J. Am. Chem. Soc. **1992**, *114*, 7560–7561

Cubic Nonlinear Optical Properties of Group 4 Metallocene Halide and Acetylide Complexes

Lori K. Myers,[†] Charles Langhoff,[‡] and
Mark E. Thompson*[,†]

Department of Chemistry, Princeton University
Princeton, New Jersey 08544
Central Research, 1776 Building
Dow Chemical Corporation, Midland, Michigan 48674

Received March 13, 1992

Third-order nonlinear optical (NLO) materials are of interest because they are potentially useful in a wide range of optical devices.[1] The study of molecular materials for third-order nonlinear optics has focused primarily on organic monomers and polymers.[1a,2] Most organic materials studied have delocalized π systems which are responsible for their large nonresonant third-order NLO susceptibilities. Recent reports of good NLO properties for group 10 metal acetylide oligomers suggest that organometallic complexes may be good candidates for NLO study.[3] Electron delocalization in these organometallic complexes is achieved by strong metal to ligand charge transfer between the filled metal orbitals and vacant acetylide π^* orbitals. A limited amount of data exists concerning the third-order NLO properties of other organometallic complexes.[4] Herein, we report on a systematic study of the third-order nonlinear optical properties of group 4 metallocene complexes, Cp_2MX_2 (M = Ti, Zr, Hf; X = F, Cl, Br, $C{\equiv}CC_6H_5$).

Group 4 metallocene complexes are formally d^0, 16-electron complexes; therefore, electron delocalization cannot take place through a MLCT process, as in the group 10 complexes discussed above. Theoretical calculations show that the LUMO in these complexes is primarily a metal-centered orbital which lies in the MX_2 plane, as shown in the Figure 1.[5,15b] Strong π donation and ligand to metal charge transfer (LMCT) involving this vacant metal orbital are observed for amide and alkoxide ligands;[6] spectroscopic evidence suggests LMCT processes may be important in acetylide complexes as well.[7] This LMCT may lead to mixing between the π systems of the acetylide ligands to produce an extended network, leading to materials with good third-order NLO properties.

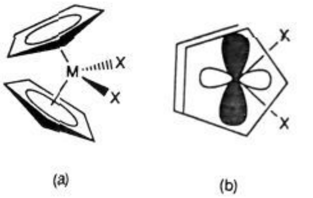

Figure 1. Structure of Cp_2MX_2 (side view) (a); proposed LUMO for Cp_2MX_2 compounds, M = Ti, Zr, Hf (top view) (b).

Table I. Third-Order NLO Coefficients Measured by Third Harmonic Generation[a]

compd (λ_{max}, nm)	solvent	γ (10^{-36} esu)[b]
Cp'_2TiF_2 (324)	$CHCl_3$	<3[c]
Cp'_2TiCl_2 (394)	$CHCl_3$	<5[c]
Cp'_2TiBr_2 (428)	$CHCl_3$	<5[c]
Cp_2ZrCl_2 (338)	$CHCl_3$	<5[c]
$Cp_2Ti(C{\equiv}C\phi)_2$ (410)	THF	92[d]
$Cp_2Zr(C{\equiv}C\phi)_2$ (390)	THF	58
$Cp_2Hf(C{\equiv}C\phi)_2$ (390)	THF	51
$\phi C{\equiv}CC{\equiv}C\phi$	THF	45[e]
$HC{\equiv}C\phi$	neat	6
$Cp_2Ti(C{\equiv}C\phi)Cl$	THF	31
$(C_5H_4\text{-}n\text{-}Bu)_2Fe$	neat	25

[a] 1.907-μm light tripled to 0.636 μm (all of the compounds are transparent at both frequencies). [b] Error bars are ±15%. [c] Upper limit based on solubility. [d] The γ of 50×10^{-36} esu previously reported for $Cp'_2Ti(C{\equiv}C\phi)_2$ ($Cp' = C_5H_4Me^-$) in $CHCl_3$ was in error due to photodecomposition in $CHCl_3$ (see ref 13). [e] See: Perry, J. W.; Stiegman, A. E.; Marder, S. R.; Coulter, D. R. In ref 2b, p 189.

Group 4 metallocene complexes were purchased or synthesized using literature procedures.[8] The third-order nonlinear optical susceptibilities, γ, were derived from the third harmonic generation (THG) efficiencies determined for solutions of a given complex.[9] The THG experiment was performed with a Raman shifted Nd:YAG laser with a fundamental of 1.9 μm. The complexes studied, the solvents used for THG experiment, and the measured γ values are given in Table I. To prevent decomposition of the Zr and Hf complexes, these solutions were prepared and the cell was loaded in a glove box. NMR (Ti compounds only) and ultraviolet–visible (UV–vis) spectra taken before and after the THG experiment show that the compounds are stable throughout the THG experiment.

We first undertook a study of the metallocene–halide complexes as a control for the metallocene–phenylacetylide complexes. The lowest lying absorptions in the UV–vis spectra of the metallocene–halides arise from Cp to metal charge transfers,[5,10] which may give electronically delocalized complexes. The third-order susceptibilities of these halide complexes, however, are too low to allow them to be measured exactly, even for saturated solutions (approximately 0.2 M). The γ values listed in Table I are the upper bounds and are on the order of 5×10^{-36} esu. For comparison, the γ measured for benzene is 4×10^{-36} esu.[11] Group 8 metallocenes give relatively larger values of γ; for example the γ of 1,1′-dibutylferrocene (BuFc) is 25×10^{-36} esu (Table I).[12]

The metallocene–phenylacetylide complexes have γ values ranging from 30×10^{-36} to 90×10^{-36} esu, as shown in Table I. These γ values are increased substantially over the values for metallocene–dihalides, and they are similar to comparable or-

---

[†] Princeton University.

[‡] Dow Chemical Corporation.

(1) (a) Prasad, P. N.; Williams, D. J. *Nonlinear Optical Effects in Molecules and Polymers*; John Wiley and Sons, Inc.: New York, 1991. (b) Ulrich, D. R. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 3. (c) Abraham, E.; Seaton, C. T.; Smith, S. D. *Sci. Am.* **1983**, *284*, No. 2, 85. (d) Pepper, D. M. *Sci. Am.* **1986**, *254*, No. 1, 74.

(2) For example, see: (a) Chemla, D. S.; Zyss, T. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press, Inc.: Orlando, FL, 1987; Vol. 2. (b) *Organic Materials for Non-Linear Optics*; Hann, R. A., Bloor, D., Eds.; Royal Society of Chemistry: London, 1989. (c) *Organic Materials for Nonlinear Optics*; Hann, R. A., Bloor, D., Eds.; Royal Society of Chemistry: London, 1991.

(3) (a) Frazier, C. C.; Guha, S.; Chen, W. P.; Cockerham, M. P.; Porter, P. L.; Chauchard, E. A.; Lee, C. H. *Polymer* **1987**, *28*, 553. (b) Frazier, C. C.; Chauchard, E. A.; Cockerham, M. P.; Porter, P. L. *Mater. Res. Symp. Proc.* **1988**, *109*, 323. (c) Guha, S.; Frazier, C. C.; Porter, P. L.; Kang, K.; Finberg, S. E. *Opt. Lett.* **1989**, *14*, 952. (d) Blau, W. J.; Byrne, H. J.; Cardin, D. J.; Davey, A. P. *J. Mater. Chem.* **1991**, *1*, 245.

(4) (a) Ghosal, S.; Samoc, M.; Prasad, P. N.; Tufariello, J. J. *J. Phys. Chem.* **1990**, *94*, 2847. (b) Cheng, L.-T.; Tam, W.; Meredith, G. R.; Marder, S. R. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 137. (c) Calabrese, J. C.; Cheng, L.-T.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc.* **1991**, *113*, 7227. (d) Kafafi, Z. H.; Lindle, C. S.; Weisbecker, C. S.; Bartoli, F. J.; Shirk, J. S.; Yoon, T. H.; Kim, O.-K. *Chem. Phys. Lett.* **1991**, *179*, 79. (e) Winter, C. S.; Oliver, S. N.; Rush, J. D.; Hill, C. A. S.; Underhill, A. E. *J. Appl. Phys.* **1992**, *71*, 512. (f) For a recent review, see: Nalwa, H. S. *Appl. Organomet. Chem.* **1991**, *5*, 349.

(5) Bruce, M. R. M.; Kenter, A.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 639. Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(6) (a) Vann Bynum, R.; Hunter, W. E.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2368. (b) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

(7) Sebald, A.; Fritz, P.; Wrackmeyer, B. *Spectrochim. Acta* **1985**, *41A*, 1405.

(8) (a) Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106. (b) Kopf, H.; Schmidt, M. *J. Organomet. Chem.* **1967**, *10*, 313. (c) Teuben, J. H.; De Liefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *17*, 87. (d) Erker, G.; Fromberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Kruger, C. *Organometallics* **1989**, *8*, 911.

(9) Kajzar, F.; Messier, J. *Rev. Sci. Instrum.* **1987**, *58*, 2081.

(10) Cauletti, C.; Clark, J. P.; Green, J. C.; Jackson, S. E.; Fragala, I. L.; Ciliberto, E.; Coleman, A. W. *J. Electron Spectrosc.* **1980**, *18*, 63.

(11) See ref 1a, p 226.

(12) Prasad reports a value for normal ferrocene (Cp_2Fe) of 16×10^{-36} esu, which was measured by degenerate four-wave mixing (see ref 4a). The difference in these numbers is likely due to differences in measurement technique and not inherent nonlinearities.

(13) Thompson, M. E.; Chiang, W.; Myers, L. K.; Langhoff, C. *Proc. SPIE* **1991**, No. 1497, 423.

0002-7863/92/1514-7560$03.00/0

J. Am. Chem. Soc. 1992, 114, 7561–7562

ganometallic molecules studied to date.[4] The γ values are also increased compared to related organic species, particularly for $Cp_2Ti(C\equiv C\phi)_2$ ($\phi = C_6H_5$). A trend of the γ value with respect to the metal atom exists: as one goes down the periodic chart, γ decreases.

One mechanism for increasing the γ values of the metallocene–phenylacetylide complexes over $HC\equiv C\phi$ is for the Cp_2M moiety to act as an electron-accepting group for the phenylacetylene ligand. Acceptor-substituted organic compounds have increased third-order susceptibilities over their unsubstituted analogs. Nitro substitution of styrene leads to a 2-fold increase in γ (β-nitrostyrene, $\gamma = 29 \times 10^{-36}$ esu;[14] styrene, $\gamma = 17 \times 10^{-36}$ esu[4a]). The increase in γ seen for the group 4 metallocenes is greater than that seen in related organic compounds. Assuming that the Cp_2TiCl fragment contributes $<5 \times 10^{-36}$ esu to γ, substitution of $HC\equiv C\phi$ with the metallocene $[Cp_2Ti(Cl)C\equiv C\phi]$ leads to an increase in γ by greater than a factor of 4.

If the Cp_2M unit is acting only as an electron-accepting group, the γ value for $Cp_2Ti(Cl)C\equiv C\phi$ should be at least half of that observed for $Cp_2Ti(C\equiv C\phi)_2$. The measured γ of $Cp_2Tl(Cl)\text{-}C\equiv C\phi$ is approximately one-third that of $Cp_2Ti(C\equiv C\phi)_2$, demonstrating that another electronic process is contributing to the third-order properties as well. The most likely candidate for the contributing process is the linking of the acetylide units via interaction of the metal d and acetylide π orbitals to form an extended π system. The decreasing trend in γ values (Ti > Zr $\gtrsim$ Hf) is rationalized by assuming that the Ti d orbitals are closer in energy to the alkynyl π orbitals than to the Zr or Hf d orbitals, which leads to more significant mixing between these orbitals for the Ti complexes as compared to the Zr of Hf complexes. The closer energy match also makes Ti a better acceptor for the alkyne π system, enforcing the observed trend. This smaller energy gap between the metal and organic ligand orbitals is seen in the absorption spectra (Ti is red shifted relative to Zr and Hf). The π symmetry orbitals of the cyclopentadienyl ligands may also be involved in the electronic structure leading to the observed NLO properties. Theoretical calculations suggest that, for group 4 bent metallocene complexes with unsaturated hydrocarbon ligands (i.e., carbene or acetylide), significant mixing occurs between the cyclopentadienyl and hydrocarbon π orbitals.[15] This mixing leads to molecular orbitals which extend over the entire molecule.

In conclusion, we have determined the third-order properties of a series of group 4 transition metal complexes. The third-order nonlinear optical properties of the metallocene–phenylacetylide complexes are tuned by the choice of metal atom, with Ti giving a larger optical nonlinearity than either Zr of Hf. We are continuing this study by exploring group 4 complexes (with and without Cp ligands) to obtain a better understanding of the origin and magnitude of the third-order nonlinearities in these materials.

Acknowledgment. This work was supported by the Dow Chemical Company, through their Cooperative Research Program, the U.S. Air Force Office of Scientific Research (AFOSR-90-0122), and the Advanced Technology Center for Photonics and Optoelectronic Materials (POEM, Princeton University).

Registry No. Cp'_2TiF_2, 38498-31-6; Cp'_2TiCl_2, 1282-40-2; Cp'_2Br_2, 72622-32-3; Cp_2ZrCl_2, 1291-32-3; $Cp_2Ti(C\equiv C\phi)_2$, 12303-93-4; $Cp_2Zr(C\equiv C\phi)_2$, 72982-57-1; $Cp_2Hf(C\equiv C\phi)_2$, 84879-48-1; $\phi C\equiv CC\equiv C\phi$, 886-66-8; $HC\equiv C\phi$, 536-74-3; $Cp_2Ti(C\equiv C\phi)Cl$, 142867-28-5; $(C_5H_4\text{-}n\text{-}Bu)_2Fe$, 1274-08-4.

Supplementary Material Available: Description of the data analysis procedures for the third harmonic generation measurements and a representative set of THG data ($Cp_2Hf(C\equiv C\phi)_2$) (9 pages). Ordering information is given on any current masthead page.

---

(14) Cheng, L.-T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 1064.

(15) (a) Francl, M. M.; Pietro, W. J.; Hout, R. F.; Hehre, W. J. *J. Organomet. Chem.* **1983**, *2*, 815. (b) Knight, E.; Myers, L. K.; Thompson, M. E. *Organometallics*, submitted for publication.

Cryptic Stereospecificity of Methane Monooxygenase

N. D. Priestley,[†] H. G. Floss,[*,†] W. A. Froland,[‡]
J. D. Lipscomb,[*,‡] P. G. Williams,[§] and H. Morimoto[§]

Department of Chemistry BG-10
University of Washington, Seattle, Washington 98195
Department of Biochemistry, Medical School
University of Minnesota
Minneapolis, Minnesota 55455
National Tritium Labeling Facility
Lawrence Berkeley Laboratory, 1 Cyclotron Road
Berkeley, California 94720

Received May 18, 1992

Methane monooxygenase (MMO, EC 1.14.13.25) catalyzes the NAD(P)H- and O_2-dependent hydroxylation of methane to methanol.[1-4] Soluble MMO from the methanotrophic bacterium, *Methylosinus trichosporium* OB3b, consists of a 245 kDa hydroxylase component containing a μ-(R/H)-oxo bridged binuclear iron cluster, a 40 kDa NAD(P)H-dependent oxidoreductase component, and a 15.8 kDa protein, component B, which has no associated cofactors.[4,5] The hydroxylase component alone can carry out the same oxidations as the reconstituted three-component system when H_2O_2 is used as the source of oxygen and reducing equivalents.[6,7]

Several mechanisms have been proposed for MMO-catalyzed alkane oxidation; these invoke an intermediate substrate radical,[4,8,10-12] an additional substrate carbocation intermediate,[13] or a concerted oxygen insertion into a substrate carbon–iron bond.[14] Recent studies support the formation of a substrate intermediate not bound to the iron;[10,11,13,15] however, they utilized diagnostic substrates that may not be representative of the natural substrate, methane. The experiments described here address this question more directly by determining the steric course of the oxidation of (*S*)- or (*R*)-$[1\text{-}^2H_1,1\text{-}^3H_1]$ethane to ethanol catalyzed by MMO.

[†] University of Washington.

[‡] University of Minnesota.

[§] Lawrence Berkeley Laboratory.

(1) Colby, J.; Dalton, H.; Whittenbury, R. *Annu. Rev. Microbiol.* **1979**, *33*, 481.

(2) Anthony, C. *The Biochemistry of the Methylotrophs*; Academic Press: London, 1982.

(3) Fox, B. G.; Lipscomb, J. D. In *Biological Oxidation Systems*; Reddy, C., Hamilton, G., Madyastha, M., Eds.; Academic Press: San Diego, CA, 1990; Vol. I, pp 367–388.

(4) Fox, B. G.; Froland, W. A.; Dege, J.; Lipscomb, J. D. *J. Biol. Chem.* **1989**, *264*, 10023.

(5) (a) Hendrich, M. P.; Munck, E.; Fox, B. G.; Lipscomb, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 5861. (b) Fox, B. G.; Surerus, K. K.; Munck, E.; Lipscomb, J. D. *J. Biol. Chem.* **1988**, *263*, 10553.

(6) Andersson, K. K.; Froland, W. A.; Lee, S. K.; Lipscomb, J. D. *New J. Chem.* **1991**, *15*, 411.

(7) Froland, W. A.; Andersson, K. K.; Lee, S. K.; Liu, Y.; Lipscomb, J. D. In *Applications of Enzyme Biotechnology*; Kelly, J. W., Baldwin, T. O., Eds.; Plenum Press: New York, 1991; pp 39–53.

(8) In analogy to the mechanism of cytochrome P450-catalyzed hydroxylations[9] in which substrate hydrogen atom abstraction by an activated oxygen atom bound to the active site iron cluster results in an intermediate substrate radical.

(9) McMurray, T. J.; Grove, J. T. In *Cytochrome P-450. Structure, Mechanism and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum Press: New York, 1986; pp 1–28.

(10) Green, J.; Dalton, H. *J. Biol. Chem.* **1989**, *264*, 17698.

(11) Fox, B. G.; Borneman, J. G.; Wackett, L. P.; Lipscomb, J. D. *Biochemistry* **1990**, *29*, 6419.

(12) Deighton, N.; Podmore, I. D.; Symons, M. C. R.; Wilkins, P. C.; Dalton, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1086.

(13) Ruzicka, F.; Huang, D.-S.; Donnelly, M. I.; Frey, P. A. *Biochemistry* **1990**, *29*, 1696.

(14) (a) Barton, D. H. R.; Csuhai, E.; Doller, D.; Ozbalik, N.; Balavoine, G. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 3401. (b) Barton, D. H. R.; Bévière, S. D.; Chavasiri, W.; Csuhai, E.; Doller, D.; Liu, W.-G. *J. Am. Chem. Soc.* **1992**, *114*, 2147.

(15) Rataj, M. J.; Kauth, J. E.; Donnelly, M. I. *J. Biol. Chem.* **1991**, *266*, 18684.

0002-7863/92/1514-7561$03.00/0