COMPETITIVE C-H ACTIVATION AND C=C COORDINATION IN THE
REACTIONS OF ACETYLENES WITH A BINUCLEAR RHODIUM COMPLEX

by

Donald H. Berry and Richard Eisenberg

Prepared for Publication
in the

Journal of the American Chemical Society

University of Rochester
Department of Chemistry
Rochester, NY 14627

January 20, 1986

Reproduction in whole, or in part, is permitted for
any purpose of the United States Government.

This document has been approved for public release
and sale; its distribution is unlimited.
The reaction leading to 2a and 3 supports the notion that this pre-equilibrium involves CO dissociation from 1. The results clearly establish that the $\mu_2$-alkyne bridged complex does not lie on the reaction path of the metal-promoted acetylene-to-vinylidene transformation, and suggests that vinylidene formation proceeds with initial C-H activation.
COMPETITIVE C-H ACTIVATION AND C-C COORDINATION IN THE REACTIONS OF ACETYLENES WITH A BINUCLEAR RHODIUM COMPLEX

Donald H. Barry and Richard Eisenberg
Department of Chemistry
University of Rochester
Rochester, New York 14627

Received

Abstract: The reaction between phenylacetylene and the binuclear complex Rh₂(CO)₂(dppe)₂, 1, has been studied in detail. At 28.5 °C in benzene, the reaction leads to formation of a phenylvinylidene bridged A-frame complex Rh₄(CO)₆(dppe)₄[C=C=CH-C≡C], 2a, while in refluxing acetone it yields the alkene bridged complex Rh₄(CO)₆(dppe)₄[C=C=CH₂], 3. The kinetics of the reaction show that vinylidene formation is cleanly first order in (PhCH₂) and in 1) with a Kf of 2.7, while formation of 3 proceeds with no significant isotope effect and a kinetic dependence on (PhCH₂) suggestive of a pre-equilibrium involving 1 only. The effect of CO on the reaction leading to 2a and 3 supports the notion that this pre-equilibrium involves CO dissociation from 1.

The results clearly establish that the μ₂-alkyne bridged complex does not lie on the reaction path of the metal-promoted acetylene-to-vinylidene transformation, and suggests that vinylidene formation proceeds with initial C-H activation.

Terminal alkynes react with transition metal complexes either by coordination of the C=C bond as a 2 e- or 4 e- donor, or by C-H bond activation to form acetylide complexes, which often undergo subsequent transformations. While examples of these modes of reactivity abound, the factors favoring one over the other have not been fully delineated, and the kinetic distribution of products arising from them is often masked by relative product stability. In this communication, we describe a detailed study of the reaction between phenylacetylene and the binuclear complex Rh₂(CO)₂(dppe)₂ (1; dppe = bis(diphenylphosphino)methane) which has recently been found to possess an 18 e-/16 e- non-A-frame structure. The present study, in which it is found that the product distribution is sensitive to reaction conditions, provides insight into the factors influencing modes of acetylene reactivity, while showing conclusively that μ² coordination between the two Rh atoms (μ₂-e²) does not lie on the reaction profile leading to C-H activation.

Complex 1 reacts readily with a 10-fold excess of PhCH₂ in benzene at 28.5 °C to form an intensely purple colored product 2a cleanly and without observable intermediates, eqn (1). This product has been established by a single crystal x-ray study to be a phenylvinylidene bridged A-frame complex having the structure shown in Fig. 1. ²a possesses approximate mirror symmetry with no formal Rh-Rh bond and square planar coordination about each Rh (see Fig. 1 caption for important distances and angles). A reaction similar to (1) also occurs between t-BuCH and 1 forming the intensely blue vinylidene complex Rh₂(CO)₂(dppe)₂[C=C≡C(t-Bu)], 2b. Both 2a and 2b have recently been
reported by Grundy following a different synthetic route involving the
cationic acetylide complexes Rh₂(µ-CCR)(CO)₂(dpmm)₂⁺ and a hydride source.⁷

The reaction between 1 and PhCCH when carried out at 80 °C, however,
yields a different product distribution as shown in eqn (2). Under these

\[
\begin{align*}
\text{[Diagram of reaction between 1 and PhCCH]} \quad 80 \degree \text{C} \quad \text{excess PhCCH} \quad 30 \text{min, C}_{6}H_{6} & \quad \text{[Product structure]} \\
\end{align*}
\]

conditions, 2a accounts for only 30% of the products, with the remainder
being a new compound 3. This compound, which is the sole initial product if 1
is reacted with PhCCH in acetone, shows a stretch at 1425 cm⁻¹ assignable to
\( \text{sp}^3 \)-coordinate C=C.⁸,⁹,¹⁰ The \(^1H\) NMR spectrum of 3 exhibits four inequivalent
dpmm methylene protons and an acetylene proton split into a triplet by two
equivalent \( \text{sp}^3 \)-hydrogens. The \(^31P\)\(^1H\) NMR spectrum shows two multiplets
indicative of two inequivalent dpmm P donor atoms. We assign an
acetylene-bridged structure to 3 based on this spectroscopic data, and the
fact that the analogous diphenylacetylene complex, \( \text{Rh}_2(µ-\text{CPhCPh})(\text{CO})_2(\text{dpmm})_2 \),
with similar spectroscopic properties has been found by x-ray crystallography
to have a \( \mu_2-\text{sp}^3 \)-acetylene-bridged structure.¹¹

The isolated vinyllene complex 2a is stable indefinitely at 80 °C in
benzene or acetone solution, while the acetylene complex 3 slowly converts to
2a under the same conditions, eqn (3). This isomerization takes place with a

\[
\begin{align*}
\text{[Diagram of isomerization of 3 to 2a]} \quad 80 \degree \text{C} \quad \text{excess PhCCH} \quad 30 \text{min, C}_{6}H_{6} & \quad \text{[Product structure]} \\
\end{align*}
\]

half-life of ca. 27 hr, in contrast with the formation of products in eqn (2)
which is complete within 15 minutes. Thus it can be concluded that the

formation of 2a and 3 in eqn (2) follows a kinetic distribution of products.

The kinetics of the reaction between 1 and PhCCH have been studied using
\(^1H\) NMR spectroscopy.¹² When the reaction is carried out under pseudo-first
order conditions (11), 13.4 - 15.6 M, (PhCCH), 0.35 - 1.52 M; benzene, 28.5°C,
the disappearance of 1 is first order in both 1 and (PhCCH), with 2a
representing >95% of the total products formed and 3 corresponding to the
remaining ~5%. When approximately equal concentrations of 1 and PhCCH are
employed, plots of \( k \) vs time are linear yielding a second order rate
constant of 4.28 \times 10⁻⁴ M⁻¹s⁻¹, but with a product ratio 2a:3 of 2.7:1.

Significantly, this ratio remains approximately constant during the course of
these runs, showing only minor change from 2.7 to 2.9 reflecting the slow
conversion established in eqn (3). The constancy of the product ratio under
second order conditions indicates that at low (PhCCH) both 2a and 3 follow a
rate dependence which is proportional to \([1]\)(PhCCH). The overall second order
rate constant can therefore be partitioned according to the observed product
ratio, yielding individual rate constants for the formation of 2a and 3 of
3.12 \times 10⁻⁴ M⁻¹s⁻¹ and 1.16 \times 10⁻⁴ M⁻¹s⁻¹, respectively.

When PhCCH is employed under approximately equimolar conditions, an
overall rate constant of 2.22 \times 10⁻⁴ M⁻¹s⁻¹ is obtained with a product
ratio \( d_1:2a:d_3:3 \) of 1:1:1. As with PhCCH, this ratio remains nearly constant
through ≈50% completion of the reaction, allowing calculation of \( k_2 \) for \( d_1:2a \)
and \( d_3:3 \) of 1.16 \times 10⁻⁴ M⁻¹s⁻¹ and 1.06 \times 10⁻⁴ M⁻¹s⁻¹, respectively.
From these data, a kinetic isotope effect \( k_d/k_0 \) for the formation of 2a is
determined to be 2.7 while that for the formation of 3 is 1.1. The ratio \( d_1:2a:d_3:3 \) is greatly influenced by CO, changing from 1:1:1 in the
absence of CO to ca. 4:1 under a CO pressure of 100 torr.¹³,¹⁴

The kinetics study shows that while the formation of 2a at both high and
low (PhCCH) is first order in phenylacetylene concentration, the kinetic
dependence on [(MCCH) for the formation of 3 exhibits a more complicated functional form, being first order in [(MCCH) only at low concentrations of the acetylene and significantly less than first order at high (MCCH). This observation together with the inhibition of d1-3 relative to d1-2a under CO strongly suggests a pre-equilibrium involving CO dissociation in the formation of 3. The formation of the vinylidene complex 2a, on the other hand, proceeds via a bimolecular process between I and PHCH with C-H activation occurring in or before the rate determining step of the reaction as indicated by the kinetic isotope effect. These mechanistic conclusions are summarized in the scheme and yield a rate expression for the reaction which can be written as:

\[ \frac{\text{d}n}{\text{d}t} = k_1[(MCCH)] + \frac{k_2[C=CH]}{k_3[(MCCH)]} \]

We conclude that at least two channels exist for the reaction of PHCH with the binuclear complex R2(CO)2(dppe)2 leading to distinctly different products, and that \( \mu_2^2 \)-coordinated acetylene does not lie on the reaction path of the metal complex promoted acetylene-to-vinylidene transformation.

Acknowledgements. We wish to thank the National Science Foundation (CHE 83-08064) and the Office of Naval Research for support of this work, and Johnson Matthey Co., Inc. for a generous loan of iridium salts.

REFERENCES and NOTES

1. Present address: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104.
2. See, for example: Dickson, R. S.; Fraser, P. J. Adv. Organomet. Chem. 1974, 12, 323-377 and references therein.
5. Spectroscopic data for 2a. \( ^3 \)NNR (CO)2 -CHC\( = \) region: \( \delta = 3.95 \) (m, 2 H), \( \delta = 2.25 \) (m, 2 H). \( ^3 \)IP (\( ^1 \)H) NMR: \( \delta = 31.21 \) (m). IR (nujol mull) v(CO): 1934 (s), 1910 (s) cm\(^{-1}\).
6. Crystal data for 2a: triclinic space group \( \text{PT} \) with cell dimensions \( a = 14.68(4) \) Å, \( b = 14.018(4) \) Å, \( c = 13.52(2) \) Å, \( \alpha = 102.56(2) \)°, \( \beta = 101.36(2) \)°, \( \gamma = 73.13(2) \)° and \( V = 2719.3 \) Å\(^3\); \( Z = 2 \). \( \text{Calc} = 1.317 \) g cm\(^{-3}\); Enraf-Nonius CAD4 diffractometer using graphite monochromatic Mo K\( \alpha \) radiation (\( \lambda = 0.71073 \) Å); 7082 unique reflections (\( f_{\text{calc}}, \alpha_f \), \( 4^\circ < 2\theta < 55^\circ \), scan range \( = 0.7 + 0.35 \) scan, scan rate \( = 1.2 - 20 \) °/min).

The \( \text{SHELX} \) computer programs were used for data reduction, structure solution (MULTAN) and least-squares refinement. Convergence achieved with \( R_1 = 0.049 \), \( R = 0.069 \) and \( GOF = 1.93 \) (281 variables, 4562 reflections with \( I > 3 \sigma(I), \) all non-hydrogen atoms anisotropic with phenyl hydrogens placed at calculated and fixed positions). Full details of the structure solution will be presented in a separate report.

8. Spectroscopic data for 3a obtained in S22 isolated yield. \( ^3 \)NNR (CO)2: \( \delta = 6.02 \) (1 H, t, \( ^2 \)J\( _\text{HH} = 6.8 \) Hz, PHNC-\( \text{H} \)), \( \delta = 4.51 \) (1 H, q, \( J_{\text{HH}} = 11 \) Hz, CH\( _2 \)), \( \delta = 3.76 \) (1 H, q, \( J_{\text{HH}} = 11 \) Hz, CH\( _2 \)), \( \delta = 3.53 \) (1 H, q, \( J_{\text{HH}} = 11 \) Hz, CH\( _2 \)). \( 31 \)P \( ^1 \)H NMR: \( \delta = 22.30 \) (m), 19.65 (m). IR v(CO): 1938 (SH), 1923 (s) cm\(^{-1}\); v(C=NC): 1425 (m) cm\(^{-1}\).
9. By comparison, v(C=NC) \( = 1425 \) cm\(^{-1}\) in the PHNCPh analog\(^1\) and 1402 cm\(^{-1}\) in CO\( _2 \)(CO)\( _3 \)(HC\( = \)C\( = \)C\( = \)). -shite, Y.; Tamura, F.; Nakamura, M. Inorg. Chem. 1985.
10. Compound 3a has been previously reported as a product in the reaction.
of Rh$_2$(CO)$_2$(dppe)$_2$H$_2$ with PhCCH: Kubat, C. P.; Woodcock, C.; Eisenberg, R. Inorg. Chem. 1978, 21, 2119.


12. Phenyl acetylene was twice distilled, freeze-pump-thawed, and stored in a nitrogen atmosphere glove box. Standard solutions of 3 in benzene-$d_6$ (0.0161–0.0165 M) were prepared and used under nitrogen. All runs were followed to 75–95% completion. NMR tube samples were flame-sealed under nitrogen. Temperatures were maintained constant within ±2°C.

13. The inhibition of 3 by CO has been shown qualitatively at 28.5°C and 80°C. A study of the kinetics under CO is currently in progress.11

14. Compound 2a appears to coordinate CO rapidly and reversibly, as evidenced by an upfield shift in the methylene protons in the $^1$H NMR spectrum and a change of the intense purple color to yellow. Coming after the slow step, this equilibrium only affects the kinetics in that the CO concentration in solution is diminished.
Figure 1. Molecular structure of 2a (only ipso-carbons of dppm phenyl rings included for clarity.) Selected bond distances (Å) and angles (degrees): Rh1-Rh2 = 3.011(1), Rh1-C3 = 2.063(7), Rh2-C3 = 2.051(7), C3-C4 = 1.326(9), Rh1-C3-Rh2 = 94.1(3), C3-C4-C7 = 126.2(7), C1-Rh1-C3 = 177.3(3), C2-Rh2-C3 = 178.0(3), P1-Rh1-P4 = 172.12(7), P2-Rh2-P3 = 152.44(8).
<table>
<thead>
<tr>
<th>Office of Naval Research</th>
<th>2</th>
<th>Dr. David Young</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attn: Code 413</td>
<td></td>
<td>Code 334</td>
</tr>
<tr>
<td>800 N. Quincy Street</td>
<td></td>
<td>NORDA</td>
</tr>
<tr>
<td>Arlington, Virginia 22217</td>
<td></td>
<td>NSTL, Mississippi 39529</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dr. Bernard Douda</th>
<th>1</th>
<th>Naval Weapons Center</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naval Weapons Support Center</td>
<td></td>
<td>Attn: Dr. Ron Atkins</td>
</tr>
<tr>
<td>Code 5042</td>
<td></td>
<td>Chemistry Division</td>
</tr>
<tr>
<td>Crane, Indiana 47522</td>
<td></td>
<td>China Lake, California 93555</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Commander, Naval Air Systems Command</th>
<th>1</th>
<th>Scientific Advisor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attn: Code 310C (H. Rosenwasser)</td>
<td></td>
<td>Commandant of the Marine Corps</td>
</tr>
<tr>
<td>Washington, D.C. 20360</td>
<td></td>
<td>Code RD-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Washington, D.C. 20380</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Naval Civil Engineering Laboratory</th>
<th>1</th>
<th>U.S. Army Research Office</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attn: Dr. R. W. Drisko</td>
<td></td>
<td>Attn: CRD-AA-IP</td>
</tr>
<tr>
<td>Port Hueneme, California 93401</td>
<td></td>
<td>P.O. Box 12211</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Research Triangle Park, NC 27709</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Defense Technical Information Center</th>
<th>12</th>
<th>Mr. John Boyle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Building 5, Cameron Station</td>
<td></td>
<td>Materials Branch</td>
</tr>
<tr>
<td>Alexandria, Virginia 22314</td>
<td></td>
<td>Naval Ship Engineering Center</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Philadelphia, Pennsylvania 19112</td>
</tr>
</tbody>
</table>

| DTNSRDC                             | 1 | Naval Ocean Systems Center |
|-------------------------------------|---|Attn: Dr. S. Yamamoto |
| Attn: Dr. G. Bosmajian              |   | Marine Sciences Division   |
| Applied Chemistry Division          |   | San Diego, California 91232 |
| Annapolis, Maryland 21401           |   |                          |

| Dr. William Tolles                  | 1 |                           |
| Superintendent                      |   |                           |
| Chemistry Division, Code 6100       |   |                           |
| Naval Research Laboratory           |   |                           |
| Washington, D.C. 20375              |   |                           |