Chart I. Preparation of Regioisomeric Artificial B$_6$ Enzymes from A,B-Capped Cyclodextrin

the conditions, total yields of amino acids were ca. 40%[4] and the enantiomeric excess observed for L-amino acid was very high, as listed in Table II.

The observed high chiral induction for **3a** may be understood on the basis of stereospecific participation[2e] of the ω-NH$_2$ grouping toward the prochiral azomethine plane fixed nearly perpendicular toward the N-lone pair during the prototropy (see eq 3), due to

$$(3)$$
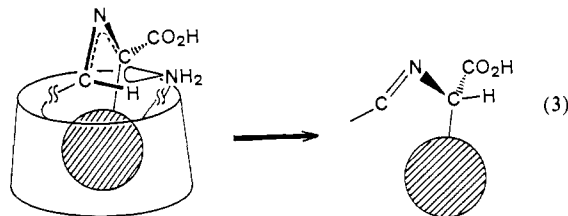
the host–guest multiple recognition.[1,5] The mechanism is further supported by the acceleration of prototropy caused by the assisting NH$_2$ group on the B ring. The observed prototropy rate ratio followed spectroscopically, k (**3**) to k (free B$_6$), was ca. 2000–2200 in the L-phenylalanine formation reaction, in a good agreement with the observed chiral induction.[6]

Table I. Characteristic Spectra of **3a**

electronic, nm (ϵ)	(aq, pH 8.0) 250 (ϵ 4400), 324 (6600)
400-MHz ^{1}H NMR; ppm from TSP	(D$_2$O, pH 4.0) SC$_6$H δ 2.55 dd (J = 12.6, 7.6 Hz), 2.82 dd (J = 12.6, 1.7 Hz). **3b:** 2.64 dd (J = 11.2 Hz, 7.7), and 3.01 dd (J = 11.2 Hz, 1.0).
100-MHz ^{13}C NMR; ppm from TSP	(D$_2$O, pH 4.0) 157.7, 144.4, 137.5, 132.5, 103.6, 102.8, 84.5, 83.2, 82.9, 74.9, 74.6, 74.3, 74.1, 73.9, 73.7, 73.5, 69.3, 62.5, 62.3, 50.2, 46.7, 37.3, 36.9, 33.7, 33.0, 16.9

(4) The present yield of **6** is neither corrected for the conversion in acylation (which may not be exactly the same for D- and L-amino acid) nor the extraction efficiency.

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(6) Or, rate ratio k (**3**) to k (B$_6$ cyclodextrin) was 10–11. Detailed analysis of complex multiphase kinetics will appear in a full-length article.

Table II. Chiral Induction in Amino Acids Formed via the Artificial B$_6$ Catalysis[a]

R–COCO$_2$H	L/D
R = PhCH$_2$	98/2
(indolyl-CH$_2$)	95/5[b]
Ph	98/2[b]

[a] At 30 °C, 2 M K$_2$HPO$_4$–KH$_2$PO$_4$ buffer, pH 8.0. [b] Recorded ratio is lowest limit.

ditions listed in Chart I. The crude mixture free from ethylenediamine was applied on a CM-25 Sephadex column. From 0.12–0.15 M NH$_4$HCO$_3$ gradient via the usual workup was obtained 64 mg of **3**·HCl (15% yield).

Separation of the two regioisomers **3a** and **3b** was successfully carried out again by CM-25 column chromatography of a prepurified **3a** + **3b** mixture (60/40 ratio) by the use of a long, thin column (5 × 1500 mm) eluted with aqueous NH$_4$HCO$_3$ (0–0.1 M gradient). The observed elution diagram obtained by measuring intensities of the absorption at 324 nm (B$_6$ chromophore) of each 3-mL fraction clearly shows that the two regioisomers are satisfactorily separated. The latter eluent was recrystallized from aqueous EtOH twice, giving pure A,B regioisomer **3a**, while from the earlier fractions, pure B,A regioisomer **3b**, was similarly obtained. Both compounds showed pyridoxamine characteristic CH$_2$ signals and ethylenediamine CH$_2$ signals in expected intensities, but the signals of **3a** SCH$_2$ at C$_6$ were found at 2.82 and 2.55 ppm while those of **3b** were at 3.01 and 2.64 ppm. Less than 1% of the contaminating signal could be seen (see further Table I).

The aminotransfer reaction smoothly proceeded between **3a** and keto acids **4a–c** under the conditions described in eq 1, giving the corresponding amino acids **5a–c**, respectively. The amino acids formed were further converted to the 3,5-dinitrobenzamides **6a–c** which were acidified (pH 3) and extracted with ether (10 mL × 3). The condensed ether layer (150 μL) was analyzed by HPLC by using a Sumipax OA-1000 chiral column eluted with a MeOH/H$_2$O/CH$_3$CO$_2$H mixture (95/5/1 vol). The two peaks of each racemic amino acid derivative were clearly resolved. Under

Formation of CO$_2$ and a Four-Membered 1,3-Dimetallacycle by Deoxygenation of a Ketone with [Rh(CO)$_2$Cl]$_2$

J. William Suggs,* Michael J. Wovkulich, and Ken S. Lee

Department of Chemistry, Brown University
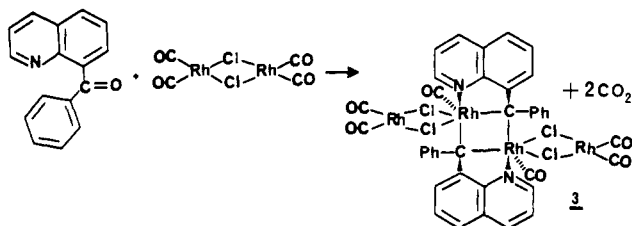*Providence, Rhode Island 02912*

8-substituted quinoline ligands have proven useful in studies of carbon–hydrogen and carbon–carbon bond activation by transition metals.[1] They allow specific ligand bonds to be brought into a metal's coordination sphere whereupon reaction can occur. We now wish to describe an unexpected example of deoxygenation of a ketone by a rhodium carbonyl complex in an 8-substituted quinoline ligand.

When 8-quinolinyl phenyl ketone (**1**) and [Rh(CO)$_2$Cl]$_2$ (**2**) are mixed in benzene at 25 °C under argon (mole ratio 1:1) the initially yellow solution darkens to a deep red color within 1 h.[2] At this time CO$_2$ evolution begins, as shown by a new IR band in the solution at 2330 cm^{-1} and by trapping of the evolved gas using Ca(OH)$_2$. The CO$_2$ evolution continues for approximately 24 h. Absorption of the CO$_2$ on Ascarite indicates slightly less than 1 mol of CO$_2$ is formed per mole of ketone. Deep red crystals of a new compound **3**, slowly formed and after 3 days these were collected (67% yield).[3] They can be handled in air, but slowly

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(2) Upon mixing, a new species with IR bands at 2098, 2080, 2026, 2011, and 1652 cm^{-1} forms. The decrease in the ketone band from 1668 cm^{-1} in **1** to 1652 cm^{-1} is consistent with bidentate N,O coordination of **1** to a rhodium species.

(3) **3**: mp 172–174 °C dec; IR (CH$_2$Cl$_2$) 2079 (s), 2057 (m), 2011 (s) cm^{-1}; NMR (250 MHz, ^{1}H, CD$_2$Cl$_2$) δ 8.28 (dd, 1 H), 7.86 (dd, 1 H), 7.50 (dd, 1 H), 7.40 (dd, 1 H), 7.4–7.3 (m 6 H), 7.01 (dd, 1 H).

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crumble due to loss of a benzene of crystallization.

Results of a single-crystal X-ray structure determination of **3** are shown in Figure 1.[4] The ketone carbonyl group has transferred its oxygen to one of the coordinated carbon monoxides of **2**, generating CO_2 and leaving behind a 1,3-dirhodiacyclobutane derivative as the final product. Oxygen atom transfer to coordinated CO from amine oxides,[5] organic nitro compounds,[6] nitrile oxides,[7] and similar compounds is well-known and has proven useful in organic and organometallic synthesis. However, this is the first example of oxygen atom transfer to CO from a functional group as weakly oxidizing as a ketone carbonyl. Recent work provides a related example of intramolecular attack of a ketone oxygen on CO in a rhodium complex to produce a metalloester, but subsequent loss of CO_2 in that case was not reported.[8]

Several features of **3**'s structure are of interest. The 1,3-dirhodiacyclobutane ring is flat to within 0.1°. Planar (M_2C_2) rings are seen in several other systems;[9] however, an analogous (Ru_2O_2) ring formed from the reaction of 8-hydroxy quinoline and $Ru_3(CO)_{12}$ was puckered.[10] The Rh(1)–Rh(1a) distance in **3** of 3.164 (1) Å does not indicate a bond between the metal atoms.[11] The Rh(1)–C(10) bond length (2.083 (6) Å) is within normal limits for a Rh(III)–alkyl bond,[12] while the Rh(1)–C(10a) distance of 2.105 (5) Å is lengthened, due to the steric hindrance between the quinoline rings. The chlorine bridges are extremely asymmetric, the Rh(2)–Cl lengths averaging 2.361 (2) Å while the Rh(1)–Cl distances average 2.626 (2) Å. This asymmetry arises from the strong trans influence of the ring carbons. The structure suggests the molecule is polarized in the direction of a $[RhCl_2(CO)_2]_2^{2-}[RhC_{17}H_{11}NO]_2^{2+}$ ion pair. The quinoline rings are tilted away from each other at a dihedral of 23°. Due to the difference in C–C vs. Rh–N bond lengths they are also twisted with respect to one another as shown in Figure 2. There are close nonbonded contacts of the atoms along the bottoms of the quinoline rings: C(8)–N(a), 2.919 (8) Å; C(9)–N(a), 2.931 (8) Å; C(9)–C(9a), 3.243 (9) Å; N–N(a), 3.147 (8) Å; C(1)–C(9a), 3.280 (8) Å. Even taking into account the smaller van der Waals radius of nitrogen vs. carbon,[13] these distances are as much as 0.4 Å less
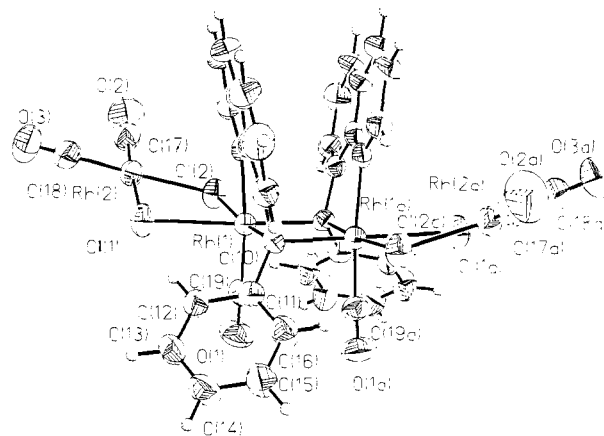
Figure 1. Molecular structure of **3**. For clarity some of the atoms are numbered here and the rest in Figure 2. Hydrogen atoms are at calculated positions. There is a C_2 axis perpendicular to the Rh_2C_2 plane. Symmetry-generated atoms are designated with (a). Selected distances (Å) and angles: Rh(2)–Cl(1) 2.364 (2), Rh(2)–Cl(2) 2.368 (2), Rh(2)–C(17) 1.847 (8), Rh(2)–C(18) 1.840 (8), Rh(1)–Cl(1) 2.657 (1), Rh(1)–Cl(2) 2.595 (2), Rh(1)–C(19) 1.867 (6), Cl(1)–Rh(2)–Cl(2) 86.9 (1)°.
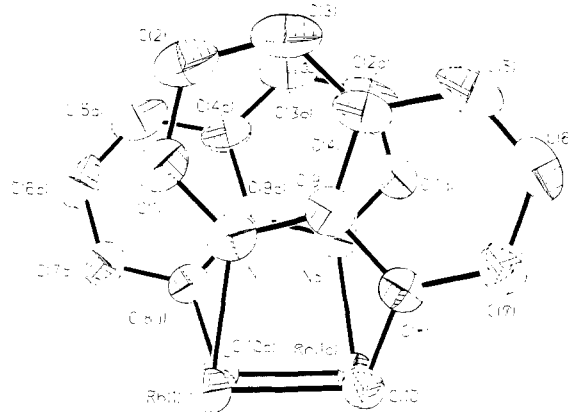

Figure 2. Molecular structure of the central ring in **3**. Selected distances (Å) and angles: Rh(1)–Rh(1a) 3.164 (1), Rh(1)–N 2.099 (4), Rh(1)–C(10) 2.083 (6), Rh(1)–C(10a) 2.105 (5), C(10)–Rh(1)–C(10a) 81.8 (3)°, Rh(1)–C(10a)–Rh(1a) 98.2 (3)°.

than the sum of van der Waals radii.

The soluble species present during the deposition of crystals of **3** exhibits carbonyl bands at 2080, 2021, and 1690 cm⁻¹. This latter band is consistant with the formation of a rhodium acyl, but it has not yet been possible to isolate precursors to **3** in crystalline form for X-ray structural analysis. In other systems, 1,3-dimetallacyclobutanes have arisen from dimerization of alkylidenes,[14] but as yet we have no evidence that such is the case here. Reactions other than ketone deoxygenation can occur with enolizable ketones. For example, we find **2** traps out the enol form of 8-quinolinyl benzyl ketone, producing a chelated enol complex as the major product.

The facile formation of **3** under ambient conditions adds another mechanistic possibility for homogeneous carbon monoxide reduction. Most schemes that have been put forward involve stepwise reduction of CO in which the CO's oxidation state decreases one unit at a time (i.e., M – CO to M – CHO to M – CH₂OH, etc.).[15] However, the isolation of **3** and the mild conditions under which it forms suggest mechanisms may exist in which the oxidation state of a CO-derived fragment can decrease in units of two. That is, an η^2-formaldehyde complex[16,17] could

(4) A deep red crystal of **3** was sealed in a capillary to prevent loss of a benzene of crystallization. By use of Mo Kα radiation and the programs supplied with the Nicolet R3ₘ/E X-ray diffractometer the crystal was assigned to the monoclinic space group $C2/c$ with unit cell parameters $a = 24.340$ (13) Å, $b = 14.261$ (7) Å, $c = 16.129$ (6) Å, $\beta = 113.63$ (3)°, $V = 5129$ Å³, $Z = 8$. There were 3873 unique observed reflections which were used with the SHELXTL series of programs to solve the structure (a linear absorption coefficient of 14.73 cm⁻¹ was used on the data). Least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms gave a structure with a final R_w based upon F^2 of 4.07% with no significant peaks in the final Fourier difference map. Hydrogen atoms were included at calculated positions and constrained to ride with the appropriate carbon atom.

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be reduced by CO to a metal alkylidene complex and CO_2 or even a metal acyl could be reduced to a metal carbyne and CO_2.[18] The heterogeneous analogue of these reactions, the disproportionation of CO to CO_2 and C (which presumably goes through a dissociative mechanism), is well-known.[19]

Supplementary Material Available: Tables of crystal and collection data, atomic coordinates and temperature factors, bond lengths and bond angles, and observed and calculated structure factors and a view of the unit cell of **3** (19 pages). Ordering information is given on any current masthead page.

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Direct Observation of the Aziridinium Imide Intermediates in the Reaction of Biadamantylidene with Triazolinediones

Stephen F. Nelsen* and Daniel L. Kapp

Samuel M. McElvain Laboratories of Organic Chemistry Department of Chemistry, University of Wisconsin Madison, Wisconsin 53706

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Greene and co-workers[1] and Adam and co-workers[2] have extensively studied the reactions of 4-substituted 1,2,4-triazolinediones **1**, R = Me, Ph, with olefins. Ene products (*N*-allylurazoles) are formed when abstractable α-hydrogens are present in the olefin, and diazetidines (formal 2 + 2 cycloaddition) when they are not, and in a few other cases (enol ethers, aryl–alkyl olefins). Rearrangements to five-membered ring urazoles are observed in some cases.[2] All of their experiments are consistent with the rate-controlling step being approach of **1** perpendicular to the plane of the olefin, forming an intermediate "with the structural characteristics of an aziridinium imide[1a]", **2**, see eq 1. The
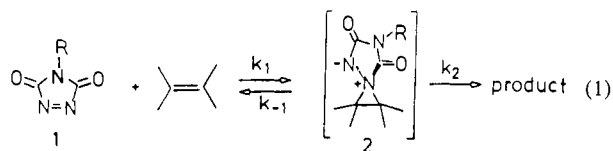
Stephenson isotope effect test provided important evidence for intermediate **2** in the ene reactions, while the reactivity pattern of various olefins which give diazetidine products was argued to be consistent with **2**. For example, norbornene is far less reactive than typical disubstituted olefins, but biadamantylidene **3** is as reactive. The activation parameters for **1**(R = Ph) + **3** were $\Delta H^{\ddagger}$
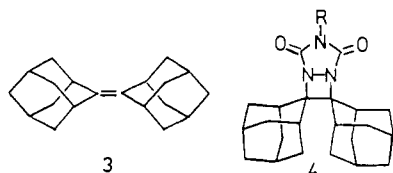

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= 10.6 kcal/mol $\Delta S^{\ddagger}$ = −33 eu[1a] in benzene, so $\Delta G^{\ddagger}$(25 °C) is 20.4 kcal/mol, corresponding to a first half-life at 0.1 M concentration of reactants of 2.6 min. The structure of the product was verified by obtaining the X-ray crystallographic structure of **4** (R = Me). The reaction goes to completion, and **4** (R = Ph) only cleaves slowly to **3** at 70 °C. We report here that, surprisingly, an intermediate that we assign as aziridinium imide **5** builds up in chloroform solution in the reaction of **3** and **1**.

When the addition of **1** (R = Me) to **3** is followed by ¹H NMR in deuteriochloroform solution, an intermediate is formed which has an N–CH_3 3 H singlet at δ 3.07, broad bridgehead 2 H signals at δ 2.75 and 3.09 (the latter overlapping with the N–CH_3 signal), and an upfield 2 H doublet at δ 1.4, as well as many other peaks which overlap with the adamantyl multiplets of **3** and **4** (R = Me). When 0.037 M **1** (R = Me) and 0.184 M **3** were mixed, the spectrum observed after 90 s showed no detectable **1** (R = Me) remaining, nor could the pink color of **1** (R = Me) be detected visually, and the ratio of intermediate to **4** was over two, as measured by integration of both the N–CH_3 and the bridgehead signals. A similar intermediate was observed in $CDCl_3$ from **1** (R = Ph) and **3**, which had bridgehead ¹H NMR absorptions at δ 2.85 and 3.17. The IR spectrum of the intermediate was obtained at room temperature under conditions where **1** (R = Me) had already disappeared, by subtracting the **4** (R = Me) signals from the observed FT-IR spectrum, giving a carbonyl region having absorptions at 1790 and 1686 cm^{-1}. These absorptions should be compared with those of the model ammonium imide **6**, reported to be 1790 and 1670 cm^{-1}.[3] Conversion of the intermediate to **4** (R = Me) is slow at −40 °C. A solution initially 0.20 M in **1** (R = Me) and 0.21 M in **3** which was reacted at room temperature for 30 s and rapidly cooled to −40 °C showed by ¹H NMR integration 15% **4** (R = Me), 2% **3**, and 83% intermediate after 2 h. The ¹³C NMR of the intermediate shows peaks at δ 159.9 and 156.6 (C=O), 81.8 (C_q), 36.8, 36.7, 35.5, 35.3, and 34.3 (CH_2), 28.6, 26.0, 25.7, and 25.5 (CH), and 26.2 (CH_3). Two of the three mirror symmetry planes which intersect at midpoint of olefin **3** have been lost in the intermediate. Our spectral data are consistent with the intermediate being **5** (R = Me).
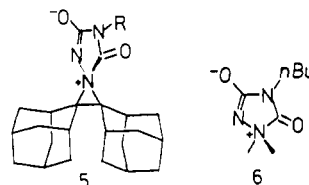
The kinetics of the reaction of **1** (R = Me) with **3** in $CDCl_3$ at 23 °C have been measured by integration of the proton NMR signals, and also by visible spectroscopy, following disappearance of **1** (R = Me) using its 536-nm (ϵ 208) band.[4] All of our data are consistent with rate constants k_1 = 0.63 ± 0.06 M^{-1} s^{-1}, k_2 = 0.0048 ± 0.0005 s^{-1} ($\Delta G_1^{\ddagger}$ = 17.7, $\Delta G_2^{\ddagger}$ = 20.6 kcal/mol). We do not yet have an accurate measure of k_{-1} but it is certainly no larger than 0.005 s^{-1} and may be substantially smaller.

We find it very surprising that **5** (R = Me) is so stable that k_1/k_{-1} is large, but our results demonstrate that it is. The unusual steric properties of **3** have made it uniquely important in the study of electrophilic additions to olefins. Wynberg and co-workers[5] originally assigned the white solids with the solubility properties of salts which are isolated upon treatment of **3** with bromine and chlorine as halonium salts, although Olah and co-workers[6] concluded on the basis of NMR studies that, in solution, only a species

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(4) At initial concentrations (M) of **1** (R = Me) and **3** respectively of 0.037 and 0.012, 0.037 and 0.043, and 0.037 and 0.184 for the NMR studies and at 0.0217 and 0.0243 and 0.00325 and 0.00328 for the UV studies.

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