in pigeons. More recently, Herbert and Mann[9] found that both the *N*-formyl and *O*-methyl groups of tuberin were labeled by [2-^{14}C]glycine, but the *N*-formyl group was not labeled by formate or methionine. In order to confirm that C-2 of glycine is the source of C-2 and C-8 in the adenine ring of **1**, as well as to define the origin of C-5 and N-7, (^{15}N,2-^{13}C)glycine was utilized as a precursor (experiment 10). The results of this experiment verify that C-5 of the adenine ring of **1** derives from C-2 of glycine and that C-2 of glycine serves as the source of C-2 and C-8 of the purine. However, no coupling was observed for the labeled carbon at C-5 suggesting complete loss of the ^{15}N label of glycine by transamination in vivo. Finally, we examined the possibility that the adenine ring of **1** is derived by catabolism of adenosine to yield free adenine[10] which is then joined to the cyclopentane moiety. Administration of [2-^{3}H,8-^{14}C]adenosine (experiment 11) showed that the adenine ring of adenosine is incorporated largely intact into the adenine ring of aristeromycin. The high incorporation figure suggests that the major route to the adenine ring of **1** may proceed via adenosine.

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Formation of $HCr(CO)_3^-$ from the Remarkable Reaction of Hydride Ion with Benzenechromium Tricarbonyl. Gas-Phase Reactions of a Novel 14-Electron Metal Anion Complex

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We wish to report here on the novel ligand displacement reaction that occurs when benzenechromium tricarbonyl (**1**) reacts with hydride ion in the gas phase. In this paper we describe our studies of the mechanism of this reaction and provide a preliminary account of the reactivity of the 14-electron metal ion product, $HCr(CO)_3^-$.

Our experiments have been carried out at 300 ± 2 K in a flowing afterglow apparatus which has been described in detail previously.[1] Hydride is produced as the major observed ion from electron impact on trace amounts of NH_3 added past an electron gun. A fast flow of helium buffer gas carries hydride ions the length of a 100 cm × 7.3 cm i.d. flow reactor where they interact with $C_6H_6Cr(CO)_3$ added to the system through a heated helium flow inlet. Hydride rapidly reacts with **1** to yield a proton-abstraction product and a benzene-displacement product, **2**, in roughly equal amounts (eq 1).[2] Production of $HCr(CO)_3^-$ can

$$H^- + \underset{\mathbf{1}}{C_6H_6Cr(CO)_3} \rightarrow C_6H_5Cr(CO)_3^- + H_2$$
$$\rightarrow \underset{\mathbf{2}}{HCr(CO)_3^-} + C_6H_6 \qquad (1)$$

be shown to be unique to hydride since OH^- and other strongly basic anions react with **1** by exclusive proton abstraction.[3]

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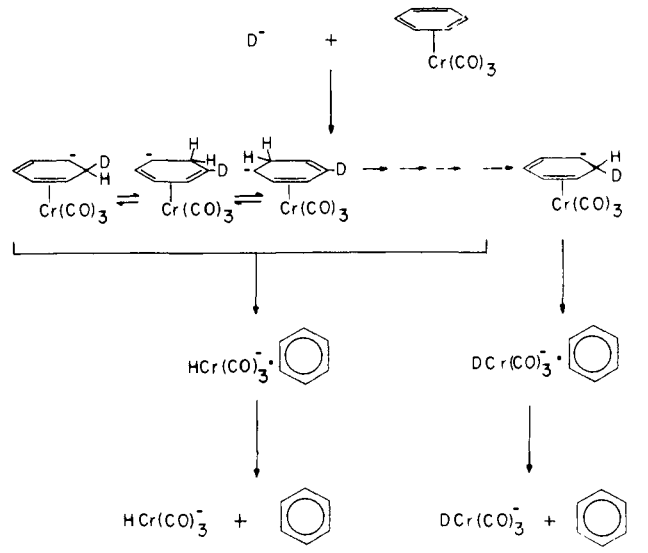
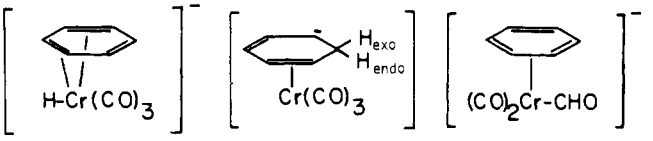
(2) An accurate rate and product distribution for eq 1 could not be determined due to the low volatility of **1** and the unavoidable presence of NH_2^- and OH^- in the system, respectively.

Scheme I



In analogy with nucleophilic addition mechanisms postulated for metal arenes in solution,[4-7] we can envisage hydride addition to complex **1** in (at least) three different ways. Direct H^- attachment to the metal requires "slippage" of the η^6-benzene ligand to η^4 (A); subsequent or simultaneous expulsion of the hydrocarbon



A B C

from the energy-rich adduct then produces $HCr(CO)_3^-$. Alternatively, initial hydride addition to the benzene ring or a carbonyl ligand may occur to produce a chromium–cyclohexadienyl anion B or chromium–formyl anion intermediate C, respectively. Intramolecular hydride migration with accompanying benzene loss may then give rise to the observed product. In solution, nucleophilic addition to compound **1** has been shown to occur predominantly to the exo face of the ring.[8-12] In order to distinguish among the conceivable intermediates shown above, we have carried out experiments using D^- produced from ND_3. If reaction 1 proceeds exclusively via intermediate A or C, then only $DCr(CO)_3^-$ would be produced. However, if reaction proceeds through intermediate B and the endo hydrogen is preferentially transferred to the metal, then only $HCr(CO)_3^-$ would be observed. A mixture of both $DCr(CO)_3^-$ and $HCr(CO)_3^-$ would appear if ring attachment occurs, but hydrogen migration is unselective. The reaction of D^- with **1** under the conditions described above affords both $HCr(CO)_3^-$ and $DCr(CO)_3^-$ in an observed ratio of 7:1. No

(3) The ΔH_{acid} of **1** is 371.5 ± 5 kcal mol^{-1}. The conjugate base anion, $C_6H_5Cr(CO)_3^-$, undergoes five H/D exchanges with D_2O, suggesting a π-arene, as opposed to a σ-phenyl structure. Lane, K. R.; Squires, R. R., unpublished results.
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free H^- is produced at low conversions of D^-, nor does $HCr(CO)_3^-$ undergo H/D exchange with the ND_3 which is present in the flow reactor. Thus, we conclude that ring attachment must occur at some point in the course of an ion–molecule collision. Moreover, from the fact that the observed $HCr(CO)_3^-/DCr(CO)_3^-$ product ratio is near the statistical value of 6:1, we can conclude that complete H/D scrambling occurs within the collision complex prior to expulsion of benzene. Our view of the mechanism is outlined in Scheme I. Initial ring addition by D^- produces a vibrationally and rotationally excited cyclohexadienyl anion complex which can undergo rapid hydrogen shifts in either a thermally allowed sigmatropic manner[13] or with mediation by the $Cr(CO)_3$ fragment. This latter possibility seems unlikely, however, since we have found that $HCr(CO)_3^-$ does *not* undergo H/D exchange in the presence of C_6D_6, although an adduct readily forms by termolecular association. This implies that a barrier exists for hydride migration from chromium to the arene ligand and, by inference, that once the metal–hydrogen bond is formed expulsion of benzene follows. Thus, H/D scrambling proceeds entirely within the benzene moiety prior to a slower chromium–hydride bond formation step which is accompanied by loss of neutral benzene.

Preliminary studies of the reactions of $HCr(CO)_3^-$ with a variety of small molecules have exposed a striking and enhanced reactivity relative to other transition-metal negative ions which have been examined previously.[14-17] For example, $HCr(CO)_3^-$ undergoes facile oxidative insertion/reductive elimination reactions with a variety of n-donor Brønsted acids (eq 2), as well as H/D exchange

$$HCr(CO)_3^- + HX \xrightarrow[HX = NH_3,\ H_2O,\ ROH]{} XCr(CO)_3^- + H_2 \quad (2)$$

in the presence of D_2.[16,17] While **2** does not appear to react with alkanes or cyclopropane, it does react readily with alkenes, cycloalkenes, and alkynes in a manner reminiscent of atomic metal cations.[18-21] For instance, propylene and many other olefins possessing allylic CH bonds give insertion/elimination products which we formulate as 16-electron π-allyl complexes (eq 3).

$$CH_2{=}CH{-}CH_3 + \underset{\mathbf{2}}{HCr(CO)_3^-} \rightarrow HC(CH_2)(CH_2){-}Cr(CO)_3^- + H_2 \quad (3)$$

Cyclic and acylic conjugated dienes react exclusively by simple adduct formation; in this case coordinatively saturated (18-electron) complexes are initially produced, so elimination of H_2 is apparently disfavored. Interestingly, acetylene also reacts with **2** by insertion/H_2 elimination, whereas ethylene produces only an adduct. A complete accounting of the rich chemistry of $HCr(CO)_3^-$ will be reported in a future publication.

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Enantioselective Lactonization of Sodium 4-Hydroxypimelate under Abiological Conditions[1]

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Enantiotopic group differentiation by biochemical methods has been shown to be a prevailing method of choice for asymmetric syntheses.[2] On the other hand, only a few abiological methods, useful for providing enantiomerically rich compounds, exist to date,[3] although considerable attention[4] has been paid since Marckwald[5] reported decarboxylation of geminal dicarboxylic acid with brucine in low enantioselectivity. Here we describe a simple and preparative method for enantiotopic group differentiation between two carboxylate groups by protonation.

Sodium 4-hydroxypimelate (**1**) has been chosen as a starting dicarboxylate because monoprotonation allows rapid cyclization in the reaction medium to afford a stable γ-lactone. Careful neutralization[6] of the ethanolic solution of **1** with (1*S*)-(+)-10-camphorsulfonic acid (*S*-CSA) monohydrate as a chiral proton source gave rise to the expected lactone **2** in nearly quantitative yield.[7] Results are summarized in Table I. The degree of

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(6) Every neutralization process was performed at −78 °C.

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