

Dinuclear Complexes with a C₂ Bridge: Synthesis, Structure, and Reactivity

Hsiu-Fu Hsu

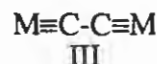
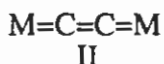
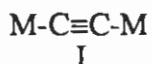
Literature Seminar

April 19, 1994

The chemistry of hydrocarbon-bridged multi-nuclear transition complexes is a subject of intense research activity, largely because information about the chemical behavior of hydrocarbon fragments in such complexes is relevant to surface chemistry of heterogeneous catalysts [1]. While metal cluster carbides are relatively common [2], complexes with dicarbide ligands that bridge to just two metals are rare. V. R. Nast reported $K_2[HC\equiv CAuC\equiv CAuCH]$ [3] as the first C₂-bridged complex in 1964. From 1980 to date, twenty additional compounds have been discovered. The development of further chemistry with these compounds has been frustrated by their poor availability.

There is no systematic strategy for the preparation of C₂ bridged compounds. In principle, this type of complex can be prepared: (a) from alkali metal acetylides and alkyl complexes or metal halides, (b) from alkyne complexes having acidic protons and metal halides or alkyl complexes, (c) from cationic complexes containing σ, π -ethynyl bridges, (d) from metal alkyls and acetylene, (e) from dihaloacetylene and carbonylmetalate ions, (f) from lithiated metal alkynes and metal halides, or (g) by oxidative addition of a dihaloacetylene, a 1,3-diyne, or "RC \equiv C⁺" to low-valent metal centers.

Three limiting valence bond descriptions of a central linear M-C-C-M moiety can be drawn as shown in I-III.



Among the known compounds, most adopt the type I bonding mode. Only $Cp_2(Me_3P)-Ti=C=C-Ti(Me_3P)Cp_2$ [4] and $(silox)_3Ta=C=C-Ta(silox)_3$ [5] adopt the type II bonding mode and $(t-BuO)_3W\equiv C-C\equiv W(O-t-Bu)_3$ [6] is the single known example of type III. The C-C bond distance within the bridging C₂ unit typically corresponds to a normal triple, double, or single C-C bond.

The MO diagrams of three compounds that illustrate each bonding mode have been calculated. The calculations for $(OC)_5Re-C\equiv C-Re(CO)_5$ [7] indicate that there is no net Re-acetylene π -interaction and that the dominant interaction between the rhenium and the C₂ unit is a σ -bond. The overall picture of an intact C \equiv C triple bond and two Re-C σ bonds agrees with the structural results. On the other hand, calculations on $(silox)_3Ta=C=C-Ta(silox)_3$ [8] suggest that there is appreciable $d_\pi \rightarrow C_2(\pi^*)$ backbonding. The difference between Re-C \equiv C-Re and Ta=C=C-Ta may be attributed to the contrasting roles played by the π acceptor CO ligands in the dirhenium complex and the π donor siloxide ligands in the ditantalum compound; these ligands help to determine the energies of the metal d_π orbitals relative to those of the C₂ fragment. The calculated frontier orbital diagram of $(t-BuO)_3W\equiv C-C\equiv W(O-t-Bu)_3$ [9] shows that the combined effects of C₂ π donation and C₂ π^* backbonding leads to significant reduction of the C-C bond order. The results indicate that the type III bonding mode is approached but not fully achieved. It is worth noting that complexes of the later transition metals cannot reduce the C-C bond order to the same extent because (a) their d_π electrons are too low in energy to back-bond effectively into the C₂ (π^*) orbital, and (b) if all the d_π metal orbitals are filled, then no net π donation from the C₂ unit to the metal is possible.

In contrast to the plentiful chemistry of C₁ species, the chemistry of C₂ species is much less developed. To date, two kinds of reactions have been described: (1) insertion of

isocyanides into the metal-carbon bond, and (2) incorporation of the dicarbide ligands into larger clusters.

Selective double insertion of isocyanides into the metal-carbon bond of $\text{Cl}(\text{PR}_3)_2\text{Pt}-\text{C}\equiv\text{C}-\text{Pd}(\text{PR}_3)_2\text{Cl}$ [10] and $\text{Cl}(\text{PR}_3)_2\text{Pd}-\text{C}\equiv\text{C}-\text{Pd}(\text{PR}_3)_2\text{Cl}$ [11] compounds has been carried out by the Takahashi group [12,13]. Multiple and successive insertion of isocyanides into the Pd-C bond of $\text{Cl}(\text{PR}_3)_2\text{Pt}-\text{C}\equiv\text{C}-\text{Pd}(\text{PR}_3)_2\text{Cl}$ has also been observed, which suggests that this reaction is a living polymerization process. Isocyanide can be also inserted into the Zr-carbon bond of $\text{Cp}(\text{Me}_3\text{P})_2\text{Ru}-\text{C}\equiv\text{C}-\text{ZrCp}_2\text{Cl}$ [14].

Several dinuclear dicarbide compounds have been used as building blocks for the construction of larger clusters containing a dicarbide ligand. For example, reaction of $\text{Cp}^*(\text{OC})_2\text{Fe}-\text{C}\equiv\text{C}-\text{Fe}(\text{CO})_2\text{Cp}^*$ with $\text{Ru}_3(\text{CO})_{12}$ results in the sequential formation of permetalated ethene and ethane derivatives [$\text{MC}\equiv\text{CM} \rightarrow \text{M}_2\text{C}=\text{CM}_2 \rightarrow \text{M}_3\text{C}-\text{CM}_3$] by formal stepwise addition of dimetallic fragments to the $\text{C}\equiv\text{C}$ bond [15]. Reaction of $\text{Co}_2(\text{CO})_8$ with $\text{Cp}^*(\text{OC})_2\text{Fe}-\text{C}\equiv\text{C}-\text{Fe}(\text{CO})_2\text{Cp}^*$ [16] or $(\text{OC})_5\text{Re}-\text{C}\equiv\text{C}-\text{Re}(\text{CO})_5$ [17] forms tetranuclear clusters containing bicarbide ligands. The thermal reaction of $\text{Cp}(\text{CO})_2\text{Ru}-\text{C}\equiv\text{C}-\text{Ru}(\text{CO})_2\text{Cp}$ [18] with $\text{Fe}_2(\text{CO})_9$ gives similar products [19]. However, reaction of $\text{Cp}^*(\text{OC})_2\text{Fe}-\text{C}\equiv\text{C}-\text{Fe}(\text{CO})_2\text{Cp}^*$ with $\text{Cp}_2\text{Ni}_2(\text{CO})_2$ results in elimination of the C_2 ligand to give the $\text{Cp}^*\text{-COFe}(\mu\text{-CO})_2\text{NiCp}$ dimer [20].

In conclusion, the three limiting bonding modes of C_2 -bridged complexes have been found. Compounds containing ethynediyl (type I) ligands constitute the majority of known compounds, and these can be useful for the synthesis of larger clusters. The reaction of isocyanides with $\text{Cl}(\text{PR}_3)_2\text{Pt}-\text{C}\equiv\text{C}-\text{Pd}(\text{PR}_3)_2\text{Cl}$ demonstrates that selective insertion and a living polymerization process can be achieved. The chemistry of complexes containing C_2 units of types II and III has yet to be developed.

References

- Halton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W., "Bridged Hydrocarbyl or Hydrocarbon Binuclear Transition Metal Complexes: Classification, Structure, and Chemistry," *Chem. Rev.* **1983**, *83*, 135-209.
 - Casey, C. P.; Audett, J. D., "Synthesis and Reactivity of Saturated Hydrocarbon-Bridged Dinuclear Complexes," *Chem. Rev.* **1986**, *86*, 339-352.
- Tachikawa, M.; Muetterties, E. L., "Metal Carbide Clusters," *Prog. Inorg. Chem.* **1981**, *28*, 203-238.
 - Bradley, J. S., "The Chemistry of Carbidocarbonyl Clusters," *Adv. Organomet. Chem.* **1983**, *22*, 1-58.
- Nast, V. R.; Kirner, U., "Alkynylverbindungen von Übergangsmetallen (XXIV)," *Z. anorg. allg. Chem.* **1964**, *330*, 311-316.
- Binger, P.; Muller, P.; Phillipps, P.; Gabor, B.; Mynott, R.; Herrmann, A. T.; Langhauser, F.; Kruger, C., "Synthese und Struktur eines neuen Bis[(trimethylphosphan)titanocen]-Komplexes mit einer verbrückenden C_2 -Einheit," *Chem. Ber.* **1992**, *125*, 2209-2212.
- LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F., "Carbon Monoxide Cleavage by $(\text{silox})_3\text{Ta}$ ($\text{silox} = t\text{-Bu}_3\text{SiO}^-$)," *J. Am. Chem. Soc.* **1986**, *108*, 6382-6384.

6. Listemann, M. L.; Schrock, R. R., "A General Route to Tri-*tert*-butoxytungsten Alkylidyne Complexes. Scission of Acetylenes by Ditungsten Hexa-*tert*-butoxide," *Organometallics* **1985**, *4*, 74-83.
7. (a) Appel, M.; Heidrich, J.; Beck, W., " σ, π -Ethinid- und σ, σ -Ethindiid-verbrucket Rheniumcarbonyl, $[(OC)_5Re(\mu-\eta^1, \eta^2-C\equiv CH)Re(CO)_5]^+BF_4^-$ und $(OC)_5Re-C\equiv C-Re(CO)_5$," *Chem. Ber.* **1987**, *120*, 1087-1089.
 (b) Heidrich, J.; Steimann, M.; Appel, M.; Beck, W.; Phillips, J. R.; Trogler, W. C., "Hydrocarbon-Bridged Complexes. 15. Molecular and Electronic Structure of $(\mu$ -Ethynediyl)bis(pentacarbonylrhenium), $(OC)_5Re-C\equiv C-Re(CO)_5$," *Organometallics*, **1990**, *9*, 1296-1300.
8. Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T., "Carbon Monoxide Cleavage by $(silox)_3Ta$ ($silox = t-Bu_3SiO^-$): Physical, Theoretical, and Mechanistic Investigations," *J. Am. Chem. Soc.* **1989**, *111*, 9056-9072.
9. Caulton, K. G.; Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B.; Xue, Z., "Structure and Bonding of $(\mu$ -Dicarbido)hexa-*tert*-butoxyditungsten, $(t-BuO)_3W\equiv C-C\equiv W(O-t-Bu)_3$," *Organometallics* **1992**, *11*, 321-326.
10. Onitsuka, K.; Joh, T.; Takahashi, S., "Syntheses and Properties of Heterodinuclear μ -Ethynediyl Complexes Containing Palladium and Platinum," *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1179-1181.
11. Ogawa, H.; Joh, T.; Takahashi, S.; Sonogashira, K., "Synthesis and Properties of μ -Ethynediyl-bis[trans-chlorobis(trimethylphosphine)metal] Complexes," *J. Chem. Soc., Chem. Commun.* **1985**, 1220-1221.
12. (a) Ogawa, H.; Joh, T.; Takahashi, S., "Selective Double Insertion of Isocyanides into the Metal-Carbon Bond of μ -Ethynediyl-dipalladium Complexes," *J. Chem. Soc., Chem. Commun.* **1988**, 561-562.
 (b) Onitsuka, K.; Ogawa, H.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H., "Reactions of μ -Ethynediyl Complexes of Transition Metals: Selective Double Insertion of Isocyanides and Molecular Structure of $[Cl(Et_3P)_2PdC\equiv CC(=NPh)-C(=NPh)Pd(PEt_3)_2Cl]$," *J. Chem. Soc., Dalton Trans.* **1991**, 1531-1536.
13. Onitsuka, K.; Ogawa, H.; Joh, T.; Takahashi, S., "Reaction of Heterodinuclear μ -Ethynediyl Complexes Containing Palladium and Platinum: Multiple and Successive Insertion of Isocyanides," *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 851-852.
14. (a) Lemke, F.; Szalda, D. J.; Bullock, R. M., "Ruthenium/Zirconium Complexes Containing C_2 Bridges with Bond Orders of 3, 2, and 1. Synthesis and Structures of $Cp(PMe_3)_2RuCH_nCH_nZrClCp_2$ ($n = 0, 1, 2$)," *J. Am. Chem. Soc.* **1991**, *113*, 8466-8477.
 (b) Lemke, F.; Bullock, R. M., "Insertion and β -Hydride Elimination Reactions of Ruthenium/Zirconium Complexes Containing C_2 Bridges with Bond Orders of 1, 2, and 3," *Organometallics* **1992**, *11*, 4261-4267.
15. Akita, M.; Sugimota, S.; Tanaka, M.; Moro-oka, Y., "Preparation, Characterization, and Sequential Transformation of Dicarbide Cluster Compounds with Permetalated Ethyne, Ethene, and Ethane Structures," *J. Am. Chem. Soc.* **1992**, *114*, 7581-7582.

16. Akita, M.; Terada, M.; Moro-oka, Y., "Interaction of Ethynyliron (Fp-C≡CH and Fp*-C≡C-H) and Ethynediyliron Complexes (Fp*-C≡C-Fp*) with Co₂(CO)₈: Formation of a Cluster Compound Which Is Fluxional via a Metal-Metal Bond Scission and Recombination Process," *Organometallics* **1992**, *11*, 1825-1830.
17. Weidmann, T.; Weinrich, V.; Wagner, B.; Robl, C.; Beck, W., "Dirhenioethin (OC)₅Re-C≡C-Re(CO)₅ als Baustein zum Aufbau von Carbonyl-Metall Clusterverbindungen," *Chem. Ber.* **1991**, *124*, 1363-1368.
18. Koutsantonis, G. A.; Selegue, J. P., "Synthesis and Structure of [{Ru(CO)₂(Cp)}₂(μ-C≡C)]: An Ethynediyl Complex Formed during Tungsten-Catalyzed Alkyne Metathesis," *J. Am. Chem. Soc.* **1991**, *113*, 2316-2317.
19. Koutsantonis, G. A.; Selegue, J. P.; Wang, J. G., "Cluster Building on a Bicarbide Fragment: [Fe₂Ru₂(μ₄-C≡C)(μ-CO)(CO)₈(η-C₅H₅)₂]," *Organometallics* **1992**, *11*, 2704-2708.
20. Akita, M.; Terada, M.; Tanaka, M.; Moro-oka, Y., "Interaction of Iron Ethynyl and Ethynediyl Complexes with Cp₂Ni₂(CO)₂: Formation of Tri- and Tetranuclear Adducts with a Multiply Bridging C₂H Ligand," *Organometallics* **1992**, *11*, 3468-3472.