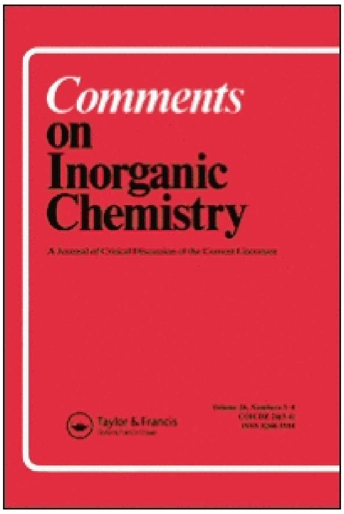

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A HALF-CENTURY OF CYCLOHEPTATRIENYLMETAL CHEMISTRY: EXPERIMENT AND THEORY

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A HALF-CENTURY OF CYCLOHEPTATRIENYLMETAL CHEMISTRY: EXPERIMENT AND THEORY

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Bruce King joined Gordon Stone's research group at Harvard University in 1957 and initiated his research on synthetic transition metal organometallic chemistry. The work that he presented at the Stone Symposium evolved during more than a half-century from his 1959 discovery of the sandwich compound $(\eta^5\text{-}C_5H_5)V(\eta^7\text{-}C_7H_7)$ while a student in Gordon Stone's Harvard laboratory. After leaving Gordon's research group Bruce King continued synthetic studies on cycloheptatrienylmetal compounds. This led to the discovery of the first trihapto derivatives $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_7H_7)$ and $(\eta^3\text{-}C_7H_7)\text{-}Co(CO)_3$, while working at the Mellon Institute (now Carnegie-Mellon University) in the 1960s. Bruce King then continued work in synthetic inorganic and organometallic chemistry and related experimental work at the University of Georgia until the late 1990s, when he closed down his experimental ("wet chemistry") laboratory to concentrate on theoretical and mathematical chemistry. At that time he initiated collaborative work in various areas of computational inorganic and organometallic chemistry, including density functional theory studies of cycloheptatrienylmetal derivatives related to some of his early synthetic successes noted above. Bruce King's work in computational inorganic chemistry evolved and expanded greatly in collaboration with groups at several Chinese universities and he now holds several adjunct academic appointments

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in China. The computational part of the research presented here is in collaboration with Prof. Hongyan Wang at Southwest Jiaotong University in Chengdu, China, and Prof. Xuejin Feng at Jiangnan University in Wuxi, China.

INTRODUCTION

The landmark discoveries of ferrocene[1–2] (η^5-$C_5H_5)_2Fe$, in 1951 and dibenzenechromium[3] (η^6-$C_6H_6)_2Cr$, in 1955 stimulated efforts to synthesize related compounds containing seven-membered carbocyclic rings, i.e., cycloheptatrienyl (tropylium) rings. Initial efforts by Wilkinson and collaborators[4] to use tropylium bromide, $C_7H_7^+Br^-$ as a source of the cycloheptatrienyl ring in reactions with a variety of transition metal complexes failed completely. In most such reactions the transition metal compound simply reduced the tropylium ion to bicycloheptatrienyl, C_7H_7–C_7H_7. Furthermore, the sandwich compound bis(cycloheptatrienyl)titanium, (η^7-$C_7H_7)_2Ti$, strictly analogous to ferrocene and dibenzenechromium, still remains elusive.

The successful synthesis of the first metal complexes with fully bonded seven-membered carbocyclic rings (i.e., η^7-C_7H_7 ligands) was first achieved by Dauben and Honnen in 1958[5–6] using the neutral hydrocarbon cycloheptatriene as the source of the C_7H_7 ring rather than a tropylium salt. Thus a thermal reaction of $Mo(CO)_6$ with cycloheptatriene was found to give (η^6-$C_7H_8)Mo(CO)_3$, a triolefin complex in which six of the seven carbon atoms of the C_7H_8 ring are bonded to the metal atom leaving the CH_2 carbon beyond direct bonding distance to the molybdenum atom (Figure 1). Subsequent hydride abstraction from (η^6-$C_7H_8)Mo(CO)_3$ with the carbonium ion $(C_6H_5)_3C^+$ gave the first true metal cycloheptatrienyl complex, namely the cation $(\eta^7 - C_7H_7)Mo\ (CO)_3^+$

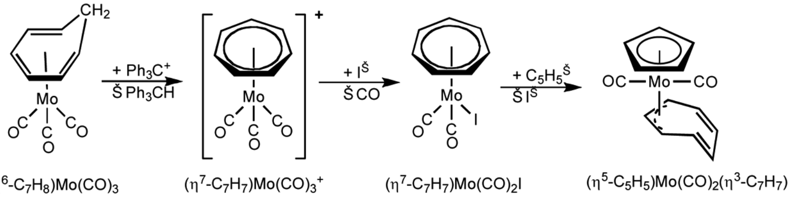


Figure 1. The relationships between cycloheptatriene and cycloheptatrienylmolybdenum derivatives.

Other metal carbonyl derivatives were found to give cycloheptatrienyl metal complexes directly upon thermal reactions with cycloheptatriene without the need for a separate hydride abstraction step (Figure 2). The first such example was the thermal reaction of (η^5-C_5H_5)V$(CO)_4$ with cycloheptatriene to give (η^5-C_5H_5)V(η^7-C_7H_7), which was discovered by the author in 1959 while a graduate student in Gordon Stone's laboratory.[7,8] Subsequently, the reaction of V$(CO)_6$ with cycloheptatriene[9] was found to give directly (η^7-C_7H_7)V$(CO)_3$.

The availability of (η^7-C_7H_7)Mo$(CO)_2$I in good yield (Figure 1)[10] suggested that it might be a good starting material for the synthesis of other (η^7-C_7H_7)Mo$(CO)_2$X derivatives, similar to the use of the likewise readily available[11] (η^5-C_5H_5)Fe$(CO)_2$I to prepare other (η^5-C_5H_5)-Fe$(CO)_2$X derivatives. This proved to be the case, at least to a limited extent. In this connection a particularly interesting reaction of (η^7-C_7H_7)Mo$(CO)_2$I is its reaction with sodium cyclopentadienide to give (η^5-C_5H_5)Mo$(CO)_2$(η^3-C_7H_7) in which the originally planar heptahapto C_7H_7 ring has become a bent trihapto C_7H_7 ring to preserve the favored 18-electron configuration of the central molybdenum atom (Figure 1). This reaction, first reported in 1963 by the author while at the Mellon Institute (now Carnegie Mellon University),[12,13] can be considered as a competition experiment between five- and seven-membered rings, which indicates that full pentahapto bonding of the C_5H_5 ring is more favorable than full heptahapto bonding of the C_7H_7 ring. Then when both rings are present in a molecule and one ring must release its M–C bonds to maintain a favorable metal electronic configuration, the C_7H_7 ring releases its M–C bonds before the C_5H_5 ring.

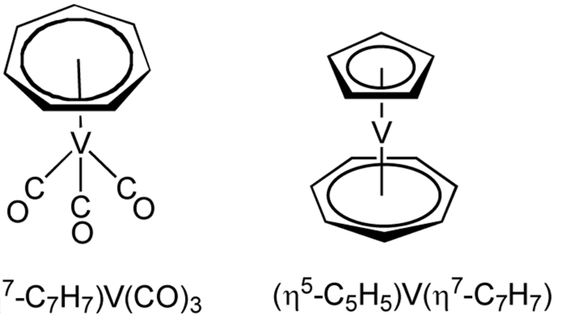


Figure 2. Some cycloheptatrienylvanadium derivatives synthesized directly from cycloheptatriene and vanadium carbonyl derivatives.

Another interesting cyclopentadienyliron derivative related to (η^5-C_5H_5)Fe$(CO)_2$I is the corresponding doubly carbonyl bridged dimer[14] (η^5-$C_5H_5)_2Fe_2(CO)_2(\mu$-$CO)_2$, a readily available compound from which (η^5-C_5H_5)Fe$(CO)_2$I is normally synthesized by reaction with iodine. In addition the unsaturated (η^5-$C_5H_5)_2Fe_2(\mu$-$CO)_3$ has been obtained by the photochemical decarbonylation of (η^5-$C_5H_5)_2Fe_2(CO)_2$-(μ-$CO)_2$. The complex (η^5-$C_5H_5)_2Fe_2(\mu$-$CO)_3$ is of particular interest since it is a stable triplet state organometallic compound[15–17] with a $\sigma + \frac{2}{2\pi}$ double bond analogous to the double bond in isolated dioxygen. Despite the stability of these binuclear cyclopentadienyliron carbonyls and the ready availability10 of (η^7-C_7H_7)Mo$(CO)_2$I, none of the analogous binuclear cycloheptatrienylmolybdenum carbonyls are currently known.

THEORETICAL METHODS

The following three density functional theory (DFT) methods were used in this work:

1. B3LYP: This hybrid Hartree-Fock (HF) Density Functional Theory (DFT) method combines Becke's three-parameter exchange functional with the Lee-Yang-Parr correlational functional[18,19] as realized in the Gaussian 94 program.
2. BP86: This pure DFT method incorporates the Becke 1988 exchange functional with Perdew's 1986 treatment of correlation.[20,21]
3. MPW1PW91: This newer-generation functional combines the modified Perdew-Wang exchange functional with the Perdew-Wang 91 gradient-correlation functional.[22]

The DFT studies on the first row transition metal derivatives $(C_7H_7)_2M$ (M = Ti, V, Cr, Mn, Fe, Co, Ni)[23] used the B3LYP and BP86 methods. All three methods were used for the study of the $(C_7H_7)_2Mo_2(CO)_n$ ($n = 6, 5, 4, 3, 2, 1$) derivatives.

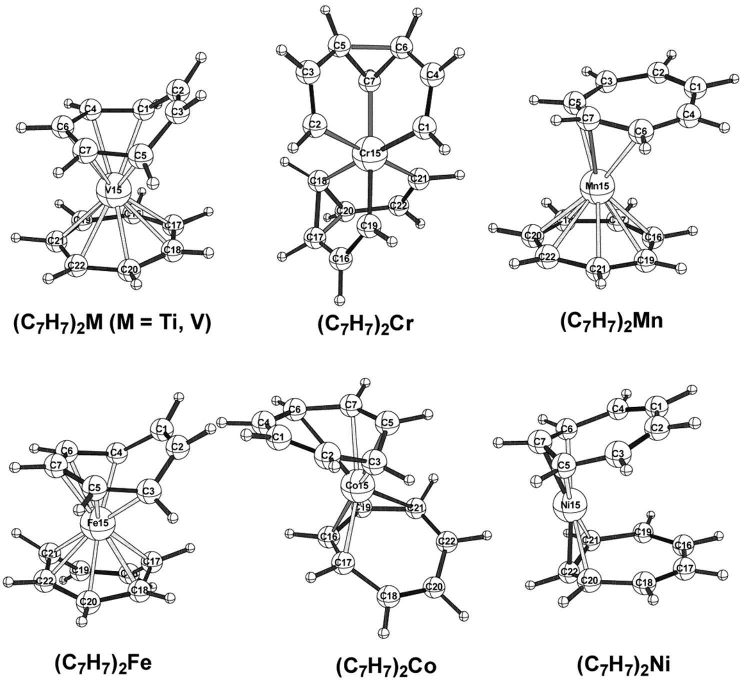
The following basis sets were used in this work:

1. For carbon and oxygen a standard Huzinaga-Dunning double-ζ basis set was used with one set of pure spherical harmonic *d* polarization functions ($\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$).[24–26]
2. For the first-row transition metals the contracted Wachters basis set was augmented by two sets of *p* functions with $\alpha = 0.2646$, 0.104 and one set of *d* functions with $\alpha = 0.1316$.[27,28]

3. For second and third row transition metals effective core potential methods were used because of the large number of electrons. The Stuttgart double-ζ basis set was used for molybdenum in the work discussed here.[29,30]

THE $(C_7H_7)_2M$ SANDWICH COMPOUNDS OF THE FIRST ROW TRANSITION METALS

Density functional theory (DFT) methods using the B3LYP and BP86 functionals predict $(\eta^7\text{-}C_7H_7)_2Ti$ to distort by ring slippage to give a singlet 16-electron complex $(\eta^7\text{-}C_7H_7)Ti(\eta^5\text{-}C_7H_7)$ having an uncomplexed C=C double bond in one of the C_7H_7 rings (Figure 3) but otherwise closely related to the known[31] $(\eta^7\text{-}C_7H_7)Ti(\eta^5\text{-}C_5H_5)$. The situation is



$(C_7H_7)_2M$ (M = Ti, V)

$(C_7H_7)_2Cr$

$(C_7H_7)_2Mn$

$(C_7H_7)_2Fe$

$(C_7H_7)_2Co$

$(C_7H_7)_2Ni$

Figure 3. The lowest energy structures predicted for $(C_7H_7)_2M$ derivatives (M = Ti, V, Cr, Mn, Fe, Co, Ni).

similar with $(C_7H_7)_2V$ except that the corresponding structures have doublet spin multiplicity. However, an analogous $(\eta^7\text{-}C_7H_7)Cr(\eta^5\text{-}C_7H_7)$ structure is not found for chromium. Instead, the most stable $(C_7H_7)_2Cr$ structure is a singlet d^0 six-coordinate formally Cr(VI) complex with two tridentate cyclopropyldivinyl C_7H_7 ligands (Figure 3). The latter rearrangement of the C_7H_7 rings bonded to chromium can involve initially a $(\eta^6\text{-}C_7H_7)_2Cr$ diradical sandwich compound followed by a bis(η^5-norcaradienyl)Cr intermediate. For the later first row transition metals the lowest energy $(C_7H_7)_2M$ structures are predicted to be doublet $(\eta^7\text{-}C_7H_7)Mn(\eta^3\text{-}C_7H_7)$ rather than $(\eta^5\text{-}C_7H_7)_2Mn$ for manganese, singlet *cis* and *trans* structures $(\eta^5\text{-}C_7H_7)_2Fe$ for iron, doublet $(\eta^3\text{-}C_7H_7)_2Co$ for cobalt, and two singlet $(\eta^3\text{-}C_7H_7)_2Ni$ stereoisomers for nickel (Figure 3).

THE BINUCLEAR CYCLOHEPTATRIENYLMOLYBDENUM CARBONYLS $(C_7H_7)_2Mo_2(CO)_n$ ($n = 6, 5, 4, 3, 2, 1$)

Theoretical studies on the binuclear cycloheptatrienylmolybdenum carbonyls $(C_7H_7)_2Mo_2(CO)_n$ ($n = 6, 5, 4, 3, 2, 1, 0$) indicate structures with fully bonded heptahapto $\eta^7\text{-}C_7H_7$ rings and four or fewer carbonyl groups to be energetically competitive.[32] This is in striking contrast to the corresponding chromium derivatives. The lowest energy such structure for $(\eta^7\text{-}C_7H_7)_2Mo_2(CO)_4$ is a singlet unbridged structure with a formal Mo–Mo single bond of length ~3.2 Å (Figure 4). A higher energy pentahapto structure $(\eta^5\text{-}C_7H_7)_2Mo_2(CO)_4$ is also predicted with a formal Mo≡Mo triple bond of length ~2.56 Å. The lowest energy structures for the corresponding cyclopentadienyliron carbonyl are the cis and trans isomers of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ with two bridging carbonyl groups. Both isomers are known experimentally and have been structurally characterized by X-ray crystallography. However, a higher energy $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ structure is also predicted with only terminal carbonyl groups similar to the lowest energy $(\eta^7\text{-}C_7H_7)_2Mo_2(CO)_4$ structure (Figure 4).

Low energy structures are predicted for $(C_7H_7)_2Mo_2(CO)_3$ with two heptahapto $\eta^7\text{-}C_7H_7$ rings, either one or two bridging carbonyl groups, and formal Mo = Mo double bonds of length ~2.8 Å (Figure 5). However, the global minimum for $(C_7H_7)_2Mo_2(CO)_3$ is a $(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_7)Mo_2(CO)_3$ structure with a formal Mo≡Mo triple bond of length ~2.53 Å. The lowest energy $Cp_2Fe_2(CO)_3$ structure is a triply

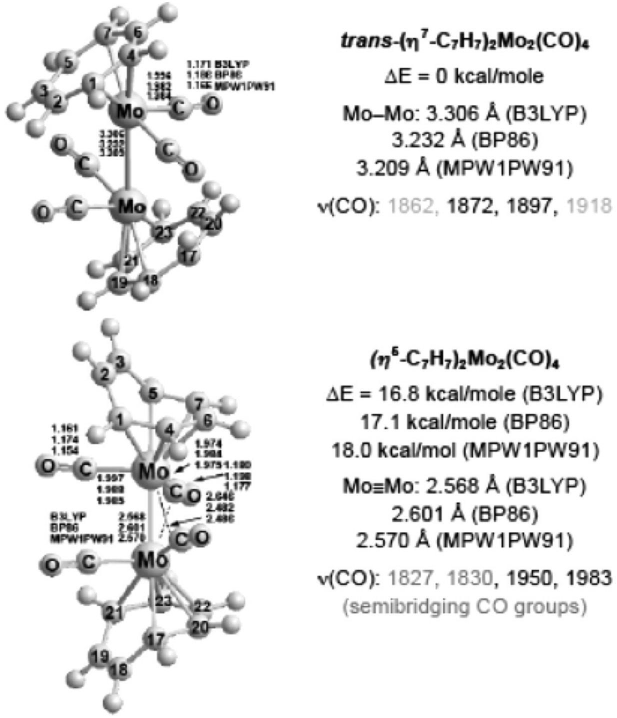


Figure 4. The lowest energy $(C_7H_7)_2Mo_2(CO)_4$ structures.

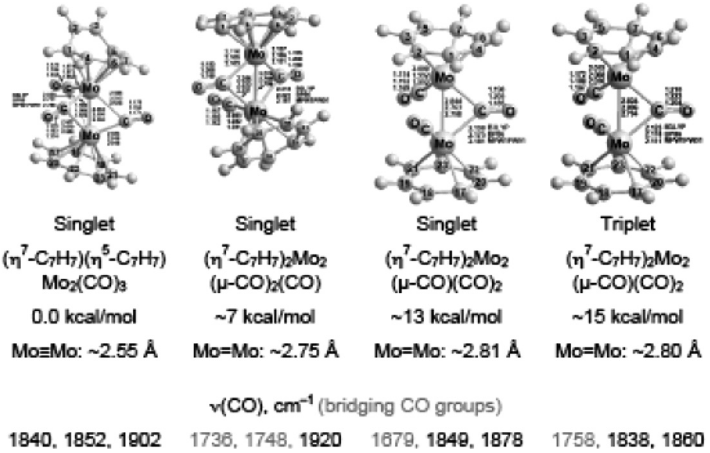


Figure 5. The lowest energy $(C_7H_7)_2Mo_2(CO)_3$ structures.

bridged triplet structure with a formal Fe = Fe double bond and the usual η^5-C_5H_5 ring.[33] The triplet spin state occurs in the double bond, which is a $\sigma + \frac{2}{2\pi}$ double bond with the unpaired electrons in the π components analogous to the O=O double bond in normal dioxygen.

The lowest energy structures for $(C_7H_7)_2Mo_2(CO)_2$ and $(C_7H_7)_2Mo_2$ (CO) have heptahapto η^7-C_7H_7 rings and predicted metal-metal distances of ~2.54 Å and ~2.31 Å, respectively, consistent with the formal triple and quadruple bonds, respectively, needed to give both metal atoms the favored 18-electron configuration. The lowest energy structures for the carbonyl-richer systems $(C_7H_7)_2Mo_2(CO)_n$ ($n = 6$, 5) contain one trihapto η^3-C_7H_7 ring and one pentahapto η^5-C_7H_7 ring.

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