. The following general procedure was employed. To a 10-mL flask in a glovebox was added 25 μL (0.14 mmol) of **3**. The flask was capped with a septum and removed from the glovebox. The septum was pierced with an N_2 inlet needle, and 1 mL of dry solvent was added. A diamine ligand (0.14 mmol) was added via syringe, and the solution was cooled to −78 °C. Freshly distilled benzaldehyde (14 μL, 0.14 mmol) was added via syringe. After 10 min, 1 mL of aqueous NH_4Cl was added and the mixture was allowed to warm to room temperature. Standard workup afforded a mixture of **6** and **7** as determined by ^1H NMR spectroscopy.[11,12] The aldols were purified by chromatography on silica gel, and a Pirkle 1A chirally-modified HPLC column[19] was employed to determine the enantiomeric excess of **7**. Data are summarized in Table II.

Michael Addition. To a 10-mL flask in a glovebox was added 102 μL (0.54 mmol) of **3**. The flask was capped with a septum and removed from the glovebox. The septum was pierced with an N_2 inlet needle, and **3** was dissolved in 1 mL of THF. Enone **9**[22] (68 mg, 0.36 mmol) in 1 mL of THF was added, and after 5 h the reaction mixture was cooled to 0 °C and quenched with saturated aqueous NH_4Cl. Standard workup afforded a gummy solid that was shown to contain less than 5% of the syn Michael adduct by ^1H NMR spectroscopy. Chromatography on silica gel

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(38) Galer, A. L.; Wilkinson, G. *Inorg. Synth.* **1979**, *19*, 253.

(39) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13–18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(4% ether/hexanes) afforded 83 mg (76%) of **10**, mp 102.5–104 °C. Anti Michael adduct **10** was identified by comparison of its ^1H NMR spectrum and melting point with those of an authentic sample.[23c]

Reaction with Benzoyl Chloride. To a 10-mL flask in a glovebox was added 106 μL (0.5 mmol) of **3**. The flask was capped with a septum and removed from the glovebox. The septum was pierced with an N_2 inlet needle, and **3** was dissolved in 1 mL of THF. Benzoyl chloride (58 μL, 0.5 mmol, distilled from $CaCO_3$) in 1 mL of THF was added at 0 °C, and after 10 min the reaction mixture was quenched with saturated aqueous $NaHCO_3$. Standard workup afforded a white solid. Chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluant provided 70 mg (65%) of a white solid, mp 89–90.5 °C. Compound **11** was identified by comparison of its ^1H NMR spectrum and melting point with those of an authentic sample.[24]

Reaction with Trimethylsilyl Chloride. To a 10-mL flask in a glovebox was added 207 μL (1 mmol) of **3**. Enolate **3** was dissolved in 2 mL of THF, and 152 μL (1.2 mmol) of trimethylsilyl chloride was added. After 15 h, the reaction mixture was diluted with 6 mL of pentane, removed form the glovebox, and partitioned between pentane and saturated aqueous $NaHCO_3$. Standard workup afforded **12** in quantitative crude yield. Bulb-to-bulb distillation (25 °C, 0.05 torr) provided 122 mg (66%) of a colorless oil. Enol silane **12** was identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[11,12]

Ethylzinc Diisopropylamide (16). To a 10-mL flask in a glovebox under N_2 was added 253 mg (2.36 mmol) of lithium diisopropylamide.[26] To this solid in 4 mL of ether was added 306 mg (2.36 mmol) of ethylzinc chloride[27] in 3 mL of ether over 2 min. The white suspension was stirred for 15 min and filtered through a fine glass frit. The solvent was removed under vacuum to afford a white foam which was dissolved in 4 mL of pentane and filtered through a fine glass frit to remove some residual lithium chloride. The solvent was removed under vacuum to afford 438 mg (95%) of a gummy, white solid: mp 132–136 °C dec; IR (C_6H_6) 3020–2760, 1465, 1385, 1368, 1160, 910 cm^{-1}; ^1H NMR (250 MHz, C_6D_6) δ 0.57 (q, 2, J = 8.1 Hz), 1.08 (d, 12, J = 6.5 Hz), 1.54 (t, 3, J = 8.1 Hz), 3.08 (heptet, 2, J = 6.5 Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 6.246, 13.350, 26.729, 49.468. Anal. Calcd for $C_8H_{19}NZn$: C, 49.37; H, 9.84; N, 7.20. Found: C, 49.44; H, 10.07; N, 7.02.

4-Bromo-2-methyl-2-((trimethylsilyl)oxy)pentan-3-one (21). To a 100-mL flask was added 15 mL of THF and 2.32 mL (16.5 mmol) of diisopropylamine (distilled from CaH_2). The solution was cooled to 0 °C, and 10.5 mL (15.8 mmol) of a 1.5 M solution of n-BuLi in hexane was added via syringe over 5 min. After being stirred 10 min, the solution was cooled to −78 °C and 3.24 mL (15 mmol) of 2-methyl-2-((trimethylsilyl)oxy)pentan-3-one[34] in 15 mL of THF was added over 10 min. After 10 min at −78 °C the reaction mixture was allowed to warm to room temperature. In a separate 100-mL flask, 930 μL (18 mmol) of bromine was added to 15 mL of THF. The solution was cooled to −78 °C, and the enolate solution was added dropwise over 20 min. An additional 10 mL of THF was added during the addition as stirring became slow. The orange bromine color was dissipated when only about half of the enolate solution had been added. The reaction was quenched with 20 mL of saturated aqueous $NaHCO_3$ after 1 min. The mixture was allowed to warm to room temperature and partitioned between pentane and aqueous $NaHSO_3$. The layers were separated, and the aqueous layer was washed with pentane. The combined organic layers were washed sequentially with aqueous $NaHSO_3$ and brine and dried (Na_2SO_4). The solvent was removed with a rotary evaporator to afford 4.39 g of a colorless oil. ^1H NMR analysis indicated that the bromo ketone was ca. 90% pure. Distillation at 25 torr caused significant decomposition; however, the pink fractions boiling between 112 and 121 °C were purified by bulb-to-bulb distillation at 0.03 torr to afford 2.58 g (64%) of **21** as a colorless oil. An unidentified impurity (<10%) remained which was not removed by subsequent distillation at 1.2 torr: IR (film) 2970, 1725, 1260, 1205, 1050, 895, 850 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.19 (s, 9), 1.35 (s, 3), 1.54 (s, 3), 1.71 (d, 3, J = 6.8 Hz), 5.18 (q, 1, J = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 2.197, 20.709, 27.882, 28.898, 39.848, 79.934, 208.947. An analytical sample was prepared by preparative GC. Anal. Calcd for $C_9H_{19}O_2BrSi$: C, 40.45; H, 7.17; Br, 29.90. Found: C, 40.33; H, 7.28; Br, 29.84.

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Synthesis, Structure, and Ligand Dynamics of $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}CH_3C{=}NCH_2CH_3)Ru_3(CO)_9$

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The reaction of triethylamine with $Ru_3(CO)_{12}$ in refluxing hexanes catalyzed by $Fe_2(CO)_4(SEt)_2(PPh_3)_2$ is shown to yield the complex $(\mu\text{-H})Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CH_3C{=}NCH_2CH_3)$ (I) as the major product (30%). An X-ray crystallographic investigation of I reveals that the organic ligand is parallel to one edge of the metal triangle and acts as a five-electron donor. The hydride was located; it symmetrically bridges the two metal atoms parallel to the C–N vector and is in the plane of the metal triangle. Compound I crystallizes in the $P\bar{1}$ space group with a = 8.396 (2) Å, b = 15.198 (3) Å, c = 8.093 (2) Å, α = 102.95 (2)°, β = 108.63 (2)°, and γ = 90.33 (2)°. Least-squares refinement based on 2867 observed reflections led to a final R value of 3.3% (R_w = 4.4%). The variable-temperature ^1H and ^{13}C NMR spectra reveal that the organic ligand is fluxional, undergoing restricted oscillatory motion which is coupled to hydride edge hopping and axial–radial exchange on two of the three ruthenium atoms.

Introduction

The cleavage of nitrogen–carbon bonds by heterogeneous transition-metal catalysts and metal cluster complexes is an area of current interest because of the importance of developing denitrification procedures for coal and petroleum refining processes.[1] Trinuclear clusters of ruthenium

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