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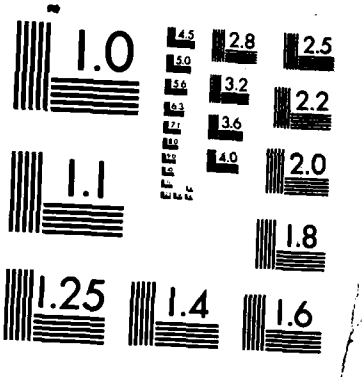

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Competitive C-H Activation and C≡C Coordination in the Reactions of Acetylenes with a Binuclear Rhodium Complex

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

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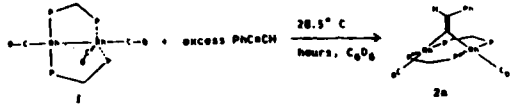
Received

Abstract: The reaction between phenylacetylene and the binuclear complex $Rh_2(CO)_3(dppm)_2$, 1, has been studied in detail. At 28.5° C in benzene, the reaction leads to formation of a phenylvinylidene bridged A-frame complex $Rh_2(CO)_2(dppm)_2(C{=}C(H)Ph)$, 2a, while in refluxing acetone it yields the alkyne bridged complex $Rh_2(\mu_2\text{-}\eta^2\text{-PhCCH})(CO)_2(dppm)_2$, 3. The kinetics of the reaction show that vinylidene formation is cleanly first order in [PhCCH] and in [1] with k_H/k_D of 2.7, while formation of 3 proceeds with no significant isotope effect and a kinetic dependence on [PhCCH] suggestive of a preequilibrium involving 1 only. The effect of CO on the reaction leading to 2a and 3 supports the notion that this preequilibrium involves CO dissociation from 1. The results clearly establish that the μ_2-η^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.

Terminal alkynes react with transition metal complexes either by coordination of the C≡C bond as a 2 e- or 4 e- donor,[2] or by C-H bond activation to form acetylide complexes, which often undergo subsequent transformations.[3] 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 $Rh_2(CO)_3(dppm)_2$ (1; dppm = bis(diphenylphosphino)methane) which has recently been found to possess an 18 e-/16 e- non-A-frame structure.[4] 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 η^2 coordination between the two Rh atoms (μ_2-η^2) does not lie on the reaction profile leading to C-H activation.

Complex 1 reacts readily with a 10-fold excess of PhCCH in benzene at 28.5° C to form an intensely purple colored product 2a cleanly and without observable intermediates, eqn (1).[5] This product has been established by a single crystal x-ray study to be a phenylvinylidene bridged A-frame complex

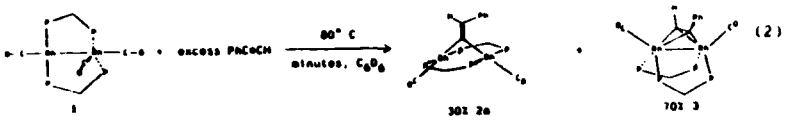


(1)

having the structure shown in Fig. 1.[6] 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-BuCCH and 1 forming the intensely blue vinylidene complex $Rh_2(CO)_2(dppm)_2(C{=}C(H)(t\text{-}Bu))$, 2b. Both 2a and 2b have recently been

reported by Grundy following a different synthetic route involving the cationic acetylide complexes $Rh_2(\mu\text{-CCR})(CO)_2(dppm)_2^+$ and a hydride source.[7]

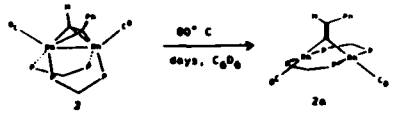
The reaction between 1 and PhCCH when carried out at 80° C, however, yields a different product distribution as shown in eqn (2). Under these



(2)

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 η^2-coordinated C≡C.[8,9,10] The ^1H NMR spectrum of 3 exhibits four inequivalent dppm methylene protons and an acetylene proton split into a triplet by two equivalent Rh nuclei. The $^{31}P\{^1H\}$ NMR spectrum shows two multiplets indicative of two inequivalent dppm P donor atoms. We assign an acetylene-bridged structure to 3 based on this spectroscopic data, and the fact that the analogous diphenylacetylene complex, $Rh_2(\mu\text{-PhCCPh})(CO)_2(dppm)_2$, with similar spectroscopic properties has been found by x-ray crystallography to have a μ_2-η^2 acetylene bridged structure.[11]

The isolated vinylidene 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



(3)

half-life of <u>ca</u>. 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 ([1], 13.4 - 15.6 mM; [PhCCH], 0.351 - 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 $[1]^{-1}$ vs time are linear yielding a second order rate constant of 4.28×10^{-4} $M^{-1}s^{-1}$, 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 to 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 3.12×10^{-4} $M^{-1}s^{-1}$ and 1.16×10^{-4} $M^{-1}s^{-1}$, respectively.

When PhCCD is employed under approximately equimolar conditions, an overall rate constant of 2.22×10^{-4} $M^{-1}s^{-1}$ is obtained with a product ratio d_1-2a:d_1-3 of 1.1:1. As with PhCCH, this ratio remains nearly constant through >85% completion of the reaction, allowing calculation of k_2 for d_1-2a and d_1-3 of 1.16×10^{-4} $M^{-1}s^{-1}$ and 1.06×10^{-4} $M^{-1}s^{-1}$, respectively. From these data, a kinetic isotope effect k_H/k_D for the formation of 2a is determined to be 2.7 while that for the formation of 3 is 1.1. The ratio of d_1-2a:d_1-3 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 [PhCCH] for the formation of 3 exhibits a more complicated functional form, being first order in [PhCCH] only at low concentrations of the acetylene and significantly less than first order at high [PhCCH]. This observation together with the inhibition of d_1-3 relative to d_1-2a under CO strongly suggests a preequilibrium 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 1 and PhCCH 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:

$$\frac{-d[1]}{dt} = k_1[1][PhCCH] + \frac{k_2k_3[1][PhCCH]}{k_{-2}[CO] + k_3[PhCCH]}$$

We conclude that at least two channels exist for the reaction of PhCCH with the binuclear complex $Rh_2(CO)_3(dppm)_2$ leading to distinctly different products, and that μ_2-η^2 coordinated acetylene does not lie on the reaction path of the metal complex promoted acetylene-to-vinylidene transformation.

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4. Woodcock, C.; Eisenberg, R. Inorg. Chem. 1985, 24, 1285.
5. Spectroscopic data for 2a. ^1H NMR (C_6D_6) $-CH_2-$ region: δ 3.85 (m, 2 H), 2.25 (m, 2 H). ^{31}P {^1H} NMR: δ 31.22 (m). IR (nujol mull) ν(CO): 1934(s), 1910(s) cm^{-1}.
6. Crystal data for 2a: triclinic space group $P\bar{1}$ with cell dimensions a = 14.684(4)Å, b = 14.818(4)Å, c = 13.527(2)Å, α = 102.56(2)°, β = 101.56(2)°, γ = 73.13(2)° and V = 2719.3 $Å^3$; Z = 2, d_{calc} = 1.377 gcm^{-3}; Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å); 7082 unique reflections (h, ±k, ±l, 4° < 2θ < 45°, scan range = .7 + 0.35(tanθ), scan rate = 1.2 - 20 °/min). The SDP+ computer programs were used for data reduction, structure solution (Multan) and least-squares refinement. Convergence achieved with R_1 = 0.048, R_w = 0.069 and GOF = 1.93 (631 variables, 4562 reflections with I > 3σ(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.
7. Deraniyagala, S. P.; Grundy, K. R. Organometallics 1985, 4, 424-426.
8. Spectroscopic data for 3a obtained in 52% isolated yield. ^1H NMR (C_6D_6): δ 6.02 (1 H, t, $^2J_{Rh-H}$ = 6.8 Hz, PhCC-H), 4.51 (1 H, q, $J_{P-H} - J_{H-H}$ = 11 Hz, CH_2), 3.76 (1 H, q, $J_{P-H} - J_{H-H}$ = 11 Hz, CH_2), 3.53 (1 H, q, $J_{P-H} - J_{H-H}$ = 11 Hz, CH_2), 3.33 (1 H, q, $J_{P-H} - J_{H-H}$ = 11 Hz, CH_2). ^{31}P {^1H} NMR: δ 22.39 (m), 19.65 (m). IR ν(CO): 1938(sh), 1923(s) cm^{-1}; ν(C≡C): 1425 (m) cm^{-1}.
9. By comparison, ν(C≡C) = 1425 cm^{-1} in the PhC≡CPh analog[11] and 1402 cm^{-1} in $Co_2(CO)_6$(HC≡CH). [illegible]shita, Y.; Tamura, F.; Nakamura, A. Inorg. Chem. 1[illegible]
10. Compound 3a has been previously reported as a product in the reaction

of $Rh_2(CO)_2(dppm)_2(H)_2$ with PhCCH: Kubiak, C. P.; Woodcock, C.; Eisenberg, R. Inorg. Chem. 1978, 21, 2119.

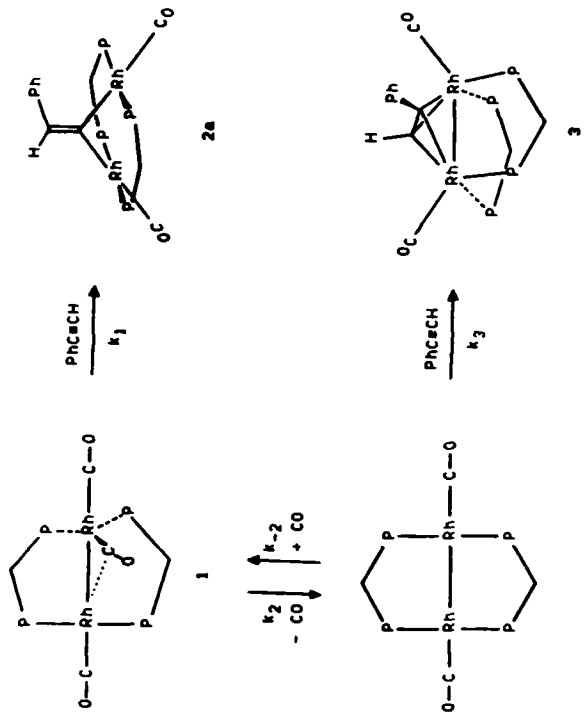
11. Berry, D. H.; Eisenberg, R. manuscript in preparation.

12. Phenyl acetylene was twice distilled, freeze-pump-thawed, and stored in a nitrogen atmosphere glove box. Standard solutions of 1 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° 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 ^1H 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.

SCHEME



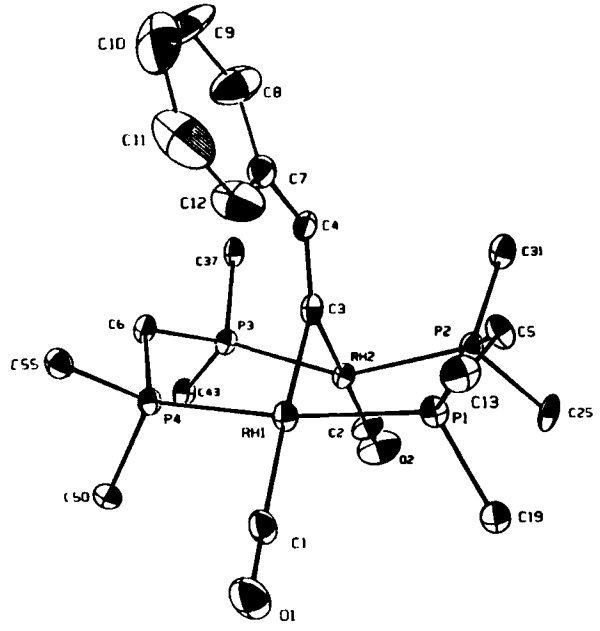


Figure 1. Molecular structure of 2a (only ipso-carbons of dppm phenyl rings included for clarity.) Selected bond distances (Å) and angles (degrees): Rh1-Rh2 = 3.011(1), Rh1-C3 = 2.063(7), Rh2-C3 = 2.051(7), C3-C4 = 1.329(9), Rh1-C3-Rh2 = 94.1(3), C3-C4-C7 = 126.2(7), C1-Rh1-C3 = 177.3(3), C2-Rh2-C3 = 178.6(3), P1-Rh1-P4 = 172.12(7), P2-Rh2-P3 = 152.44(8).

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