STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIII, 2, 2008

UNSATURATION IN BINUCLEAR FIRST ROW CYCLOPENTADIENYLMETAL CARBONYLS AS STUDIED BY DENSITY FUNCTIONAL THEORY

R. BRUCE KING[a], HENRY F. SCHAEFER[a], YAOMING XIE[a],
QIAN-SHU LI[b], XIUHUI ZHANG[b], HONGYAN WANG[c]

ABSTRACT. The geometries of binuclear cyclopentadienylmetal carbonyls $Cp_2M_2(CO)_n$ as well as related metal nitrosyl and cyclobutadienemetal derivatives have been optimized by using B3LYP and BP86 methods from density functional theory. New examples of metal-metal multiple bonding and four-electron donor carbonyl groups have been found in unsaturated molecules of this type.

Keywords: *metal carbonyls, metal nitrosyls, cyclopentadienylmetal derivatives, cyclobutadienemetal derivatives, metal-metal bonding, DFT calculations.*

INTRODUCTION

The first example of an unsaturated metal carbonyl derivative was the molybdenum complex $(\eta^5\text{-}Me_5C_5)_2Mo_2(CO)_4$ first synthesized by King and Bisnette [1] in 1967 and structurally characterized by Huang and Dahl [2] a number of years later. The relatively short Mo≡Mo distance of 2.488 Å found in this complex was interpreted to be the metal-metal triple bond required to give both metal atoms the favored 18-electron rare gas electronic configuration. Subsequently other unsaturated binuclear cyclopentadienylmetal carbonyl derivatives with formal metal-metal triple bonds such as $(\eta^5\text{-}C_5R_5)_2V_2(CO)_5$,[3,4] $(\eta^5\text{-}C_5R_5)_2Cr_2(CO)_4$, [5,6,7] and $(\eta^5\text{-}C_5R_5)_2M'_2(CO)_3$ (M´= Mn, [8] Re [9]) were synthesized. In addition, $Cp_2Co_2(CO)_2$ [10] and $Cp_2Fe_2(CO)_3$ [11] with formal metal-metal double bonds have been synthesized and characterized structurally. Table 1 summarizes the possible unsaturated binuclear cyclopentadienylmetal carbonyls of the first row transition metals listed according to the formal metal-metal bond order assuming 18-electron configurations for the metal atoms and only two-electron donor carbonyl groups. Compounds in Table 1 that are sufficiently stable for isolation and structural characterization by X-ray diffraction are listed in **bold** type.

---

[a] *Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia, USA, rbking@chem.uga.edu*

[b] *Institute of Chemical Physics, Beijing Institute of Technology, Beijing 100081, P. R. China*

[c] *College of Sciences, Southwest Jiaotong University, Chengdu 610031, P. R. China*

Table 1.

Possible unsaturated cyclopentadienylmetal carbonyls of the first row transition metals

M–M	M=M	M≡M	$M_{=},^{=}M$
$Cp_2Ti_2(CO)_8$	$Cp_2Ti_2(CO)_7$	$Cp_2Ti_2(CO)_6$	$Cp_2Ti_2(CO)_5$
$Cp_2V_2(CO)_7$	$Cp_2V_2(CO)_6$	**$Cp_2V_2(CO)_5$**	$Cp_2V_2(CO)_4$
$Cp_2Cr_2(CO)_6$	$Cp_2Cr_2(CO)_5$	**$Cp_2Cr_2(CO)_4$**	$Cp_2Cr_2(CO)_3$
$Cp_2Mn_2(CO)_5$	$Cp_2Mn_2(CO)_4$	**$Cp_2Mn_2(CO)_3$**	$Cp_2Mn_2(CO)_2$
$Cp_2Fe_2(CO)_4$	**$Cp_2Fe_2(CO)_3$**	$Cp_2Fe_2(CO)_2$	$Cp_2Fe_2(CO)$
$Cp_2Co_2(CO)_3$	**$Cp_2Co_2(CO)_2$**	$Cp_2Co_2(CO)$	
$Cp_2Ni_2(CO)_2$	$Cp_2Ni_2(CO)$		
$Cp_2Cu_2(CO)$			

Stable metal carbonyl derivatives usually have 18-electron configurations corresponding to filling each the nine orbitals of the sp^3d^5 valence orbital manifold with electron pairs. Unsaturated binuclear metal carbonyls and cyclopentadienylmetal carbonyls may be regarded as analogues of ethylene and acetylene. Whereas the unsaturation in ethylene and acetylene always leads to carbon-carbon double and triple bonds in stable compounds, unsaturation in metal carbonyl derivatives can, at least in principle, be manifested in several different ways including the following: (1) Formation of metal-metal multiple bonds retaining the favored 18-electron metal configuration; (2) Four-electron bridging carbonyl groups involving not only donation of an electron pair through a carbon-metal dative σ-bond but also donation of a second electron pair from a filled π orbital of the C≡O triple bond in a carbonyl ligand; (3) Metal electronic configurations less than 18 electrons of which a 16-electron configuration for d^8 metal atoms is the most common. Unsaturated binuclear metal carbonyls $M_2(CO)_n$ containing only carbonyl ligands are not stable and have only been observed in low-temperature matrices. However, a number of unsaturated cyclopentadienylmetal carbonyls are stable as indicated above.

This paper summarizes some of our recent work on cyclopentadienylmetal carbonyl derivatives of first row transition metals V, [12,13] Cr, [14] Fe,[15] Co, [16] Ni [17] as well as related cyclobutadienylmetal nitrosyl[17] and cyclobutadiene cobalt carbonyl [18] derivatives. It is based on a lecture by RBK given at the MOLMOD 2007 conference held at Arcalia near Bistrița in July, 2007. At the time of the conference our work on binuclear cyclopentadienylmanganese carbonyls [19] was not complete so they were not discussed in this lecture and thus are not included in this paper.

THEORETICAL METHODS

Two DFT functionals were used in this work. The first functional is the B3LYP method, which is the hybrid HF/DFT method using the combination of the three-parameter Becke functional (B3) with the Lee-Yang-Parr (LYP) generalized gradient correlation functional [20,21]. The other DFT method used was BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86) [22,23]. All calculations were performed using the double-ζ plus polarization (DZP) basis sets. The DZP basis sets used for carbon and oxygen add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$ to the standard Huzinaga-Dunning contracted DZ sets [24,25] and are designated as 9s5p1d/4s2p1d.. For hydrogen, a set of p polarization functions $\alpha_p(H) = 0.75$ is added to the Huzinaga-Dunning DZ set. The loosely contracted DZP basis set for the transition metals is the Wachters primitive set [26] augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer, and Schaefer,[27] designated (14s11p6d/ 10s8p3d).

RESULTS AND DISCUSSION

The results with the binuclear cyclopentadienylmetal carbonyls can be summarized as follows:

(1) $Cp_2Ni_2(CO)_n$. The experimentally known [28] doubly bridged structure was found to be the lowest energy structure for $Cp_2Ni_2(CO)_2$ with alternative triplet structures having considerably higher energies. Singly bridged structures were found to be of lowest energy for $Cp_2Ni_2(CO)$.

(2) $Cp_2Co_2(CO)_n$. For $Cp_2Co_2(CO)_3$ singly bridged and triply bridged structures with formal Co–Co single bonds have similar energies; the singly bridged structure is the one known experimentally [29]. The strongly preferred structure for $Cp_2Co_2(CO)_2$ is the doubly bridged structure with a formal Co=Co double bond; this structure has also been realized experimentally.[10] The preferred structure for $Cp_2Co(CO)$ is a singly bridged structure with a formal Co≡Co triple bond. This species has not been isolated but is a probable reaction intermediate in the pyrolysis [30] of $Cp_3Co_3(\mu\text{-}CO)_3$ to give the tetranuclear derivative $Cp_4Co_4(\mu_3\text{-}CO)_2$.

(4) $Cp_2Fe_2(CO)_n$. The *trans-* and *cis*-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ isomers of $Cp_2Fe_2(CO)_4$ known experimentally are predicted to be genuine minima with very similar energies consistent with the experimental observation of an equilibrium between these isomers in solution [31-34]. An intermediate in the interconversion

of the *trans*- and *cis*-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ doubly bridged isomers of $Cp_2Fe_2(CO)_4$ can be the *trans* unbridged isomer of $Cp_2Fe_2(CO)_4$ calculated to be 2.3 kcal/mole (B3LYP) or 9.1 kcal/mole (BP86) above the global minimum *trans*-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$. For the unsaturated $Cp_2Fe_2(CO)_3$ the known[11] triplet isomer $Cp_2Fe_2(\mu\text{-}CO)_3$ with an Fe=Fe double bond similar to the O=O double bond in O_2 is found to be the global minimum. The lowest energy structure for the even more unsaturated $Cp_2Fe_2(CO)_2$ is a doubly bridged structure $Cp_2Fe_2(\mu\text{-}CO)_2$ with a short iron-iron distance suggesting the Fe≡Fe triple bond required to give both iron atoms the favored 18-electron configuration. This species has not been synthesized but is a probable reaction intermediate in the pyrolysis of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ to give $Cp_4Fe_4(\mu_3\text{-}CO)_4$ [31]. The lowest energy structure for $Cp_2Fe_2(CO)$ is a triplet unsymmetrically bridged structure $Cp_2Fe_2(\mu\text{-}CO)$ with a short iron-iron distance (~2.1 Å) suggestive of the Fe$^{=}$,$_{=}$Fe quadruple bond required to give both iron atoms the favored 18-electron rare gas configuration.

(5) $Cp_2Cr_2(CO)_n$. The experimentally realized structures of the stable singlet $Cp_2Cr_2(CO)_6$ with a formal Cr–Cr single bond and singlet $Cp_2Cr_2(CO)_4$ with a formal Cr≡Cr triple bond correspond to the global minima found by DFT methods [14]. The global minimum for $Cp_2Cr_2(CO)_5$, expected to have a formal Cr=Cr double bond, is a triplet, which is thermodynamically unstable with respect to disproportionation into the stable $Cp_2Cr_2(CO)_6$ and $Cp_2Cr_2(CO)_4$ with formal Cr–Cr single and Cr≡Cr triple bonds, respectively. This instability of $Cp_2Cr_2(CO)_5$ has been verified experimentally [14]. Triplet and singlet structures are found for the tricarbonyl $Cp_2Cr_2(CO)_3$ with the triplet isomer having an apparent Cr≡Cr triple bond (2.295 Å by BP86) predicted to have lower energy than the singlet isomer having an apparent Cr$^{=}$,$_{=}$Cr quadruple bond (2.191 Å by BP86). Quintet, septet, and singlet structures as well as a highly spin contaminated triplet structure were found for the dicarbonyl $Cp_2Cr_2(CO)_2$. In all of the $Cp_2Cr_2(CO)_n$ (n = 3, 2) structures the carbonyls are asymmetric semibridging groups, typically with differences of 0.3 to 0.5 Å between the shortest and longest M–C distances.

(6) $Cp_2V_2(CO)_n$. An optimized structure for $Cp_2V_2(CO)_7$ is found with one symmetrical bridging carbonyl group and a V–V distance of 3.306 Å (BP86) suggesting a single bond [12]. This structure is predicted to be unstable with respect to dissociation into $CpV(CO)_4$ + $CpV(CO)_3$. Energetically competitive structures for $Cp_2V_2(CO)_6$ include a doubly symmetrically bridged singlet structure with only two-electron donor carbonyl groups, a triplet doubly semibridged structure, and a singlet structure with one four-electron donor bridging carbonyl group [12]. The global minimum for $Cp_2V_2(CO)_5$ with a V≡V distance of 2.452 Å (BP86) [13] is essentially the same as the structure

of the known $Cp_2V_2(CO)_5$ determined by X-ray diffraction [14]. The global minimum for $Cp_2V_2(CO)_4$ is a triplet electronic state with a V≡V distance of 2.444 Å (BP86). However, slightly higher energy singlet $Cp_2V_2(CO)_4$ structures are found either with a V≡V distance of 2.547 Å (BP86) and one four-electron donor bridging CO group or with a $V^{=},{=}V$ distance of 2.313 Å (BP86) and all two-electron donor bridging CO groups. Four-electron donor bridging carbonyl groups become more prevalent upon further decarbonylation leading ultimately to three singlet $Cp_2V_2(\eta^2\text{-}\mu\text{-}CO)_2$ isomers as well as triplet, quintet, and septet structures of $Cp_2V_2(CO)$ with extremely low ν(CO) frequencies around 1400 cm^{-1}.

Similar DFT studies were also performed on the binuclear cyclobutadienecobalt carbonyl derivatives[18] $(\eta^4\text{-}C_4H_4)_2Co_2(CO)_n$ (n = 4, 3, 2, 1) for comparison with the isoelectronic $Cp_2Fe_2(CO)_n$ derivatives discussed above. The singlet doubly bridged and unbridged isomers of $(\eta^4\text{-}C_4H_4)_2Co_2(CO)_4$ are nearly degenerate suggesting a highly fluxional system similar to the experimentally known and closely related $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^4\text{-diene})_2Co_2(CO)_4$ systems. The global minimum of $(C_4H_4)_2Co_2(CO)_3$ is a doubly bridged singlet isomer $(\eta^4\text{-}C_4H_4)_2Co_2(CO)(\mu\text{-}CO)_2$ in contrast to the isoelectronic $(C_5H_5)_2Fe_2(CO)_3$ where the global minimum is a triply bridged triplet isomer $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3$ analogous to dioxygen. A related triply bridged triplet isomer of $(C_4H_4)_2Co_2(CO)_3$ is also found, but at 9.6 kcal/mol (B3LYP) or 5.1 kcal/mol (BP86) above the global minimum. The $(C_4H_4)_2Co_2(CO)_2$ system behaves analogously to the corresponding $(C_5H_5)_2Fe_2(CO)_2$ system in that its lowest energy structure is a doubly bridged isomer $(\eta^4\text{-}C_4H_4)_2Co_2(\mu\text{-}CO)_2$ with a short cobalt-cobalt distance suggestive of the Co≡Co triple bond required to give both cobalt atoms the favored 18-electron configuration. Both axial and perpendicular metallocene structures are found for $(C_4H_4)_2Co_2(CO)$, including a low energy $(\eta^4\text{-}C_4H_4)_2Co_2(\eta^2\text{-}\mu\text{-}CO)$ structure with a four-electron donor bridging CO group and a cobalt-cobalt distance suggestive of a Co≡Co triple bond.

Some DFT studies on binuclear late transition metal cyclopentadienylmetal nitrosyls $Cp_2M_2(NO)_n$ (M = Fe, Co, Ni) were also carried out for comparison with related carbonyl derivatives.[17] However, in such metal nitrosyls the neutral NO ligands can formally be either three-electron or one-electron donors. For terminal NO groups, three-electron donors have linear M–N≡O configurations whereas one-electron donors have bent M–N=O configurations. Similarly for bridging NO groups three electron donors have planar M_2NO configurations whereas one-electron donors have pyramidal M_2NO configurations. The global minima for $Cp_2M_2(NO)_2$ (M = Fe, Co) are found to have closely related structures with two symmetrically bridging nitrosyl ligands but variable planarity of the central M(μ-NO)$_2$M units. Similarly the single nitrosyl ligands in the global minima for Cp$_2$M$_2$(NO) are found to bridge symmetrically the pair of metal atoms. An unusual dimer Cp$_2$Ni$_2$(μ-NO)$_2$ was found with a Ni–Ni bond distance suggestive of a single bond and geometry corresponding to one one-electron donor bridging NO group and one three-electron donor bridging NO group. However, dissociation of Cp$_2$Ni$_2$(μ-NO)$_2$ into the well-known stable monomer CpNiNO is highly favored energetically.

CONCLUSIONS

Structures with metal-metal multiple bonds are preferred over structures with four-electron donor bridging carbonyl groups for the Cp$_2$M$_2$(CO)$_n$ derivatives studied in this work except for highly unsaturated derivatives of the early transition metal vanadium. Among these structures, those with formal M≡M triple bonds appear to be particularly favorable and are found in a number of stable Cp$_2$M$_2$(CO)$_n$ derivatives such as Cp$_2$V$_2$(CO)$_5$, Cp$_2$Cr$_2$(CO)$_4$, and Cp$_2$Mn$_2$(CO)$_3$. Furthermore, Cp$_2$Cr$_2$(CO)$_5$, with a formal Cr=Cr double bond is known both experimentally and theoretically to disproportionate into Cp$_2$Cr$_2$(CO)$_6$ and Cp$_2$Cr$_2$(CO)$_4$ with Cr–Cr single and Cr≡Cr triple bonds, respectively.

ACKNOWLEDGMENTS

We are indebted to the the U. S. National Science Foundation (Grants CHE-0209857, CHE-0451445, and CHE-0716718) for support of the work at the University of Georgia, the 111 Project (B07012) in China for the support of the work at the Beijing Institute of Technology, and the Chinese National Science Foundation (Grant 10774104) for the support of the portion of the work at Southwest Jiaotong University.

REFERENCES

1. R. B. King, M. B. Bisnette, *J. Organometal. Chem.* **1967**, *8*, 129.
2. J. S.Huang, L. F. Dahl, *J. Organometal. Chem.* **1983**, *243*, 57.
3. F. A. Cotton, L. Kruczynski, B. A. Frenz, *J. Organometal. Chem.* **1978**, *160*, 93.
4. J. C. Huffman, L. N. Lewis, K. G. Caulton, *Inorg. Chem.* **1980**, *19*, 2755.
5. M. D. Curtis, W. M. Butler, *J. Organometal. Chem.* **1978**, *155*, 131.
6. R. B. King, A. Efraty, W. M. Douglas, *J. Organometal. Chem.* **1973**, *60*, 125.
7. J. Potenza, P. Giordano, D. Mastropaolo, A. Efraty, *Inorg. Chem.* **1974**, *13*, 254.

8. W. A. Herrmann, R. Serrano, J. Weichmann, *J. Organometal. Chem.* **1983**, *246*, C57.
9. J. K. Hoyano, W. A. G. Graham, *Chem. Comm*. **1982***,* 27.
10. W. I. Bailey Jr., D. M. Collins, F. A. Cotton, J. C. Baldwin, *J. Organometal. Chem.* **1979**, *165*, 373.
11. J. P. Blaha, B. E. Bursten, J. C. Dewan, R. B. Frankel, C. L. Randolph, B. A. Wilson, M. S. Wrighton, *J. Am. Chem. Soc.* **1985**, *107*, 4561.
12. Q. Li, X. Zhang, Y. Xie, R. B. King, H. F. Schaefer, III *Eur. J. Inorg. Chem.*, **2007**, 1599.
13. QLi, X. Zhang, Y. Xie, R. B. King, H. F. Schaefer, *J. Am. Chem. Soc.*, **2007***, 129*, 3433.
14. G. C. Fortman, T. Kégl, Q.-S. Li, X. Zhang, H. F. Schaefer, Y. Xie, R. B. King, J. Telser, C. D. Hoff, *J. Am. Chem. Soc.*, **2007**, *129*, 14388.
15. H. Y. Wang, Y. Xie, R. B. King, H. F. Schaefer, *Inorg. Chem.*, **2006**, *45*, 3384.
16. H. Wang, Y. Xie, R. B. King, . F. Schaefer, H, III *J. Am. Chem. Soc.*, **2005**, *127*, 11564.
17. H. Wang, Y. Xie, R. B. King, H. F. Schaefer, , III *Inorg. Chem.*, **2006**, *45*, 5621.
18. H. Wang, Y. Xie, R. B. King, H. F. Schaefer, III *Organometallics*, **2007**, *26*, 1393.
19. X. Zhang, Q.-S. Li, Y. Xie, R. B. King, H. F. Schaefer, *Organometallics*, **2008**, *27*, 61.
20. A. D. Becke, *J. Chem. Phys*. **1993**, *98*, 5648.
21. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
22. A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
23. J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.
24. T. H. Dunning, *J. Chem. Phys*. **1970**, *53*, 2823.
25. S. *J.* Huzinaga, *Chem. Phys*. **1965**, *42*, 1293.
26. A. J. H. Wachters, *J. Chem. Phys.* **1970**, *52*, 1033.
27. D. M. Hood, R. M. Pitzer, H. F. Schaefer, *J. Chem. Phys.* **1979**, *71*, 705.
28. L. R. Byers, L. F. Dahl, *Inorg. Chem.* **1980**, *19*, 680.
29. F. R. Anderson, M. S. Wrighton, *Inorg. Chem*., **1986**, *25*, 112.
30. S. Gambarotta, C. Floriani, A. Chiesi-Viulla, C. Guastini, *J. Organometal. Chem.* **1985**, *296*, C6.
31. R. B. King, *Inorg. Chem.* **1966**, *5*, 2227.