cidation of the $NiH_{-2}L{-}O_2$ and the reaction mechanism and synthetic applications of aromatic hydroxylations.[24]

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Registry No. $Ni^{II}H_{-2}L^1$, 80400-19-7; $Ni^{II}H_{-2}L^2$, 80389-72-6; $Ni^{II}L^3$, 77321-28-9; $Ni^{III}H_{-2}L^2$, 82135-48-6; $Ni^{II}H_{-2}L^2{-}O_2$, 82149-93-7; $Cu^{II}H_{-2}L^1$, 80386-21-6; $Cu^{II}H_{-2}L^2$, 80386-22-7; $Cu^{II}L_3$, 80389-68-0; $Cu^{II}L_6$, 52304-87-7.

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(23) The electrochemically generated $Ni^{III}H_{-2}L$ species are not active at all in the oxygenation of benzene. In the $NiH_{-2}L{-}O_2$ reactions, the ligand L^1 and L^2 are gradually oxidized to dehydrogenated species (determined by the mass spectroscopy), which results in loss of activity in the oxygenation of benzene. It is common that Ni(III) complexes tend to undergo self oxidation–reduction in which the ligands are frequently dehydrogenated (Kirksey, S. T.; Neubecker, T. A.; Margerum, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 1631).

(24) A strong superoxide dismutase activity was recently discovered with $Ni^{II}H_{-2}L^1$ and $Ni^{II}H_{-2}L^2$ complexes: Kimura, E.; Sakonaka, A.; Nakamoto, M. *Biochim. Biophys. Acta* **1981**, *678*, 172.

Selective Formation of Trans Olefins by a Catalytic Hydrogenation of Alkynes Mediated at Two Adjacent Metal Centers

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Cis olefins are the ubiquitous first products in catalytic alkyne hydrogenations with metals and also mononuclear metal complexes; appearance of trans olefins in such reactions usually can be traced to a subsequent step of olefin isomerization. Earlier, we[1] noted the possibility that trans olefins could be initial products in homogeneous systems if there were two metal centers involved in the catalytic sequence. We describe here a system in which trans olefins are so formed with a dinuclear metal catalyst. A late step in the catalytic cycle was rate determining, enabling a definition of intermediates in the catalytic cycle,[2] including the key bridging vinyl intermediate with trans substituents, through low-temperature studies and by spectroscopic and crystallographic investigations. This novel catalytic system has no synthetic utility because of a short catalyst lifetime. However, utility is not the immediate issue; the key scientific point is that a unique catalytic outcome at adjacent metal centers in a polynuclear complex has been unequivocally demonstrated.

Alkynes are converted[3] to olefins at low rates (~1 turnover/min) at 20 °C and <1 atm by the catalyst precursor $(\mu\text{-}H)_2Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ (**1**), a bridged square-planar[4] dinuclear complex. This dimer[3] has been shown to undergo fast, reversible reaction with hydrogen to form $(\mu\text{-}H)_3(H)Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ (**2**). We have found that the dimer also reacts with alkynes (but not with olefins) in the absence of hydrogen to form first $(\mu\text{-}H)_2(\eta^2\text{-}\mu\text{-}RC_2R)Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$, which then transforms to a bridged vinyl complex. Relative rates of reaction of **1** with H_2 and with alkynes is H_2 > dialkylacetylenes > diarylacetylenes. The tetrahydride **2** also reacted with alkynes to form hydrogen and the bridged vinyl complex, but more rapidly than did dimer **1** form the vinyl complex directly from alkyne.

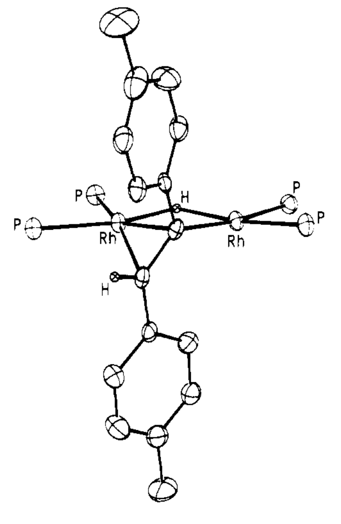

Figure 1. Core structure of $HRh_2(CH_3C_6H_4C{=}C(H)C_6H_4CH_3)[P(O\text{-}i\text{-}C_3H_7)_3]_4$ with isopropoxy groups omitted for clarity. The *p*-tolyl groups are oriented trans to one another in the bridging vinyl linkage. The X-ray crystal structure of $HRh_2(CH_3C{=}C(H)CH_3)[P(O\text{-}i\text{-}C_3H_7)_3]_4$ revealed an essentially identical structure for the core atoms. Isostructural also is the vinyl complex derived from $C_6H_5C{\equiv}CC_6H_5$ as determined by NMR spectroscopy (see supplementary material). The full details of these crystal structures will be described elsewhere.

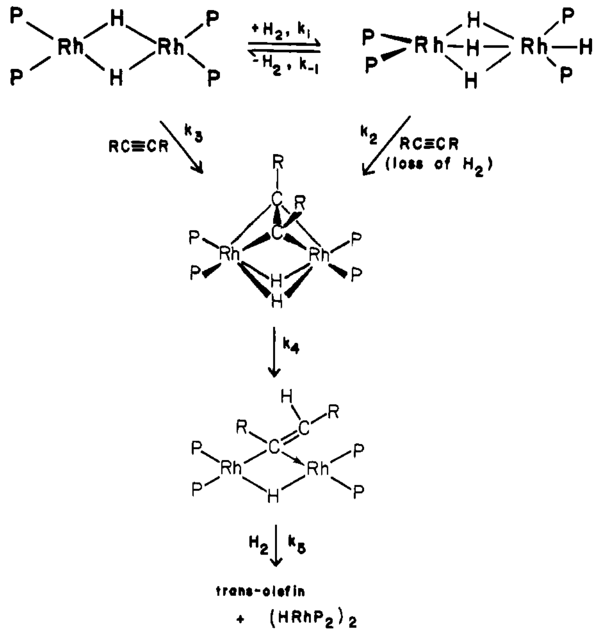

Figure 2. Scheme depicting the catalytic hydrogenation of acetylene to olefins by $(\mu\text{-}H)_2Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$. In the bridging vinyl structure, the arrow represents a π bonding of the vinyl carbon atoms to the rhodium atom on the right (see Figure 1). All compounds shown in this scheme have been spectroscopically or crystallographically defined. For $R = C_6H_5$ or $CH_3C_6H_4$, $k_1 > k_2 > k_4 > k_3 > k_5$; for $R = CH_3$, $k_1 > k_2 > k_4 \cong k_3 > k_5$. Undetected in these reactions have been $H_4Rh_2(RC{\equiv}CR)[P(O\text{-}i\text{-}C_3H_7)_3]_4$ (from reaction of $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ with $RC{\equiv}CR$) and $H_3Rh_2(RC{=}C(H)R)[P(O\text{-}i\text{-}C_3H_7)_3]_4$ (from reaction of the vinyl complexes with H_2). The last step of the cycle undoubtedly comprises several elementary steps including hydrogen addition, carbon–hydrogen bond formation, and olefin elimination. The first of these elementary steps is probably the rate-determining step.

The bridged vinyl complexes derived from various dialkyl- and diarylacetylenes appeared to be structurally identical by NMR data, but the stereochemistry in the vinyl group could not be

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(2) No homogeneous catalytic hydrogenation of alkynes had been mechanistically established in reasonable detail prior to this study.

(3) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

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established from the NMR data. Accordingly, the crystal structures of the vinyl complexes derived from 2-butyne, **3**, and from di-*p*-tolylacetylene, **4**, were determined. Both vinyl derivatives had trans stereochemistry (Figure 1). There are precedents for bridging vinyl ligands in clusters but all, crystallographically defined, have cis stereochemistry.[5]

One equivalent of hydrogen converted the vinyl complexes to the corresponding trans olefin and the original dimer, **1**. In a catalytic mode, the product was the trans olefin (see the degradation sequence described below). With the vinyl complexes as the catalyst, the results were the same. Our data provide a firm basis for the catalytic sequence presented in Figure 2. The rate-determining step appears to be hydrogen addition to the vinyl intermediate since the catalytic reaction rate is a sensitive function of H_2 pressure. Olefin elimination directly from this vinyl intermediate does not appear to be a kinetically significant process, at least for diarylacetylenes in either the presence or absence of H_2.

Unfortunately, alkynes also react with the bridged vinyl intermediate.[6] This process, competitive with hydrogen addition to form the trans olefin, leads to the degradation of the dinuclear complex within 5 min under catalytic conditions. The details of the chemistry that ensues vary with the nature of the acetylene; for brevity, the description here is limited to diphenylacetylene chemistry. Addition of the latter to the vinyl complex forms the mononuclear, square-planar complex[7] $Rh[\pi\text{-}(H)(R^1)C{=}C(R^2)C(R^3){=}C(R^4)][P(O\text{-}i\text{-}C_3H_7)_3]_2$ (**5**), which has been crystallographically defined (details of which will be presented in a separate article) and which has the R^1 and R^2 aryl groups trans and R^3 and R^4 cis. This latter complex was shown to be a catalyst precursor for the hydrogenation of diphenylacetylene to *cis*-stilbene. Thus, alkyne hydrogenation initiated by **1** transforms from selective trans-olefin to selective cis-olefin formation. Attempts to prevent the effective alkyne competition for the vinyl intermediate by raising the hydrogen pressure from 1 to 100 atm were only partially successful (the degradation rate was suppressed but the overall rate was so greatly enhanced that all alkyne was consumed in ~60 s, and under these conditions, substantial amounts of the first formed olefins were converted to alkanes).

Alkyne hydrogenations catalyzed by other dinuclear and also polynuclear complex precursors have been described,[8-12] but in all these reported systems, cis olefins have been the main products. However, the nuclearity of the actual catalyst intermediates was not defined in these systems although labeling studies[8] for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\eta^2\text{-}\mu\text{-}RC_2R)$ indicated that fragmentation of the dimer was not a significant process. In any case, the presence of reactive, adjacent metal centers is not a sufficient condition[1] for trans-olefin formation in alkyne hydrogenation—the stereochemical outcome obviously depends on the intimate stereochemistry of the intermediates in the catalytic cycle. The precise electronic and steric factors that govern stereochemistry[1] in the formation of the bridging vinyl ligand are not evident from available data. Having demonstrated a principle concerning catalysis at two adjacent metal centers and having reasonably outlined the mechanistic character of the catalytic cycle, we now seek a robust trans-olefin catalytic system by dispersing and supporting dinuclear metal complexes on metal oxides.

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Registry No. 1, 65176-62-7; **2**, 70727-45-6; **3**, 82135-63-5; **4**, 82135-62-4; **5** (R = Ph), 82135-61-3; $HRh_2(C_6H_5C{=}C(H)C_6H_5)[P(O\text{-}i\text{-}C_3H_7)_3]_4$, 82135-60-2; $(\mu\text{-}H)_2(\eta^2\text{-}\mu\text{-}C_6H_5C_2C_6H_5)Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]^4$, 82135-59-9; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5; di-*p*-tolylacetylene, 2789-88-0.

Supplementary Material Available: Synthesis and characterization data for $(\mu\text{-}H)_2(\eta^2\text{-}\mu\text{-}C_6H_5C_2C_6H_5)Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$, the bridged vinyl species derived from 2-butyne, diphenylacetylene, and di-*p*-tolylacetylene, and for $[(i\text{-}C_3H_7O)_3P]_2Rh(C(C_6H_5){=}C(C_6H_5){-}C(C_6H_5){=}C(H)(C_6H_5))$ (6 pages). Ordering information is given on any current masthead page.

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Reduction of CH_3NC and CH_3CN by the Reduced Species of $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$: Model Reactions to Nitrogenase

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Recently, we reported that C_2H_2 is reduced by the electrochemically reduced species of $[Fe_4S_4(SPh)_4]^{2-}$ ($[4\text{-}Fe]^{2-}$)[1] or $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ ($[Mo\text{-}Fe]^{3-}$)[2] catalytically in MeOH/THF to give C_2H_4 selectively without evolving H_2 gas and that C_2D_2 is reduced by the same catalyst in H_2O at pH 6.0 to afford *cis*-$C_2D_2H_2$ stereoselectively.[3] The close similarity of these reactions to the nitrogenase reaction has driven us to study the reduction of CH_3NC and CH_3CN by the same catalysts. Isonitrile and nitrile molecules seem to be more practical substrates than acetylene for nitrogenase model reactions, since the reductions of CH_3NC to CH_4 and CH_3NH_2[4-9] and of CH_3CN to C_2H_6 and NH_3[8-10] require six electrons as in the reduction of N_2 to NH_3. In the reduction of RNC and RCN catalyzed by some molybdenum complexes reported so far,[11-13] the amounts of CH_3NH_2 and NH_3 formed have not been determined at all. This com-

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