

Binuclear Transition Metal Derivatives of 1,2-Bis(indenyl)ethane.

Ramin Khayatpoor

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The mononuclear *ansa*-metallocenes have been utilized effectively as stereoselective catalysts in a number of processes.¹ Variations involving linked indenyl ligands have undergone considerable development in the context of providing chiral environments for such mononuclear transition metal catalysts;²⁻⁶ however, they have received scant attention as ligands for binuclear compounds.⁷⁻¹⁰ Our objective was to investigate the preparation of binuclear transition metal derivatives of 1,2-bis(indenyl)ethane and their subsequent chemistry.

The addition of doubly deprotonated 1,2-bis(indenyl)ethane to two equivalents of $W(CO)_5(THF)$, followed by reflux and subsequent oxidation by ferrocenium, leads to the di-tungsten complex $\{(\eta^5-C_9H_6)_2(C_2H_4)\}W_2(CO)_6$. The structure of this compound is shown in Figure 1. Another product, characterized principally by its 1H NMR spectrum, contained two linked ligands, each coordinated to one $W(CO)_3$ moiety flanking a central metal-metal bond. The Mo analogues are also prepared in the same way. Isolation of the byproduct, which contains a M-M bond linking two different ligands, is an expected general feature of the synthesis, *if a metal-metal bond can readily form*. The W_2 complex $\{(\eta^5-C_9H_6)_2(C_2H_4)\}W_2(CO)_6$ undergoes a facile transformation in chlorinated solvents. Cleavage of the metal-metal bond is concomitant with oxidative addition of one metal center to the C-H bond of the five-member ring attached to the adjacent tungsten center. The structure of the transformed product is shown in Figure 2. This transformation is not observed for the molybdenum analogue; however, it exhibits an interesting fluxional behavior.

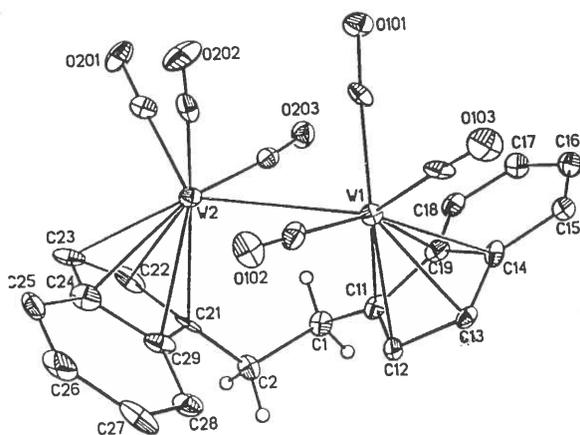


Figure 1. A molecular structure diagram of $\{(\eta^5-C_9H_6)_2(C_2H_4)\}W_2(CO)_6$

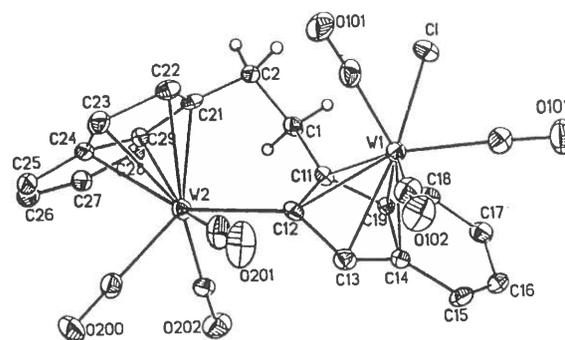
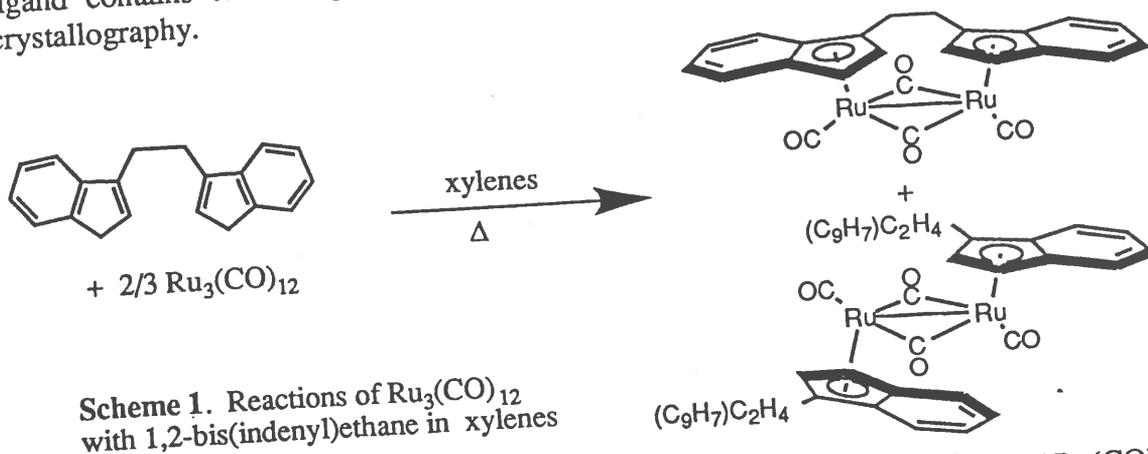


Figure 2. A molecular structure diagram of $W(CO)_3\{(\eta^1:\eta^5-C_9H_5)(C_2H_4)(\eta^5-C_9H_6)\}WCl(CO)_3$

The Ru₂ and Fe₂ compounds are prepared by the heating the metal carbonyl with the ligand in xylenes (Scheme 1). As mentioned above, two products containing two metal centers are possible, and that is what is observed. The binuclear product based on one ligand contains two bridging carbonyls in the solid state, as determined by X-ray crystallography.



Heating Re₂(CO)₁₀ in indene at high temperature leads to (η⁵-C₉H₇)Re(CO)₃. Similarly, heating rhenium carbonyl with 1,2-bis(indenyl)ethane in decalin provides both mono- and di-metalated complexes, which are η⁵ coordinated via the five-membered rings to the Re(CO)₃ moieties. The structure of {(η⁵-C₉H₆)₂C₂H₄}Re₂(CO)₆ is shown in Figure 3. The Mn compounds were prepared similarly using Mn₂(CO)₁₀.

Photolysis of the Re₂ compound {(η⁵-C₉H₆)₂C₂H₄}Re₂(CO)₆ in ether leads to two products. One follows from the *rearrangement* of a carbonyl ligand from one metal center to another, concomitant with oxidative addition of the C-H bond of the opposing five-member ring to that metal, migratory insertion of the hydride to the adjacent carbon in the ring, and formation of a Re-Re bond. The structure of Re₂(CO)₆{μ-(η¹,η²-C₉H₆)C₂H₄(η⁵-C₉H₆)} is shown in Figure 4. The other product results from the *loss* of a carbonyl ligand, leading to the η² coordination of the opposite six-membered ring.

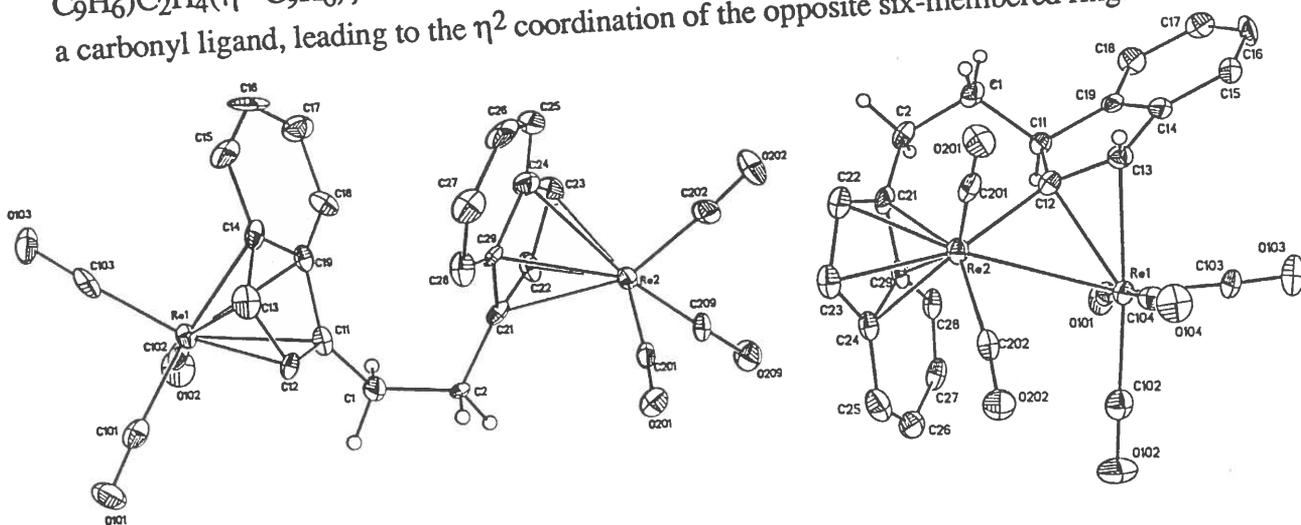


Figure 3. A molecular structure diagram of {(η⁵-C₉H₆)₂C₂H₄}Re₂(CO)₆

Figure 4. A molecular structure diagram of Re₂(CO)₆{μ-(η¹,η²-C₉H₆)C₂H₄(η⁵-C₉H₆)}

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