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Metal Clusters in Catalysis. 14.¹ The Chemistry of Dinuclear Metal–Acetylene Complexes

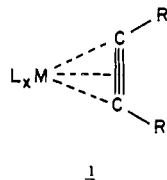
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Abstract: Acetylene and diaryl- and dialkylacetylenes are uniformly bound in a μ_2 - η^2 fashion in dinuclear metal complexes so as to generate an M_2C_2 tetrahedral core structure with a substantially increased acetylenic C–C bond distance. One class of these dinuclear complexes, $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR})$, was shown to react at 20 °C with hydrogen and with hydrogen plus $\text{RC}\equiv\text{CR}$, respectively, to form stoichiometrically and catalytically the cis alkene (>95% selectivity). In contrast, $\text{Fe}_2(\text{CO})_6$ - $[(\text{CH}_3)_3\text{CC}\equiv\text{CC}(\text{CH}_3)_3]$ reacted only stoichiometrically with hydrogen at 20 °C in the presence of free di-*tert*-butylacetylene with conversion of only the initially bound acetylene to a mixture of hydrocarbons comprised of trans and cis alkenes and traces of the alkane. The trans alkene predominated in this iron system. The coordinately saturated complexes, $\text{Co}_2(\text{CO})_6$ - $(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ and $\text{Ni}_2(\text{C}_5\text{H}_5)_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$, showed neither reactivity toward hydrogen at 20–80 °C nor acetylene ligand exchange in solutions with $\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7$ at 50 °C. These chemically distinguished features are discussed and some relationships of this acetylene chemistry to acetylene–metal surface chemistry are examined. Acetylene ligand lability, established for the $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR})$ species, arises from a monomer–dimer equilibrium: $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR}) + \text{RC}\equiv\text{CR} \rightleftharpoons 2 \text{Ni}(\text{COD})(\text{RC}\equiv\text{CR})$. The monomer is probably the active catalyst in the observed acetylene trimerization reaction whereas the dimer appears to be the primary solution species that interacts with hydrogen.

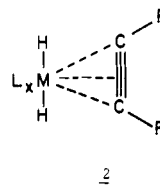
Introduction

Complexation of acetylenes by a single transition metal in a molecular complex is adequately described in terms of σ and π bonding interactions that involve the π and π^* orbitals of the acetylene.³ These complexes schematically represented in **1** are designated as η^2 acetylene complexes following the



hapto notation proposed by Cotton.⁴ Structural data for these complexes have been critically reviewed by Ittel and Ibers.⁵ In all instances, the acetylenic C–C bond distances increase from the ~ 1.20 Å reference for free acetylenes to 1.30 ± 0.70 Å.⁶ All structural data are limited to acetylene and dialkyl- or diarylacetylenes; no data are available for $\text{RC}\equiv\text{CH}$.⁶ This bond order reduction on complexation should be and is sufficient to activate the acetylene for reduction or specifically for hydrogenation.^{7,8} For example, Osborne and Schrock⁹ have shown that complexes of the form $\text{Rh}(\text{norbornadiene})\text{L}_2^+$

effectively and selectively catalyze the hydrogenation of acetylenes to cis alkenes ostensibly through intermediates formally analogous to **1** and **2**.



In the binding of acetylenes to transition metals in dinuclear or polynuclear (cluster) complexes, the prevailing mode is not of form **1** but rather a cluster form where there is a rehybridization of the carbon orbitals so that relatively strong metal–carbon σ bonds are formed between the acetylenic carbon atoms and two or more metal atoms as illustrated in **3** for the

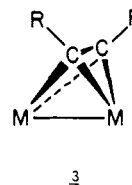


Table I. Dinuclear Metal Acetylene Complexes

Complex	M-M	M-C	C-C ^a	Ref
Mo ₂ (C ₅ H ₅) ₂ (CO) ₄ (HC≡CH)	2.984	1.967 (av)	1.338	13a
Mo ₂ (C ₅ H ₅) ₂ (CO) ₄ (C ₂ H ₅ C≡CC ₂ H ₅)	2.977	1.961 (av)	1.335	13b
Mo ₂ (C ₅ H ₅) ₂ (CO) ₄ (C ₆ H ₅ C≡CC ₆ H ₅)	2.956	2.20 (av)	1.329	13c
Fe ₂ (CO) ₆ [(CH ₃) ₃ CC≡CC(CH ₃) ₃]	2.316	2.08 (av)	1.311	14
Co ₂ (CO) ₆ [(CH ₃) ₃ CC≡CC(CH ₃) ₃]	2.463	2.00 (av)	1.335	14
Co ₂ (CO) ₆ (C ₆ H ₅ C≡CC ₆ H ₅)	2.47	1.96 (av)	1.369	14, 15
Rh ₂ (PF ₃) ₄ (P(C ₆ H ₅) ₃) ₂ (C ₆ H ₅ C≡CC ₆ H ₅)	2.740	2.11 (av)	1.369	16
Ni ₂ (C ₅ H ₅) ₂ (HC≡CH)	2.345	1.884	1.341	17
Ni ₂ (C ₅ H ₅) ₂ (C ₆ H ₅ C≡CC ₆ H ₅)	2.329	1.89 (av)	1.35	18a
Ni ₂ (COD) ₂ (C ₆ H ₅ C≡CC ₆ H ₅) ^b	2.617	1.93 (av)	1.386	12
Pd ₂ [(C ₆ H ₅) ₃ C ₅] ₂ (C ₆ H ₅ C≡CC ₆ H ₅)	2.639	2.05 (av)	1.33	18b

^a C-C = "acetylene" carbon-carbon bond distance. ^b COD = 1,5-cyclooctadiene.

simplest case, the dinuclear complexes. Bond order reduction, as sensed by C-C bond elongation, seems to increase as the number of interacting metal atoms is increased from one in **1** to two in **3** and three or four in cluster-acetylene complexes.⁸ In some but not all of these dinuclear and polynuclear complexes, the acetylene is susceptible to hydrogenation to an olefin, and in a few cases, the complexes themselves serve as catalysts for acetylene hydrogenation. We see two important aspects of this chemistry. The structural features, well established from crystallographic studies, may to a first approximation provide reasonable models of the binding of an acetylene, specifically a disubstituted acetylene, to some metal surfaces^{7,8,10-12} but they do not necessarily relate to the binding of HC≡CH or an RC≡CH acetylene to a metal surface (vide infra). Since the reactivity of these acetylene complexes toward hydrogen (hydrogenation) varies, there is an opportunity here to examine the various factors, e.g., ligand lability, acetylene ligand exchange (in an intramolecular and intermolecular context), and metal-metal bond reactivity, that may affect the susceptibility of the bound acetylene to a hydrogenation reaction. Some aspects of this chemistry have been considered for metal clusters.^{7,8,10-12} Here we discuss the chemistry of the relatively large and structurally well-defined¹²⁻¹⁹ dinuclear metal-acetylene complexes. Table I provides a concise summary of these complexes and the salient structural features;¹²⁻¹⁹ all complexes have the basic tetrahedral M₂C₂ structural framework, **3**. The dinuclear metal acetylene complexes may be decomposed into four discrete electronic classes: (1) the class of d⁹-d⁹ complexes in which there is a single metal-metal bond and full coordination saturation within the complex, e.g., Co₂(CO)₆(RC≡CR), (C₅H₅Ni)₂(RC≡CR), and C₅H₅Ni(RC≡CR)Co(CO)₃, (2) the class of coordinately saturated d⁵-d⁵ molybdenum complexes [C₅H₅Mo(CO)₂]₂(RC≡CR), which have a single Mo-Mo bond, (3) the d⁸-d⁸ class with a metal-metal double bond as exemplified by [Fe(CO)₃]₂(RC≡CR), and (4) the d¹⁰-d¹⁰ class in which the metal-metal interaction is relatively weak, for example, [Ni(COD)]₂(RC≡CR). As discussed below only the last two classes exhibit a reactivity toward hydrogen under moderate conditions of temperature and pressure.

Results and Discussion

Earlier we reported¹² the synthesis of Ni₂(1,5-cyclooctadiene)₂(C₆H₅C≡CC₆H₅), a dinuclear acetylene complex whose established structure is presented in Figure 1. Because this complex readily undergoes reduction and also serves as a catalyst for acetylene hydrogenation, we discuss the chemistry of this complex, and related complexes, first and then extend the discussion and questioning about reactivity to other well-established dinuclear metal-acetylene complexes.

Reaction of diphenylacetylene and bis(1,5-cyclooctadiene)nickel, Ni(COD)₂, in a 1:2 molar ratio yielded Ni₂(COD)₂(C₆H₅C≡CC₆H₅) in high yield; in fact, single

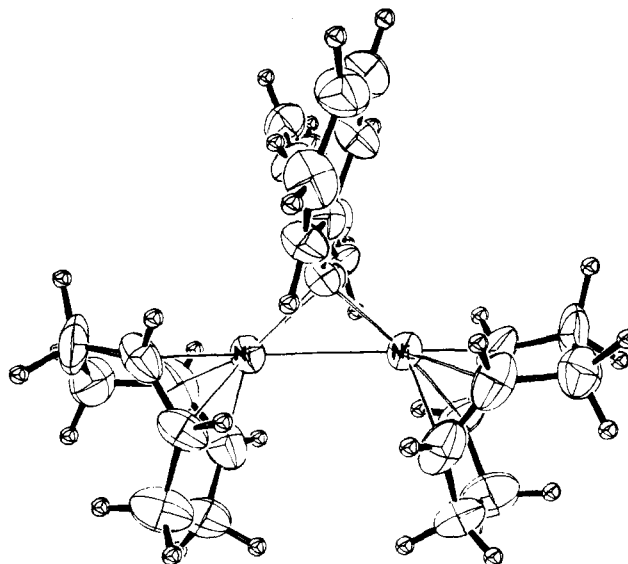


Figure 1. A perspective drawing, adapted from an ORTEP plot, of the (1,5-cyclooctadiene)₂-diphenylacetylene structure. This perspective only partially illustrates the relative ligand shielding of each nickel atom because acetylene and diene hydrogen atom positions are not depicted in the drawing.

crystals of the complex slowly separated from the reaction solution.¹² In a similar fashion, the di-*p*-tolylacetylene analogue was prepared. A preliminary description of the molecular structure of the former has appeared¹² (see Figure 1) and the full details of the crystallographic study of both complexes will be reported separately.¹⁹ The key features of the molecular structure of the diphenylacetylene complex are the basic Ni₂C₂ tetrahedral core, an acetylenic C-C distance of 1.39 Å, a Ni-Ni distance of 2.62 Å, and a rather effective shielding of the nickel atoms by the organic ligands.

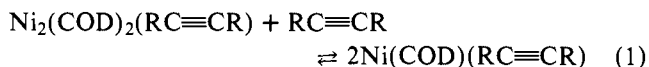
Dialkylacetylenes reacted with Ni(COD)₂ to form Ni₂(COD)₂(RC≡CR) as established by ¹H NMR studies of the reaction system. Our attempts to isolate these complexes were unsuccessful because (1) the reaction is reversible and (2) we employed quite volatile dialkylacetylenes like 2-butyne and 3-hexyne; these reaction systems yielded starting materials where conventional isolation procedures were employed. Acetylene and monosubstituted acetylenes did not yield tractable complexes ostensibly because of the reactivity of the acetylenic C-H bond.

In a formal context, the dinickel-acetylene complexes are coordinately unsaturated 32- or 34-electron species (see Conclusion section below) and the general chemical features of these complexes are consistent with such a formal characterization. Unlike the coordinately saturated Co₂(CO)₆(C₆H₅C≡CC₆H₅) and Ni₂(C₅H₅)₂(C₆H₅C≡CC₆H₅) com-

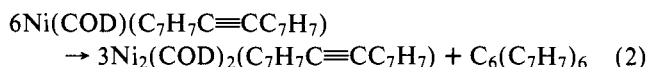
plexes, the $\text{Ni}_2(\text{COD})_2(\text{acetylene})$ structures were extremely reactive toward oxygen in the solution state. Reaction of the dinuclear nickel-acetylene complexes with donor ligands was fast. Isocyanides and phosphites instantaneously converted the complexes at 20 °C to mixtures of mononuclear species. With excess trimethyl phosphite, the product was $\text{Ni}[\text{P}(\text{OCH}_3)_3]_4$ plus free acetylene and cyclooctadiene.

Hydrogen reacted at a modest rate with solutions of $\text{Ni}_2(\text{COD})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$. Nickel metal formation was visually evident after about 30 min at 20 °C and the acetylene was completely converted to *cis*-stilbene (95% or greater *cis*) within 1 h. Attempts to observe hydride intermediates by ^1H NMR at -40 to 20 °C and hydrogen pressures up to 5 atm were unsuccessful. It appears that in this reaction system the hydrogen addition step is much slower than the hydrogen transfer (to the acetylene) step. A reaction system composed of diphenylacetylene, hydrogen, and $\text{Ni}_2(\text{COD})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ was catalytic (~two turnovers per hour) for the hydrogenation of the acetylene to *cis*-stilbene but cyclotrimerization of the acetylene to hexaphenylbenzene was a minor competing reaction. Similarly, the nickel complex catalyzed the hydrogenation of 3-hexyne to 3-hexene (99% *cis* and 1% *trans*) at a slightly higher rate (~three turnovers per hour). In this system, cyclotrimerization of the acetylene to hexaethylbenzene occurred at about the same rate as the hydrogenation reaction. In the absence of hydrogen, the nickel complexes catalyzed the cyclotrimerization of dialkylacetylenes and diarylacetylenes as did $\text{Ni}(\text{COD})_2$ itself.

In solution, the dimer appears to be robust; the ^1H NMR spectrum was essentially invariant over a temperature range of 50 to -50 °C and the only resonances detected are assignable to protons in the dimer structure. However, the acetylene ligands in these nickel complexes are highly labile as was shown by NMR studies of mixtures of $\text{Ni}_2(\text{COD})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ and di-*p*-tolylacetylene, $\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7$. This exchange proceeds through the formation of a mononuclear complex. There is a rapid equilibrium between the dinuclear complex and a mononuclear species when excess acetylene is present,

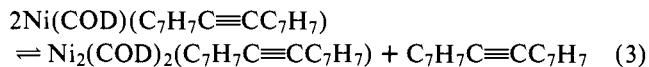


and the mononuclear complex with di-*p*-tolylacetylene has been isolated and characterized. On standing, such solutions reformed the dimer $\text{Ni}_2(\text{COD})_2(\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7)$ because the excess acetylene slowly was trimerized to hexa-*p*-tolylbenzene.



The diphenylacetylene complex exhibited an analogous initial behavior and the $\text{Ni}(\text{COD})(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ complex formed (eq 1); however, this solution on standing for 24 h produced detectable (NMR) quantities of free 1,5-cyclooctadiene in addition to the dimer and hexaphenylbenzene. This liberation of cyclooctadiene may have reflected the formation of small amounts of $\text{Ni}(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)_2$.

Dissolution of the mononuclear di-*p*-tolylacetylene complex rapidly established an equilibrium with free acetylene and the dimeric complex.

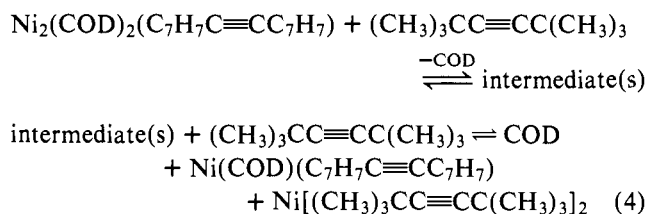


A ^1H NMR study of the di-*p*-tolylacetylene system gave an equilibrium constant of 0.12 ± 0.04 for eq 3 at 20 °C.

Reaction of $\text{Ni}(\text{COD})_2$ with other unsaturated molecules provided a range of results. Azobenzene yielded an isolable mononuclear complex, $\text{Ni}(\text{COD})(\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5)$, and simple olefins gave neither isolable products nor spectroscopic

(NMR) evidence of reaction or interaction between the olefin and the complex. An NMR study of the $\text{Ni}(\text{COD})_2$ -2-butene system and of the $\text{Ni}_2(\text{COD})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ -2-butene system showed neither evidence for the formation of $\text{Ni}_2(\text{COD})_2(2\text{-butene})$ or $\text{Ni}(\text{COD})(2\text{-butene})$ nor for olefin isomerization. Trace impurities (possibly peroxides) in olefins often elicited a catalytic decomposition of $\text{Ni}(\text{COD})_2$ to give a nickel mirror.

Di-*tert*-butylacetylene displayed a substantially different rate and mode of interaction with the nickel dimer complex, $\text{Ni}_2(\text{COD})_2(\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7)$. Using NMR to monitor the reaction, it was found that new resonances other than those of the reactants slowly appeared, ~10% reaction in 1 h at 20 °C; one set could be ascribed to free cyclooctadiene and one resonance line to a di-*tert*-butylacetylene-nickel complex. Isolation studies showed that $\text{Ni}(\text{COD})(\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7)$ was definitely formed in the reaction. Also isolated in small amounts was a yellow, relatively unstable oil. The ^1H NMR spectrum of the oil showed only a single resonance for a complexed di-*tert*-butylacetylene. The data suggest the following reaction sequence:



Reaction of $\text{Ni}_2(\text{COD})_2(\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7)$ with di-*tert*-butylacetylene and hydrogen led to the formation of a nickel mirror and *cis*- and *trans*-di-*tert*-butylethylene (2,2,5,5-tetramethyl-3-hexene). Immediately after visual observation of a nickel mirror, the isomer ratio was ~7 *cis* to 3 *trans* with the bulk of the added acetylene unreacted. The nickel mirror was apparently formed only after significant quantities of the diarylacetylene were hydrogenated and then this mirror heterogeneously catalyzed the hydrogenation of the di-*tert*-butylacetylene. Separate studies with nickel mirrors and the di-*tert*-butylacetylene established that a catalyzed hydrogenation does occur and the olefin isomer ratio ranged from about 7 *cis* to 1 *trans* to 3 *cis* to 1 *trans*. This mirror does not catalyze the isomerization of these olefins.

Since the equilibrium between the $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR})$ complexes and $\text{RC}\equiv\text{CR}$ with the corresponding mononuclear $\text{Ni}(\text{COD})(\text{RC}\equiv\text{CR})$ complexes has been unequivocally established and since a facile acetylene cyclotrimerization was observed for solutions of the monomer but not of the dimer and also for the catalytic reactions (especially for dialkylacetylenes), the $\text{Ni}(\text{COD})(\text{RC}\equiv\text{CR})$ complex, or possibly $\text{Ni}(\text{RC}\equiv\text{CR})_2$ which could be present at very low (spectroscopically undetectable) concentrations, is probably the first intermediate in the cyclotrimerization cycle. Attempts to prepare $\text{Ni}(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)_2$ from the $\text{Ni}(\text{COD})_2$ reaction system were unsuccessful, although the studies of the di-*tert*-butylacetylene reaction with $\text{Ni}_2(\text{COD})_2(\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7)$ suggest the formation of $\text{Ni}[(\text{CH}_3)_3\text{CC}\equiv\text{CC}(\text{CH}_3)_3]_2$.

A careful study of the 16-electron mononuclear acetylene complex $[(\text{CH}_3)_3\text{CNC}]_2\text{Ni}(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ in its reactions (1) with hydrogen, (2) with diphenylacetylene, and (3) with diphenylacetylene and hydrogen showed that there is no hydrogenation of the bound acetylene and no catalytic hydrogenation or cyclotrimerization of the acetylene from 0 to ~60 °C. Above 60 °C, a low rate of cyclotrimerization was observed and at 80-100 °C a low rate of hydrogenation was observed but these reactions did not proceed until deep coloration and formation of a nickel cluster occurred. We conclude that this mononuclear complex is largely inactive in these reaction re-

gimes but these observations do not allow the conclusion that the mononuclear $\text{Ni}(\text{COD})(\text{RC}\equiv\text{CR})$ complexes would be inert toward hydrogen or a catalytic cycle comprising acetylene hydrogenation. Facile interconversions in solution have complicated a precise quantitative comparative study of the $\text{Ni}(\text{COD})(\text{RC}\equiv\text{CR})$ and $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR})$ reactivities toward hydrogen. However, the rate of hydrogen addition to $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR})$, which is a singular (to at least ~98%) species in solution, is relatively constant at 20 °C. In contrast, a solution of a 1:2 molar mixture of $\text{Ni}_2(\text{COD})_2(\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7)$ and $\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7$, which would have less than ~10% of dimer present in solution, exhibited an initially very low or zero rate of reaction with hydrogen to about a 5-min reaction time and then showed sharp rate increases after ~6 and 15 min. At about the same time, solids were visually detected, but this system formed no nickel mirror, whereas the dimer yielded a mirror after about 15 min. The sharp rate increase at ~5 min could be ascribed to catalysis by small nickel particles. The results suggest that hydrogen addition to the dimer, or an intermediate derived from the dimer, is the primary initial reaction path for hydrogenation in this labile system.

There is a curious puzzle in the reactions of the nickel dimers, $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR})$. Hydrogen addition is moderately fast at 20 °C. However, the reaction of a diarylacetylene with these dinuclear nickel-diarylacetylene complexes is faster. Within mixing times, the reaction to form the $\text{Ni}(\text{COD})(\text{RC}\equiv\text{CR})$ monomer is complete. Electronically, these results present no puzzle. Steric considerations are, however, quite another matter as a casual inspection of the dimer structure (Figure 1) will quickly show.

In order to explore further the issue of reactivity in dinuclear metal acetylene complexes and to assess the significance in terms of the $\mu_2\text{-}\eta^2$ acetylene-metal binding, the reactions of other dinuclear metal complexes have been examined.

One of the more interesting dinuclear metal acetylene complexes is $\text{Fe}_2(\text{CO})_6[(\text{CH}_3)_3\text{CC}\equiv\text{CC}(\text{CH}_3)_3]$. Formally this complex is analogous to the $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR})$ complexes in that it is a 32-electron species. However, the structural studies showed that the Fe-Fe separation is very short, 2.32 Å, which is suggestive of an iron-iron double bond, even given the ambiguity associated with bond order-bond distance relationships in coupled (ligand coupled) metal-metal bonded systems. In support of this proposal, theoretical calculations do in fact indicate a closed shell configuration with multiple iron-iron interactions. A question of considerable general significance is the reactivity of this multiple-bonded metal system in oxidative addition reactions.

Hydrogen reacted rapidly at 20 °C with solutions of $\text{Fe}_2(\text{CO})_6[(\text{CH}_3)_3\text{CC}\equiv\text{CC}(\text{CH}_3)_3]$ with hydrogenation of the acetylene and the formation of $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$. Major amounts of intractable solids were also formed but these showed no activity as catalysts for the hydrogenation of the di-*tert*-butylacetylene. In fact, the reaction system was not catalytic: the extent of acetylene hydrogenation was the same whether free acetylene (tenfold excess) was present or not and the reaction was complete within less than 2 h. The major hydrogenation product was the trans alkene; the trans to cis ratio of the alkenes was 9:1. Only traces of the alkane, 2,2,5,5-tetramethylhexane, were formed in this reaction. No significant variations in the three hydrocarbon concentrations were detected over reaction periods that ranged from 2 to 24 h. These results clearly demonstrate that an oxidative addition at an iron-iron multiple bond is possible; in this case, there is an oxidative addition of hydrogen. Unfortunately, the hydrogenation sequence for the iron system follows a pathway from which re-formation of $\text{Fe}_2(\text{CO})_6[(\text{CH}_3)_3\text{CC}\equiv\text{CC}(\text{CH}_3)_3]$ is either not feasible or is slow relative to $\text{Fe}_3(\text{CO})_{12}$ formation and a catalytic cycle is not followed.

The cobalt complex, $\text{Co}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$, is coordinately saturated. An active site for hydrogen addition requires a loss of CO, a rearrangement, or a fragmentation of the Co_2C_2 cluster substructure. If such processes were to proceed at reasonable rates below the decomposition temperature of the complex, then hydrogen addition should proceed. Actually, this cobalt complex underwent no reaction with hydrogen in the presence of excess diphenylacetylene at 20–60 °C, although some catalytic cyclotrimerization of the acetylene to hexaphenylbenzene was observed at 60 °C. The dinuclear complex was recovered unchanged under these reaction conditions. Hydrogen alone underwent no reaction with $\text{Co}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ at 20–60 °C but there was some conversion of the dinuclear complex to the tetranuclear complex, $\text{Co}_4(\text{CO})_{10}(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$. As a further check on this cobalt-acetylene system, the reactions of the tetranuclear complex were examined and no reactivity toward hydrogen was detected. At 60 °C, diphenylacetylene converted the tetranuclear to the dinuclear acetylene complex. Separate studies (NMR) on the lability of the acetylene ligand in the dicobalt system showed that di-*p*-tolylacetylene did not detectably displace diphenylacetylene from $\text{Co}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ at 20 °C within a 2-day period and at 50 °C within a 1-day period, although in the higher temperature experiment there was evidence (NMR) for a small amount of acetylene trimerization.

$(\text{C}_5\text{H}_5)_2\text{Ni}_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$, like the cobalt analogue, is a coordinately saturated complex. A reactive site for hydrogen addition could be generated in this complex by a $\eta^5\text{-C}_5\text{H}_5\text{Ni} = \eta^3\text{-C}_5\text{H}_5\text{Ni}$ process or by rearrangement or fragmentation of the skeletal Ni_2C_2 cluster. However, we found no reactivity of this complex toward hydrogen in the 20–80 °C temperature range. Also, the novel mixed cluster, $\text{Ni}(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_3(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$, was inactive toward hydrogen. The acetylene ligand in $\text{Ni}(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_3(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ was not labile at 25 °C but there was ligand exchange between this complex and free di-*p*-tolylacetylene at a temperature of 50 °C over a 1-day reaction period. $(\text{C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$ ¹³ and $(\text{C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$ react with acetylene and monosubstituted and disubstituted acetylenes to form $(\text{C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{RC}\equiv\text{CR})$. These coordinately saturated acetylene complexes were also unreactive toward hydrogen and also did not exhibit acetylene ligand lability in solutions containing excess acetylene at 20–70 °C,^{20a} but the C_2H_2 complex was active at 100 °C^{20b} for acetylene exchange and acetylene hydrogenation.

Conclusions

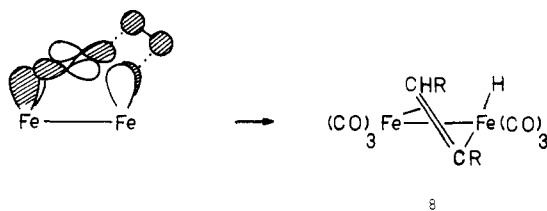
Facile hydrogenation of acetylene bound in a $\mu_2\text{-}\eta^2$ mode with a basic M_2C_2 skeletal cluster core in dinuclear metal-acetylene complexes is explicitly observed only where a formal degree of coordination unsaturation is extant, including a formal metal-metal multiple bond, classes (3) and (4) described in the Introduction. Thus, the coordinately saturated $\text{Co}_2(\text{CO})_6(\text{RC}\equiv\text{CR})$, $\text{Ni}_2(\text{C}_5\text{H}_5)_2(\text{RC}\equiv\text{CR})$, and $\text{Co}(\text{CO})_3\text{-Ni}(\text{C}_5\text{H}_5)(\text{RC}\equiv\text{CR})$ complexes underwent no hydrogenation at 20–80 °C whereas the unsaturated $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR})$ and $\text{Fe}_2(\text{CO})_6(\text{RC}\equiv\text{CR})$ complexes did at 20 °C. The major qualitative differences in the hydrogenation behavior between $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR})$ and $\text{Fe}_2(\text{CO})_6[(\text{CH}_3)_3\text{CC}\equiv\text{CC}(\text{CH}_3)_3]$ were (1) the near exclusive formation of the cis alkene in the nickel system and trans alkene in the iron system and (2) a catalytic mode for the nickel and a stoichiometric mode for the iron system. The latter qualitative differentiation probably reflects the difficulty in the trapping of the sterically encumbered di-*tert*-butylacetylene by a hydrogenation intermediate. In fact, it appears that a hydrogenation of this acetylene was not achieved (nickel metal formed in the reaction appeared to be the catalyst) with $\text{Ni}_2(\text{COD})_2\text{-}$

($C_6H_5C\equiv CC_6H_5$) which had provided a catalytic hydrogenation system for diaryl- and di-*n*-alkylacetylenes. Differentiation in the stereochemistry of the alkenes produced in the iron and nickel systems clearly delineates a different mechanistic pathway for these systems. Results of molecular orbital calculations discussed below suggest the possibility of an initial hydrogen addition across the M-M and M-C bonds for the nickel and iron systems, respectively.

Molecular-orbital studies²¹⁻²⁴ of the electronic structures of these acetylene-bridged metal dimers provide some useful insights into their reactivities and structures. One requirement for a facile reaction of a complex with hydrogen is some sort of coordination unsaturation. Electronically, this means that the complex should provide a low-lying empty molecular orbital which has the proper symmetry to accept electron density from the H-H σ_g bonding orbital.

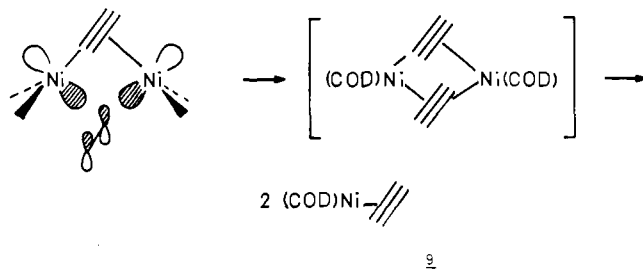
Theoretical treatments of the $Co_2(CO)_6$ (acetylene)²¹⁻²³ and $Ni_2(C_5H_5)_2$ (acetylene)²⁴ systems reveal no such empty orbitals. These complexes are d^9-d^9 dimers with a two-electron "bent" metal-metal σ orbital. The empty σ^* orbital, while it may be low lying, cannot overlap well with the σ_g orbital of an incoming H_2 molecule (in the maximum symmetry, there cannot be any overlap at all). It is reasonable that these complexes are essentially inert to hydrogenation at moderate temperatures.

Removing two electrons attains the d^8-d^8 electron count of $Fe_2(CO)_6(RC\equiv CR)$. The orbital being vacated is basically metal-metal π^* , so the complex possesses formal σ and π bonds. However, the empty molecular orbital is fairly low lying and contains a sizable contribution from the acetylene carbons, and is bonding between the iron and acetylene-carbon atoms. This orbital was originally suggested to provide a mechanism for attack by another acetylene to form a ferrole,²³ but it also provides a likely site for the initial addition of a hydrogen molecule to the complex, **8**. The resulting vinyl-iron-hydride intermediate could eventually release the trans olefin.



While the $Ni_2(COD)_2(ArC\equiv CAr)$ complexes are nominally isoelectronic with the $Fe_2(CO)_6(RC\equiv CR)$ complex, the actual electronic structures of the two systems are very different. The nickel atoms are both d^{10} centers and the dimeric complex essentially consists of two 16-electron NiL_2 "olefin" complexes, where in this case the two NiL_2 fragments bond with orthogonal π systems of the same acetylene. Strong bonding interactions between the nickel atoms are definitely absent; the calculated Ni-Ni overlap population is slightly negative, and the nickel atoms are held in proximity by the bridging acetylene.²⁴

Hydrogen addition across the metal-acetylene carbon bond is no longer a likely mode of reactivity in this nickel dimer. Since both metal atoms are in a d^{10} configuration, the $d-\pi^*$ orbital considered above—while still present—is now filled, and would repel the incoming H-H σ_g orbital. The lowest empty molecular orbitals in this dimer include the bonding and antibonding combination of the two vacant Ni " p_z " orbitals. These empty MOs permit an incoming acetylene molecule to bond between the nickel atoms and split the dimer into monomers, as drawn in **9**. This is also a very reasonable site of attack by a hydrogen molecule, leading to an intermediate μ -acetylene-($HNiCOD$)₂ species which could ultimately yield the cis olefin.



The pervasive $\mu_2-\eta^2$ binding of acetylene in these dinuclear systems suggests that similar binding modes may be found for metal surface-acetylene states, although μ_3 or $\mu_4-\eta^2$ binding may prove more common than the $\mu_2-\eta^2$ forms, especially for the 111 faces of close-packed metals as exemplified in the proposed²⁵ $\mu_3-\eta^2$ binding for C_2H_2 on Pt(111). One potentially complicating feature in any acetylene-metal surface chemistry is facile C-H bond scission, an oxidative addition reaction of C-H bonds^{26,27} to surface metal atoms, which is not common to dinuclear metal complex or metal cluster chemistry for disubstituted acetylenes, although oxidative addition reactions are documented²⁸ for monosubstituted acetylenes in cluster chemistry.

The general resistance of the $\mu_2-\eta^2$ bonded acetylene in the dinuclear metal complexes (the $d^{10}-d^{10}$ nickel complex is uniquely labile) to acetylene ligand exchange is an observation of quite general importance in metal complex and metal surface chemistry. These results suggest that analogously bonded acetylenes on metal surfaces also will be strongly bound and will not be readily susceptible to displacement reactions²⁷ or to thermal displacement. In fact, both acetylene and 2-butyne are strongly chemisorbed on the Ni(111) surface and are displaced neither by other strong donor-acceptor molecules like isocyanides nor by rapid heating of the crystal (all under high vacuum, 10^{-9} - 10^{-10} Torr, systems).²⁹ This may prove to be a rather general behavior for acetylenes chemisorbed on clean transition metal surfaces. In contrast, acetylene is only weakly chemisorbed³⁰ on the 111, 110, and 100 faces of copper metal suggesting a weak σ donor- π acceptor (as in **1**) rather than the rehybridized strong M-C σ interactions (as in **3**) established for the dinuclear metal-acetylene complexes.

In the hydrogenation of acetylenes on metal surfaces, cis alkenes generally predominate over trans alkenes and the ratio of alkene to alkane can be raised by certain pretreatment (sulfur or nitrogen compounds³¹) of the metal surface. Some of the variations in hydrogenation products could be accounted for by geometric features and by selective site poisoning (surface pretreatment). The results of our studies on these dinuclear metal-acetylene complexes raise the possibility of hydrogen addition across M-C as well as across M-M bonds and that these alternative addition modes may initially yield different alkene isomers. Perhaps the alternative M-C addition mode is operative in some metal surface catalyzed acetylene hydrogenations.

Experimental Section

General. All manipulations were performed using standard vacuum techniques or a Vacuum Atmosphere Dri-Lab in a N_2 or argon atmosphere. Solvents were purified by refluxing over sodium and benzophenone or calcium hydride and distillation under vacuum (owing to the sensitivity of the compounds, scrupulous exclusion of O_2 was necessary). The 1H NMR spectra were recorded on Varian A-60A and EM-390 instruments, equipped with variable temperature probes. Infrared spectra were recorded on a Perkin-Elmer IR337 instrument with KBr windows. Routine separation and identification of volatile compounds in catalytic reactions were effected with a Perkin-Elmer 990 gas chromatograph. Positive identification of compounds was obtained by analysis with a Finnigan gas chromatograph/mass spectrometer Model 3300 with a System Industries-150 interface. Column material was squalane (3%, 12 ft) and ethyl *N,N*-dimeth-

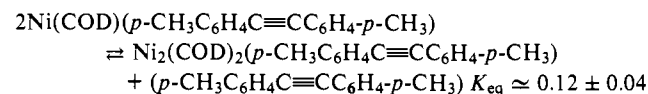
ylloxamate (20%, 7 ft) joined in series which was especially effective for the separation of hexane, the isomeric hexenes, and *cis*- and *trans*-2-hexene, and OV-101 (15%, 12 ft) for separation of di-*tert*-butylacetylene hydrogenation products. A silver nitrate column was used for the separation of *cis*- and *trans*-3-hexene. *tert*-Butyl isocyanide was dried by vacuum distillation from 4A molecular sieves. The preferred purification procedure for dialkylacetylenes and for olefins involved treatment with CaH₂, vacuum distillation, and passage down an activated alumina (grade 1) column. Diphenylacetylene was sublimed prior to use. Ni(COD)₂ was prepared as described by Schunn³² and was then stored in an argon atmosphere. Literature procedures were employed for the preparations of Co₂(CO)₆(C₆H₅C≡CC₆H₅),³³ Co₄(CO)₁₀(C₆H₅C≡CC₆H₅),³⁴ Fe₂(CO)₉[(CH₃)₃CC≡CC-(CH₃)₃],¹⁴ (C₅H₅Ni)₂(C₆H₅C≡CC₆H₅),³⁵ and [(CH₃)₃CNC]₂-Ni(C₆H₅C≡CC₆H₅).³⁶ A GC standard for the di-*tert*-butylacetylene hydrogenation products was obtained by hydrogenation of this acetylene over palladium metal conditioned with quinoline; without the conditioning, the products were *cis* and *trans* olefins and traces of the alkane.

Preparation of Ni₂(COD)₂(C₆H₅C≡CC₆H₅). Addition of Ni(COD)₂ (275 mg, 1 mmol) to a solution of C₆H₅C≡CC₆H₅ (98 mg, 0.55 mmol) in 50 mL of pentane at 25 °C led to the formation of a deep burgundy-red solution within 5 min. Over a 24-h period, small, dark red octahedra separated from this solution; many of the octahedra were of single crystal form. The crystals, recovered by filtration, were washed with five 5-mL portions of pentane; yield was 94%, mp 173–175 °C. Anal. Calcd for Ni₂C₃₀H₃₄: Ni, 22.93; C, 70.37; H, 6.69. Found: Ni, 22.78; C, 70.70; H, 7.03. ¹H NMR (benzene-*d*₆, internal (CH₃)₄Si reference) 1.82 (–CH₂–, b, 8), 2.27 (–CH₂–, b, 8), 4.73 (=CH–, b, 4), 5.13 (=CH–, b, 4), 7.14 (aromatic, m, 6), 7.40 ppm (aromatic, m, 4).

Preparation of Ni₂(COD)₂(*p*-CH₃C₆H₄C≡CC₆H₄-*p*-CH₃). The above procedure was employed with di-*p*-tolylacetylene at twice the scale and with 40 mL of pentane solvent. Three days after the mixing of reagents, large, dark red crystals were recovered by filtration and were then washed with three 2-mL portions of pentane, mp soften 138, melt 149–152 °C. Anal. Calcd for Ni₂C₃₂H₃₈: Ni, 21.74; C, 71.17; H, 7.09. Found: Ni, 21.26; C, 71.46; H, 7.15. ¹H NMR (benzene-*d*₆, internal (CH₃)₄Si reference) 1.85 (–CH₂–, b, 8), 2.13 (–CH₂–, b, 8), 2.17 (CH₃, s, 6), 4.78 (=CH=, b, 4), 5.15 (=CH–, b, 4), 7.21 ppm (aromatic, pseudo-q, 8).

Preparation of Ni(COD)(C₆H₅N=NC₆H₅). Azobenzene (364 mg, 2 mmol) and Ni(COD)₂ (550 mg, 2 mmol) were dissolved in 40 mL of pentane to give a deep red solution. After 24 h, dark red crystals were recovered by filtration and were then washed with three 2-mL portions of pentane. Anal. Calcd for NiC₂₀H₂₂N₂: Ni, 16.81; C, 68.81; H, 6.35; N, 8.03. Found: Ni, 16.72; C, 68.40; H, 6.51; N, 8.19. In reactions effected with high ratios of Ni(COD)₂ to azobenzene the isolated species were NiC₂₀H₂₂N₂ and unreacted Ni(COD)₂. There was no evidence for species of the form (COD)₂Ni₂-C₆H₅N=NC₆H₅.

Preparation of Ni(COD)(*p*-CH₃C₆H₄C≡CC₆H₄-*p*-CH₃). Ni(COD)₂ (360 mg, 1.3 mmol) and di-*p*-tolylacetylene (270 mg, 1.3 mmol) were added to ca. 60 mL of pentane and swirled at room temperature. The solution very rapidly turned red, and within 10 min precipitated 120 mg of orange-yellow, microcrystalline material (0.3 mmol, 25% yield). Cooling and evaporating the mother liquor deposited additional amounts of a reddish-brown compound for which the NMR was identical. Anal. Calcd for NiC₂₄H₂₆: Ni, 15.73; C, 77.25; H, 7.02. Found: Ni, 14.81; C, 76.64; H, 6.97. ¹H NMR (C₆D₆–(CH₃)₄Si internal reference) 2.01, 2.12 (s, 15), 5.55 (=CH–, b, 4), 7.36 ppm (aromatic, quartet, 8). Heating to 120 °C caused the compound to blacken, with melting at 133–135 °C. In solution this compound rapidly established an equilibrium with Ni₂(COD)₂(*p*-CH₃C₆H₄C≡CC₆H₄-*p*-CH₃) and the free acetylene:



(The NMR spectrum showed the expected peaks for all components.) Addition of the free acetylene to Ni₂(COD)₂(*p*-CH₃C₆H₄C≡CC₆H₄-*p*-CH₃) immediately formed Ni(COD)(*p*-CH₃C₆H₄C≡CC₆H₄-*p*-CH₃) as evidenced by NMR.

Preparation of η⁵-C₅H₅NiCo(CO)₃(C₆H₅C≡CC₆H₅). A mixture of Co₂(CO)₈ (342 mg, 1 mmol), [C₅H₅Ni(CO)]₂ (304 mg, 1 mmol),

diphenylacetylene (427 mg, 2.4 mmol), and toluene (40 mL) was warmed to 50 °C for 1 h. On cooling to 20 °C, the reaction mixture was filtered to remove the insoluble acetylene trimer, hexaphenylbenzene, and then the solution was vacuum evaporated. The residue was dissolved in pentane. This pentane solution on cooling to –30 °C yielded large, dark crystals which were collected by filtration and were then washed with three 2-mL portions of cold pentane (yield ~10%). Anal. Calcd for CoNiC₂₂H₁₅O₃: Co, 13.24; Ni, 13.19; C, 59.38; H, 3.40. Found: Co, 13.93; Ni, 11.28; C, 59.28; H, 3.48. ¹H NMR (C₆D₆–(CH₃)₄Si internal reference) 5.07 (C₅H₅, s, 5), 7.19 (ortho CH, m, 4), and 7.74 ppm (meta and para CH, m, 6). IR 1998 (s) and 2050 cm^{–1} (s) ν CO.

Preparation of (η⁵-C₅H₅Ni)₂Fe(CO)₃(C₆H₅C≡CC₆H₅). A mixture of Fe₂(CO)₉ (364 mg, 2.2 mmol), [C₅H₅NiCO]₂ (302 mg, 1 mmol), diphenylacetylene 390 mg, 2.2 mmol), and toluene (40 mL) was heated to 50 °C until gas evolution ceased, ca. 1 h. The reaction mixture was separated from solvent by vacuum rotary evaporation. The residue was dissolved in toluene and then the solution was chromatographed (alumina grade 1). Seven distinct compounds were detected including (C₅H₅Ni)₂(C₆H₅C≡CC₆H₅), various (Fe(CO)₃)_x(C₆H₅C≡CC₆H₅) complexes, and unreacted starting materials. An olive-colored fraction was subjected to a second toluene elution from an alumina column. The product was recrystallized from a pentane–toluene solution at –30 °C (yield ~10%). Anal. Calcd for FeNi₂C₂₇H₂₀O₃: Fe, 9.87; Ni, 20.77; C, 57.32; H, 3.52. Found: Fe, 9.66; Ni, 20.35; C, 56.62; H, 3.56. ¹H NMR (C₆H₅–(CH₃)₄Si internal reference) 5.02 (C₅H₅, s, 10), 7.06, 7.54 ppm (aromatic, m, 10). Tilney-Bassett³⁷ described this compound as brown.

Reaction of Ni(COD)₂ and Alkylacetylenes. Reaction of Ni(COD)₂ and dialkylacetylenes (e.g., 2-butyne and 3-hexyne) in pentane or toluene with a range of reactant ratios gave burgundy-red solutions that, without exception, yielded, on isolation procedures, unreacted Ni(COD)₂, the acetylene, and the acetylene trimer, the corresponding hexaalkylbenzene.

The ¹H NMR spectrum of a 2:1 molar mixture of Ni(COD)₂ and 3-hexyne in C₆D₆ consisted of resonances identical with those of Ni(COD)₂ and free COD plus two =CH– multiplets, and ethyl multiplets at 1.20 and 2.64 ppm (free hexyne ethyl multiplets are at 1.00 and 2.06 ppm). Similar results were observed for benzene-*d*₆ solutions of Ni(COD)₂ with C₆H₅C≡CC₆H₅ and 2-butyne. Di-*tert*-butylacetylene and Ni(COD)₂ did not react at 20 °C; at elevated temperatures a trace of red color, characteristic of the dinuclear complexes, slowly appeared. Phenylacetylene reacted with Ni(COD)₂ to form a nearly black, intractable solid that analyzed approximately for NiC₁₂H₁₂.

Perfluoro-2-butyne and Ni(COD)₂ formed Ni₂(COD)₂C₆(CF₃)₆ as reported by Stone et al.³⁸

Reaction of Ni(COD)₂ and excess dialkyl-, diaryl-, and alkyl-arylacetylenes led to an extensive trimerization reaction as established by NMR studies and by isolation and characterization of the corresponding substituted benzenes. Reaction of Ni₂(COD)₂ArC≡CAr complexes with substituted acetylenes also led to trimerization of the acetylenes.

Reaction of Ni(COD)₂, (C₅H₅NiCO)₂, and C₆H₅C≡CC₆H₅. A mixture of Ni(COD)₂, (C₅H₅NiCO)₂, and C₆H₅C≡CC₆H₅ (each in 1-mmol quantities) in 40 mL of toluene was stirred at 25 °C. The solution slowly turned from red to green over a period of 6 h; carbon monoxide was evolved and this gas formation ceased after about 24 h. The reaction solution was evaporated at 20 °C in vacuo. A portion of the residue was dissolved in C₆D₆. This solution exhibited very broad ¹H NMR resonance in the aromatic and C₅H₅ regions. On standing for 1 week, the remaining solid residue underwent decomposition with the formation of nickel metal. A pentane extraction yielded (η⁵-C₅H₅Ni)₂C₆H₅C≡CC₆H₅. Residual black solids, of high reactivity, were not successfully purified and identified.

A toluene solution of (C₅H₅NiCO)₂ (2 mmol) and C₆H₅C≡CC₆H₅ (1 mmol) yielded no (η⁵-C₅H₅Ni)₂C₆H₅C≡CC₆H₅ at 20 °C but did form the dinuclear complex at reaction temperatures of 70–90 °C.

Hydrogenation of the Dinuclear Acetylene Complexes and Catalytic Hydrogenation of Acetylenes. A solution of Ni₂(COD)₂-C₆H₅C≡CC₆H₅ (0.02 mmol) in 3 mL of toluene was evacuated at –196 °C and then warmed to 20 °C. Hydrogen was introduced to a pressure of ~400 Torr. Hydrogen uptake was relatively rapid but then began to level off at about 0.5–1.0 mol of H₂/mol of nickel complex. At this plateau, nickel metal began to separate out as a mirror and then

hydrogen absorption rate increased slightly. This reaction was repeated on a larger scale, ca. 1 mmol, and the organic products were recovered at the point that a nickel mirror began to form. The products consisted of cyclooctadiene and *cis*-stilbene (NMR analysis). Reaction of the complex with hydrogen (~1200 Torr) and excess acetylene (10:1) gave a homogeneous catalytic formation of *cis*-stilbene and of hexaphenylbenzene.

A solution of $\text{Ni}_2(\text{COD})_2\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$ (0.02 mmol) in toluene (2 mL) and 3-hexyne (2 mL) reacted with hydrogen (~1200 Torr) to produce 3-hexene and hexaethylbenzene. Rates of hydrogenation and of trimerization were the same order of magnitude. Gas chromatographic analysis of the hexene showed ~99% *cis* and 1% *trans* isomers. The turnover rate for the hydrogenation was about four per hour.

A solution of $(\text{C}_5\text{H}_5\text{Ni})_2\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$ (0.02 mmol) in toluene (2 mL) underwent no reaction with hydrogen (1200 Torr) at 25 and at 80 °C. A similar result was obtained for $\text{C}_5\text{H}_5\text{NiCo}(\text{CO})_3\text{-C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$.

A solution of 20 mg of $\text{Fe}_2(\text{CO})_6(\text{di-}i\text{-tert-butylacetylene})$ (chromatographed on silica, pentane elution, to remove residual $\text{Fe}_3(\text{CO})_{12}$) in 2 mL of toluene rapidly reacted with hydrogen (1200 Torr, 20 °C) to give the *trans* olefin (ca. 90%), *cis* olefin (ca. 10%), and traces of alkane. Similar reaction products were observed for reaction times of 2, 18, and 24 h. The metal residues were $\text{Fe}(\text{CO})_5$, $\text{Fe}_3(\text{CO})_{12}$ (characterized by IR), and unidentified solids which showed no ability to hydrogenate *di-}i\text{-tert-butylacetylene}* under similar conditions. In the presence of an added tenfold excess of the free *di-}i\text{-tert-butylacetylene}*, little or none of the free acetylene was hydrogenated in the presence of the dinuclear complex over a period of 12 h. Added *cis* olefin was not isomerized by the residues.

Three basic reactions were examined with the two cobalt acetylene complexes, $\text{Co}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ and $\text{Co}_4(\text{CO})_{10}(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$: (a) thermal stability in solution with a N_2 or argon atmosphere; (b) reaction with hydrogen (~500 Torr); and (c) reaction with excess diphenylacetylene. These were carried out in glass equipment equipped with Kontes Teflon stopcocks; nearly saturated solution of the complexes in pentane were used. The results for reactions (a) and (b) were the same at 20 and 60 °C; there was no evidence of hydrogen consumption or formation of either stilbene or dibenzyl. $\text{Co}_4(\text{CO})_{10}(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ was unchanged in reactions (a) and (b) at 20 °C over week reaction periods and was nearly unchanged at 60 °C under these conditions (traces of an insoluble brown cobalt complex were detected). The dicobalt complex formed $\text{Co}_4(\text{CO})_{10}(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ under reaction conditions (a) and (b) at 60 °C; no hydrogen consumption or stilbene-dibenzyl formation was detected in reaction (b). Reaction (c) of the dinuclear complex with either a hydrogen or nitrogen atmosphere gave a slow formation at 60 °C of hexaphenylbenzene (comparison with standard sample and mass spectrometric analysis); the dinuclear complex was recovered largely unchanged. A similar result was obtained with the tetranuclear complex, except that the tetranuclear complex was converted to $\text{Co}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ (established by IR analysis).

Hydrogenation of $\text{Ni}_2(\text{COD})_2(\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7)$. The experiments were performed by reaction of H_2 (1 atm) with 1.0-mL solutions of $\text{Ni}_2(\text{COD})_2(\text{di-}p\text{-tolylacetylene})$ in toluene (0.10 M) at 27.1 ± 0.3 °C. The reaction chamber had an estimated volume of 50 mL, and H_2 uptake was monitored by following pressure changes with a mercury manometer (2 mm i.d.). To measure H_2 uptake by the monomer $\text{Ni}(\text{COD})(\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7)$, excess *di-}p\text{-tolylacetylene}* was added to the solutions of the dimer (2 mol added acetylene per mol of monomer) immediately prior to addition of H_2 . The apparatus was carefully cleaned (HNO_3 followed by HF) after each run. Blank runs with only solvent gave the expected zero-slope straight lines. For $\text{Ni}_2(\text{COD})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$, the H_2 consumption was linear with time; the rate was about 0.04 mol of hydrogen per min per mol of dimer. Rate of hydrogen addition to the monomer $\text{Ni}(\text{COD})(\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7)$ was small or zero to ~6 min time where the rate was measurable and then as solid appeared the rate increased sharply to a near linear form of about 0.24 mol of hydrogen per mol of initial monomer.

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