Synthesis and Structures of Two Thermally Stable Sodides with the Macrocyclic Complexant Hexamethyl Hexacyclen

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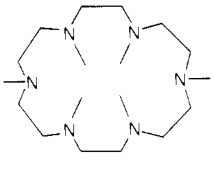
Abstract: Although a number of salts with alkali-metal anions (alkalides) or trapped electrons (electrides) are known, previously all were thermally unstable to irreversible decomposition of the cation complexant (crown ether or cryptand). By using the fully methylated nitrogen analogue of 18-crown-6, hexamethyl hexacyclen (HMHCY), two crystalline sodides, $K^+(HMHCY)Na^-$ (I) and $Cs^+(HMHCY)Na^-$ (II), have been synthesized and their crystal structures determined. The remarkable feature of HMHCY is its extreme resistance to reductive decomposition. Differential scanning calorimetry shows that compound I melts without decomposition at ~40 °C and decomplexes to yield liquid HMHCY and the alkali metals at ~74 °C while compound II melts at ~8 °C and decomplexes at ~40 °C. For both compounds, irreversible decomposition does not occur until ~140 °C. The two compounds are isostructural in the orthorhombic space group, and their crystal structures show that in each case Na^- is very nearly in contact with one alkali-metal cation. The solid may be viewed as containing closest packed contact ion pairs in which the cation is embedded in the complexant but is exposed on one face to the sodide anion. The optical spectra of thin films and the ^{23}Na MAS-NMR spectrum confirmed the presence of Na^-. The compounds are very soluble in dimethyl ether and somewhat soluble in diethyl ether and in trimethylamine. Solutions in dimethyl ether are remarkably stable. These studies point to a strategy for synthesizing thermally stable alkalides and electrides in which tertiary amine cyclic or bicyclic complexants are used to enhance stability. The limiting factor is weak cation complexation that tends to yield the free complexant and the alkali metals at elevated temperatures.

The existence of crystalline alkalides has been known since 1974[1,2] and that of crystalline electrides since 1983.[3,4] The optical and magnetic properties and a number of crystal structures of these materials have provided a great deal of insight into the nature of trapped electrons and alkali-metal anions.[5] The applicability of solutions that contain these species to organic reduction processes[6-11] and to the doping of organic semiconductors[12] has already been demonstrated. The utility of alkalides and electrides has been limited, however, by their tendency to decompose thermally. Their inherently strong reducing character requires that they be handled under an inert atmosphere or in vacuo, problems that can readily be overcome. The irreversible decomposition of these compounds at room temperatures (in times ranging from a few seconds to several days, depending on the system) poses far more severe handling and storage problems. To date, all reported alkalides and electrides have utilized either of two classes of complexing agents, crown ethers or cryptands. The thermal instability of the ionic alkalides and electrides results from reductive attack on the ether complexant by the unbound or weakly bound electrons. The cleavage of ethers by alkali metals is a complex but much-studied phenomenon.[13] This thermal instability led us to search for more robust complexing agents that would permit crystallization of alkalides and electrides yet not be as easily destroyed by reduction. This paper describes the synthesis, structure, and thermal properties of two new alkalides that utilize the complexing agent, hexamethyl hexacyclen (HMHCY, **1**; the fully methylated aza- analogue of 18-crown-6). HMHCY is extraordinarily resistant to reductive decomposition even in the presence of alkali metals at temperatures exceeding 120 °C.



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The parent unmethylated compound, hexacyclen, has been shown to complex metal cations, including alkali cations, in solution.[14] However, the somewhat acidic amino protons are readily attacked by alkali-metal anions and solvated electrons. The work of Barrett et al.[7] and Pez et al.[10] showed that it is possible to form stable dark blue solutions from mixtures of potassium, sodium, and hexamethyl hexacyclen, suggesting that this complexant might overcome the stability problems that plague alkalide-electride research.

Experimental Section

Synthesis of HMHCY. The Eschweiler-Clark methylation procedure[7] was used to prepare HMHCY, 1,4,7,10,13,16-hexaaza-1,4,7,10,13,16-hexamethylcyclooctadecane. A 5-g sample of 1,4,7,10,13,16-hexaazacyclooctadecane trisulfate (hexacyclen trisulfate; Aldrich Chemical Co.) was refluxed with formic acid (60 mL, 88%) and paraformaldehyde (12 g) for 70 h. The mixture then was dried under vacuum and brought to a pH of ~12 with 50% NaOH. The crude product was collected by solvent extraction with THF as the solvent over a period of 24 h. Vacuum distillation at ~130 °C and a manifold pressure of 2×10^{-5} Torr yielded a viscous liquid with a yellow tint. Further purification was accomplished by allowing the liquid to contact a film of potassium and sodium, followed by vacuum distillation at 100 °C (2×10^{-5} Torr). This procedure yielded a slightly less viscous clear liquid. After the initial distillation, all manipulations were performed under inert atmosphere or in vacuo to prevent contamination by water or oxygen.

Sodide Syntheses. Potassium hexamethyl hexacyclen sodide [$K^+(HMHCY)Na^-$], I, and cesium hexamethyl hexacyclen sodide [$Cs^+(HMHCY)Na^-$], II, were synthesized in a "K-Cell" by using previously reported techniques.[15-17] Dimethyl ether served as the primary solvent

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and trimethylamine as a cosolvent in both cases. Crystals with a red-orange metallic appearance for I and a dark red metallic appearance for II were obtained by slow evaporation of the solvent at −78 °C, which tended to increase the concentration of the less polar trimethylamine. Neither trimethylamine nor diethyl ether could be used as washing solvents because of high solubilities of both compounds in these solvents. The compounds were insoluble in *n*-pentane, which was therefore used as a washing solvent. All solvent was then removed, and the crystals were dried under vacuum (2×10^{-5} Torr) overnight.

Analysis. The stoichiometry was determined by hydrogen evolution, pH titration, flame emission, and ^{1}H NMR as previously described.[18] The titration curve was analyzed by acidifying with a known excess of HCl and titrating with sodium hydroxide. It was observed that acidified pure HMHCY is a triprotic species with inflection points at pH values of 4.5, 6.8, and 9.5. The inflection point at pH 4.5 is due to the excess acid, while the inflection points at pH 6.8 and 9.5 represent titrations of an additional 1 and 2 equiv of HMHCY, respectively. With the added hydroxide ions formed by reaction of Na^- with water, the titration curve was identical with the free acidified amine but shifted by an amount proportional to the number of moles of hydroxide present. Analysis of each compound was consistent with the formulas $K^+(HMHCY)Na^-$ and $Cs^+(HMHCY)Na^-$, which were confirmed by the crystal structures.

The anionic species were identified by optical absorption spectroscopy and magic angle spinning nuclear magnetic resonance (MAS-NMR). Optical spectra were obtained by dissolving a crystalline sample in methylamine and then rapidly evaporating the solvent into a side arm at liquid-nitrogen temperatures while splashing the solution onto the windows of a quartz optical cell.[19,20] A cold nitrogen gas stream (−50 °C) was used to cool the sample cell while the spectra were determined with a Beckman DK-2 spectrophotometer. The spectrum of $K^+(HMHCY)Na^-$ has a sharp peak at 15 000 cm^{-1} (660 nm) with a shoulder at 18 900 cm^{-1} (530 nm), while $Cs^+(HMHCY)Na^-$ has a broad peak at 14 900 cm^{-1} (675 nm) with a shoulder at 16 900 cm^{-1} (590 nm). These results are consistent with the spectra of previously reported sodides[15,19,20] and demonstrate the presence of Na^- in both compounds and the absence of K^- in I and Cs^- in II.

MAS-NMR spectra were obtained on polycrystalline samples. The regions of both ^{39}K and ^{23}Na were examined for I with a Bruker 180-MHz NMR (proton-frequency) spectrometer. ^{23}Na MAS-NMR gave a single resonance at −60.8 ppm [relative to Na^+(aq)], a chemical shift that is characteristic of all sodide salts.[21,22] No peaks of Na^+ or of K^- were observed. As expected on the basis of its large quadrupole broadening,[23] the signal of complexed K^+ was not seen.

For compound II, the regions of ^{133}Cs and ^{23}Na were examined. Again, ^{23}Na MAS-NMR gave a single resonance at −60 ppm [relative to Na^+(aq)]. Surprisingly, MAS-NMR gave no discernable peaks of ^{133}Cs even though Cs^+ is normally detectable in other crystalline alkalides and electrides.[21,24] No peaks were observed for Na^+ or Cs^-.

Thermal Analysis. The thermal properties of both compounds were determined by visual observation with a Thomas Hoover capillary melting point apparatus and by differential scanning calorimetry (DSC) using an E. I. du Pont de Nemours 9900 Series thermal analysis system. In the former study, the capillary tubes were loaded at room temperature under a helium atmosphere and then evacuated and flame-sealed while keeping the sample in liquid nitrogen. The observations were started at room temperature, by allowing the sample to come to equilibrium first and then heating at ~20°/min until the sample noticeably decomposed. The DSC samples were prepared under nitrogen and hermetically sealed in anodized aluminum sample pans.

Structure Determination. For $K^+(HMHCY)Na^-$, a crystalline sample was prepared as described above and then transferred in a nitrogen-filled glovebag to a copper block kept at −45 °C. The crystals were then covered with cold, purified *n*-octane to protect them from the atmosphere of the glovebag long enough for a well-formed crystal to be selected by microscopic examination. Once a suitable crystal had been found, it was mounted on the end of a glass fiber with Celvacene (medium) high-vacuum grease and transferred under a stream of cold nitrogen gas (−60 °C) to a Nicolet P3F diffractometer. The crystal was kept under a cold nitrogen gas stream (−67 °C) throughout the entire data collection to prevent thermal decomposition or oxidation. Data were recorded with Mo Kα radiation by using θ–2θ scanning techniques. The space group is orthorhombic primitive $P2_12_12_1$ with a = 11.091 (3), b = 11.172 (4), and c = 22.531 (7) Å. The refinement was initiated by using the Patterson heavy-atom method to locate the potassium positions, followed by least-squares refinement to position the sodium, carbon, and nitrogen atoms. The hydrogens were allowed to ride on their respective hosts. Final agreement factors of R = 4.5% and R_w = 5.5% were obtained for 2092 unique reflections.[25]

The structure of $Cs^+(HMHCY)Na^-$ was determined by using the same methods as for $K^+(HMHCY)Na^-$. The two sodides are isostructural with a = 11.021 (4), b = 11.411 (4), and c = 22.886 (6) Å for $Cs^+(HMHCY)Na^-$. The structure was solved by least-squares refinement using the coordinates of the atoms for $K^+(HMHCY)Na^-$ as starting values. For this compound, the hydrogens were allowed to refine. Final agreement factors of R = 3.5% and R_w = 3.6% were obtained for 4697 unique reflections.[25]

Results and Discussion

Structure. Nitrogens 4, 7, 13, and 16 in the HMHCY ring are coplanar within ±0.09 Å for I and ±0.03 Å for II, with the corresponding four methyl groups forming a cage around the alkali cation. Nitrogens 1 and 10 are below the plane 1.62 and 1.23 Å for I and 1.43 and 1.14 Å for II, with methyl groups effectively closing off the bottom of the ring. The cation is located 0.29 and 0.91 Å above the center of the plane for I and II, respectively. The cations are coordinated to all six nitrogens with K–N distances ranging from 2.90 to 3.01 Å for I and Cs–N distances ranging from 3.17 to 3.35 Å for II. The sodide anion is 4.28 Å from the potassium cation in I and 4.26 Å from the cesium cation in II.

The most unusual feature of these molecular structures is the close cation–anion distance, especially in $Cs^+(HMHCY)Na^-$. Taking the effective radii of K^+ and Cs^+ to be 1.33 and 1.69 Å, respectively[26] and the effective radius of Na^- to be between 2.50 and 2.70 Å (determined from the anionic cavity size of other sodides[2,27]), the cation–anion van der Waals separation is between 0.25 and 0.45 Å for I and between −0.13 and 0.07 Å for II. This is the first evidence for contact ion pairs between alkali-metal cations and alkali-metal anions in alkalides. It is remarkable that, in spite of their close proximity, the optical and NMR properties of Na^- show no evidence of appreciable charge transfer to the cation; that is, the properties are the same as for sodides in which Na^- is well isolated from the cation. The absence of an NMR signal for ^{133}Cs, however, may be due to a strong perturbation of the p electrons in Cs^+ as a result of this close proximity to Na^-.

In the unit cell, the molecules are ordered in a staggered arrangement to give a distorted octahedral coordination between the complexed cations and the sodium anions. The distances between K^+ and the six nearest Na^- neighbors are 4.28 Å for the "ion pair" and from 6.99 to 8.31 Å for the next five closest neighbors in I. The distances between Cs^+ and the six nearest Na^- neighbors are 4.26 Å for the ion pair and from 7.23 to 8.63 Å for the next five closest neighbors in II. Also, the sodium anions are effectively shielded from each other by the large complexed cations. The distances between Na^- and the six nearest neighboring anions range from 8.66 to 9.94 Å for I and 9.94 to 10.00 Å for II. Two views of the packing are shown in Figure 1 [these views are for $K^+(HMHCY)Na^-$; however, $Cs^+(HMHCY)Na^-$ would appear the same except for small dimensional changes].

Thermal Properties. Probably the most noteworthy feature of these materials is their resistance to thermal decomposition. When a microcrystalline sample of $K^+(HMHCY)Na^-$ is heated, as monitored by DSC (Figure 2a), it begins to melt at ~42 °C and decomplexes into the alkali metals (presumably NaK[28]) and free amine at ~74 °C. Further heating yields no sign of decomposition

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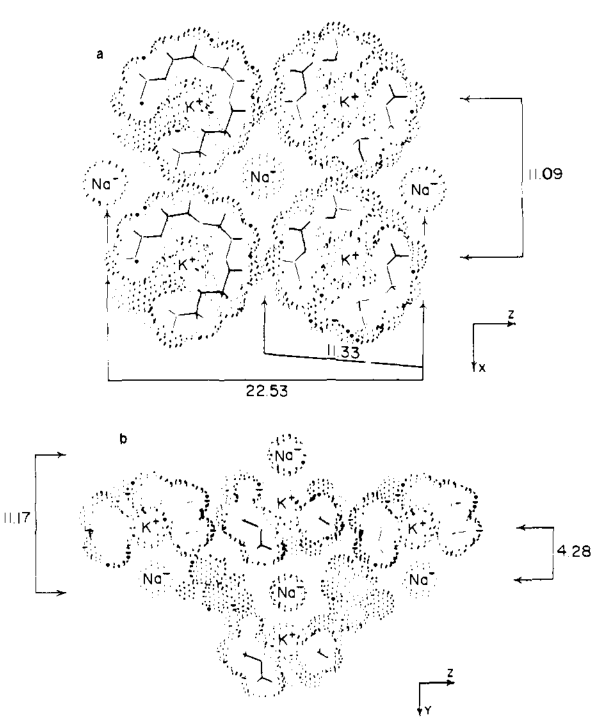

Figure 1. Two cutaway views of the cation–anion packing in $K^+(HMHCY)Na^-$ produced on an Evans and Sutherland PS-300 system with the program FRODO. The dots represent van der Waals surfaces except that Na^- is not to scale but rather fills the vacancy. View a is down the *y*-axis through the nearly coplanar array of cations and anions. View b is down the *x*-axis and shows the near contact between Na^- and K^+. Distances are in angstroms. The structure of $Cs^+(HMHCY)Na^-$ is similar.

of the complexant at temperatures up to 120 °C. To verify that the transitions indicated by DSC were melting and decomplexation, respectively, a visual observation of the heating process was also made. At approximately 40 °C, the red-orange metallic-appearing crystals melted to a form a deep blue liquid. At this point, if the sample was removed from the hot bath and immersed in liquid nitrogen, a red-orange film could be obtained. The melting and freezing were repeatable over more than one cycle. Continued heating of the sample to ~60 °C resulted in the appearance of a silvery metallic substance and a light blue liquid, which eventually became clear. The metal and complexant appeared stable until the temperature reached ~140 °C, at which point the solution became dark and a gas was evolved. In a separate experiment, the crystals were heated until they decomplexed to give a slightly pale blue solution and then cooled to −78 °C. Upon addition of dimethyl ether, the solution became dark blue, the color expected for a solvated alkali-metal anion, and red-orange films could be seen on the walls of the glass cell. These observations indicate that the endothermic process that occurs at ~74 °C in the DSC pattern is decomplexation. Further, since the exothermic decomposition does not occur until over 120 °C, HMHCY is resistant to reductive attack in the presence of alkali metals at temperatures well above 100 °C.

After the melting point was measured in the DSC, the sample was cooled to below −20 °C and reheated. This was repeated several times, but the endothermic peak at the melting point was absent except for a small dip in the base line. If, however, on the second heating the temperature was allowed to continue to increase, decomplexation occurred at the normal temperature of 74 °C. If the sample was held just above the melting point for several hours, it would remain stable until the temperature was increased to the decomplexation point. It is our belief that the crystalline compound melts at 42 °C to give a liquid, but when it is recooled, it remains in the glassy state so that no melting transition can be detected. Crystals of $K^+(HMHCY)Na^-$ that are left at room temperature decomplex after 4 days. This indicates that the solid compound is thermodynamically unstable to decomplexation at room temperature, even though it must be stable at the temperature of formation (−50 °C). The remarkable stability of the melt below 74 °C suggests that the decomplexation process must be very slow, even in the liquid state.

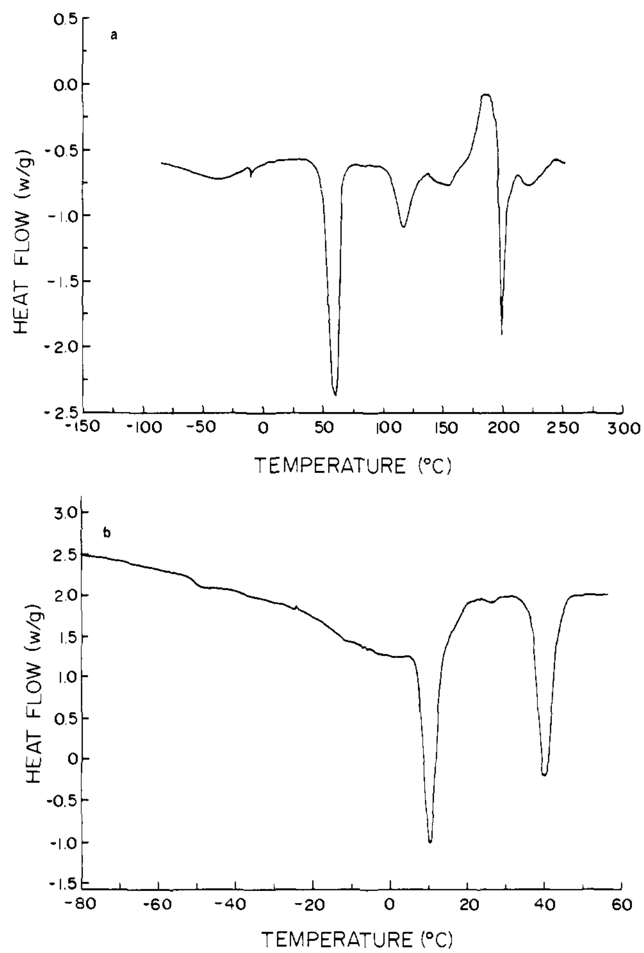

Figure 2. Differential scanning calorimetry traces at 10° min^{-1} for two sodides: (a) $K^+(HMHCY)Na^-$; (b) $Cs^+(HMHCY)Na^-$. Endothermic values are negative.

THERMODYNAMIC CYCLE

$$\begin{tikzcd}
\underline{M_{(s)} + Na_{(s)}} + \arrow[d, "1"'] & HMHCY_{(s)} \arrow[r, "5"] \arrow[d, "2"] & M^+(HMHCY)\text{-}Na^-_{(s)} \\
MNa_{(l)} + & HMHCY_{(l)} \arrow[r, "3"] & M^+(HMHCY)\text{-}Na^-_{(l)} \arrow[u, "4"']
\end{tikzcd}$$

Figure 3. Thermodynamic cycle used to calculate heats of formation of $K^+(HMHCY)Na^-$ and $Cs^+(HMHCY)Na^-$ from the metals and complexant.

Polycrystalline samples of $Cs^+(HMHCY)Na^-$ appear to melt at ~8 °C and decomplex into alkali metals [presumably Na(s) + Cs(l)] and free amine at ~37 °C (Figure 2b). NaCs forms a liquid alloy at ~45 °C,[28] near the end of the decomplexation process. As with compound I, a visual melting point was obtained for this material, which agreed with these assignments. This compound also decomplexes if left at room temperature for about 4 days. Thus, decomplexation of the melt is slow in this case also.

To estimate the heats of formation of these two alkalides from the DSC information, the thermodynamic cycle shown in Figure 3 was used. The heat of formation of the liquid alloy was obtained by summing the heat of mixing of the liquid metal[29] and the heat of fusion of the metal involved. The value obtained for NaK in this way was comparable to the value reported by McKisson and Bromley.[30] The heat of fusion of HMHCY was also obtained

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Table I. Summary of Enthalpy Changes for Various Steps in the Thermodynamic Cycle Shown in Figure 3

step	$K^+(HMHCY)Na^-$, kJ mol^{-1}	$Cs^+(HMHCY)Na^-$, kJ mol^{-1}
1	6.0	5.6
2	5.9	5.9
3	−28.9	−31.0
4	−35.1	−35.1
5	−52.1	−54.6

from DSC measurements. We did not include the heat capacities for the various components as terms that contain them should nearly cancel out in the cycle. The results are given in Table I.

By examining the measured enthalpy of decomplexation at various temperatures and the entropies of melting of $K^+(HMHCY)Na^-$, HMHCY, and NaK, we can understand why the compound is stable to decomplexation at 225 K but decomplexes (slowly) at 300 K and above. Stability at 225 K with $\Delta H = +52.3$ kJ mol^{-1} for decomplexation implies $\Delta S < 232$ J mol^{-1} K^{-1} at this temperature. Slow decomplexation of the solid compound at 300 K with $\Delta H = +64$ kJ mol^{-1} implies $\Delta S > 213$ J mol^{-1} K^{-1} at this temperature. At 300 K, the products of decomposition are both liquids (NaK and HMHCY). Adding their entropies of crystallization (−22.6 and −21.8 J mol^{-1} K^{-1}, respectively) requires that $\Delta S > 169$ J mol^{-1} K^{-1} for the decomplexation process at 225 K. Thus, at the temperature of formation of the crystalline compound, 169 J mol^{-1} K^{-1} < ΔS < 232 J mol^{-1} K^{-1}. Decomplexation above the melting points of the products would occur for any value of ΔS between these limits.

Conclusions

HMHCY has proven to be a "robust" complexing agent not easily reduced by alkali-metal anions. That decomplexation occurs without decomposition indicates that the problems with long-term stability of the sodides arise from the small complexation constants of the two alkali-metal cations K^+ and Cs^+ with HMHCY and not from the reducibility of HMHCY.

Aside from the unique thermal properties, this compound has also provided the first evidence for contact ion-pair formation between an alkali-metal cation and an alkali-metal anion, a process that occurs without destroying the essential character of the ions.

The extraordinary stability of tertiary amine complexants should permit the synthesis of thermally stable alkalides and electrides, a property that has not been achieved with crown ethers and cryptands. A strategy for such syntheses would be to use tertiary amine complexants designed to yield more stable cationic complexes, such as bicyclic tertiary amines or aza crowns that are linked together to permit the formation of "hinged" sandwich complexes. Such studies are currently under way in our laboratory.[31]

Another noteworthy feature is the remarkable stability of solutions of these compounds in a solvent such as dimethyl ether. This provides an opportunity to study concentrated stable metal solutions. Such solutions may be useful for aprotic reductions.

Of special importance would be the ability to synthesize thermally stable electrides. The wide variety of optical, magnetic, and electron emission properties of electrides might make them useful in device applications if the problem of autocatalytic decomposition can be overcome. Initial studies of a lithium-based electride that employs a cyclic methylated polyaza complexant are very encouraging in this regard.[31]

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Synthesis of η^1 Oxygen-Bound Rhodium Enolates. Applications to Catalytic Aldol Chemistry[1]

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Abstract: Oxygen-bound rhodium enolate complexes are prepared by metathesis of carbonylbis(phosphine)rhodium(I) halides and potassium enolates, **3**–**6**. Rhodium enolates of acetophenone (**7**), propiophenone (**9**), ethyl mesityl ketone (**10**), and ethyl *tert*-butyl ketone (**11**) were prepared and fully characterized. Complex **11** condenses with benzaldehyde under a variety of conditions to produce isolable rhodium aldolate complex **12**. Cleavage of **12** with trimethylsilyl chloride yields aldol silyl ether and rhodium chloride. Similar treatment of **12** with an enol silane affords the aldol silyl ether and a rhodium enolate. A catalytic aldol reaction involving enol silanes, silylketene acetals, and benzaldehyde under rhodium catalysis is presented. Deuterium, phosphorus, and carbon NMR were used to demonstrate the intermediacy of rhodium enolates and aldolates in the aldol process and to elucidate the gross mechanistic features of the catalytic cycle.

Asymmetric induction in the synthesis of organic molecules is a topic of considerable current interest.[2] Significant progress has been made, particularly in oxidation and reduction reactions, where efficient catalytic processes are known that give high levels of asymmetric induction. Less progress has been made in achieving good levels of asymmetric induction in carbon–carbon bond-forming processes such as the aldol addition reaction. For this important reaction, several excellent enantioselective methods have been developed wherein the chiral auxiliary is used stoichiometrically,[3] and there is one report of good asymmetric induction involving a noncovalently bound chiral auxiliary.[4] However, there

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