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THIRD ORDER NONLINEAR OPTICAL PROPERTIES OF GROUP 4 METALLOCENES*

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Abstract—The third order nonlinear optical (NLO) coefficients (γ) of Ti, Zr, and Hf metallocene halides, acetylides and alkenylzirconocene compounds were measured with a third harmonic generation technique with a fundamental laser frequency of 1908 nm. Metallocene halide compounds have γ of less than 5×10^{-36} esu. Titanocene bisphenylacetylide has the largest γ (92×10^{-36} esu) of the metallocene acetylide compounds. The γ of the metallocene acetylide complexes are significantly larger than the sum of the free organic acetylene and the metallocene halide compounds. $Cp_2Zr(Cl)CH{=}CH$-1,4-phenyl-$CH{=}CH(Cl)ZrCp_2$ has the largest γ (154×10^{-36} esu) of any of the group 4 metallocene compounds studied. The origin of this optical nonlinearity is most likely due to a conjugated π system, which involves the Cp–metal bonding network and like symmetry orbitals of the vinyl and acetylide ligands.

Third order nonlinear optical (NLO) materials are of interest because of their potential use in a wide range of optical devices.[2] The third order nonlinear optical properties of a material can be characterized by two coefficients. The microscopic NLO properties of a molecular material (i.e. the properties of a single molecule) are described by a coefficient γ, while the properties of a bulk solid are described by the coefficient $\chi^{(3)}$. The $\chi^{(3)}$ values of a molecular material are related to the γ values of the individual molecules and how the molecules are packed in the solid state. Contrary to the situation found for second order optical nonlinearities, there is *not* a requirement that the material to be studied have a noncentrosymmetric structure, thus molecular materials can be conveniently studied as dilute solutions.

One roadblock to designing materials with larger third order properties is the lack of a detailed understanding of the effect of molecular structure on the third order NLO response. This is in contrast to second order NLO materials where specific molecular properties affect the second order NLO properties in predictable ways.[2a] Researchers designing molecular materials for third order NLO applications have focused mainly on the properties of conjugated organic polymers and oligomers.[3] The large NLO coefficients for these materials are due to highly polarizable electronic networks in their delocalized π systems. It is also known that increasing the conjugation length of an organic polymer increases the measured γ per repeat unit.[3] A more generalized description of the effects of specific substitutions to conjugated organic systems has only recently begun to be developed.[4] A theoretical study

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* This paper is dedicated to Professor John E. Bercaw, on the occasion of his 50th birthday, quite possibly the most awesome organometallic chemist on the planet.

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by Beratan suggests that the introduction of substituents, such as donors or acceptors, which create midgap states in a polymer can lead to an increase in third order properties.[5] Midgap states can be readily introduced into organic systems by substitution with transition metals.[5]

Organometallic compounds have highly polarizable *d* orbitals. In addition, ligand and metal orbitals can interact strongly, either in the ground or excited states. This interaction may lead to highly polarizable compounds with good third order properties. The metal/ligand interaction is tuned by varying the metal atom, the oxidation state of the metal or the surrounding ligands. It may be possible to exploit the good electronic variability of organometallic compounds to develop new third order NLO materials.

Recent reports of good NLO properties for group 10 (Ni, Pd, Pt) metal acetylide oligomers[6] and other organometallic complexes[7] suggest that organometallic compounds may indeed be good candidates for NLO study. Filled *d* orbitals of the metal interact strongly with the acetylide π^* orbitals, resulting in a polarizable network.[6,8,9] A limited number of systematic studies of the third order NLO properties of other organometallic species have been conducted, so that little is known about their potential as third order NLO materials. This paper reports on our study of the third order nonlinear optical properties of tetravalent group 4 (Ti, Zr, Hf) metallocene compounds, including halides, acetylides and alkenylzirconocenes.[10]

Tetravalent group 4 metallocenes have been highly studied[11] since the initial report of their syntheses in the 1950s.[12] The typical structure of these bent metallocene compounds is shown in Fig. 1(a), where X can be a variety of organic and inorganic ligands. These compounds are formally d^0, 16 electron species. Metallocene complexes have been shown to be useful as polymerization catalysts and stoichiometric organic synthetic reagents.[13] The electronic structure of metallocene halides have been studied by several different theoretical and experimental techniques.[14] These studies have shown that the LUMO in these complexes is composed mainly of Ti centered *d* orbitals, which lie in the X—M—X plane. This is shown schematically in Fig. 1(b). The lowest energy transitions in these complexes arise from ligand to metal charge transfer (LMCT). The HOMO is composed of mainly Cp centered orbitals when X = F, Cl, Br or mainly X centered orbitals when X = I, methyl.

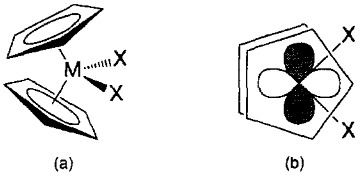

Fig. 1. (a) General structure of Cp_2MX_2, (b) LUMO orbital of group 4 bent metallocenes.

The electronic structure of the group 4 metallocenes is very different from that of the group 10 metal acetylide complexes. In the group 10 acetylides, filled metal *d* orbitals interact with organic orbitals. Group 4 metallocenes, on the other hand, have a low lying vacant *d* orbital which may interact with filled orbitals of the ligands. Evidence of this has been reported for Cp_2TiX_2, X = amide, alkoxide.[15] We are interested in studying the effect of these types of ligand/metal interactions on the NLO properties in group 4 metallocene halides, acetylides and alkenylzirconocenes.

RESULTS AND DISCUSSION

All of the metallocene complexes discussed in this paper were prepared by literature procedures or modifications thereof and are described in the experimental section. $Cp_2Ti(C{\equiv}C\phi)_2$ ($\phi = C_6H_5$) is very air stable and can be stored in the air (at *ca* 10°C) for months with minimal decomposition. $Cp_2Ti(C{\equiv}C\text{-butyl})_2$, however, decomposes in the air over several days with the concomitant formation of hexyne. The butyl acetylide derivatives are also not stable in an inert atmosphere at room temperature. The orange compound decomposes to a green species over a period of several days. $Cp_2Zr(C{\equiv}C\text{-}\phi)_2$ and $Cp_2Hf(C{\equiv}C\text{-}\phi)_2$ decompose readily in the air, but are stable in inert atmosphere. $Cp_2Zr(C_4\phi_4)$ (Fig. 2a) has been synthesized by several methods. The method of Negishi *et al.*[16] has proven to be the most convenient, and involved treating Cp_2ZrCl_2 with butyllithium at low temperature followed by diphenyl acetylene. The alkenylzirconocene compounds shown in Fig. 2(b) and (c) are synthesized from $Cp_2Zr(Cl)H$ and the appropriate diethynylbenzene. Alkenylzirconocene compounds react with H_2O to form the Zr μ-oxo dimer ($[Cp_2ZrCl]_2O$). The alkenylzirconocene compounds in this study were typically contaminated with 1–5% Zr μ-oxo dimer. Therefore, it was necessary to measure the γ of the Zr μ-oxo dimer compound for comparison to the γ of the alkenylzirconocene compounds.

As discussed above, the Cp → M charge transfer is the lowest energy transition in the X = F, Cl, Br compounds and X → M charge transfer in the X = I compound. The energy of these transitions fall in a large range from 410 nm for X = F to 590 nm for X = I in the titanium complexes. The energy of

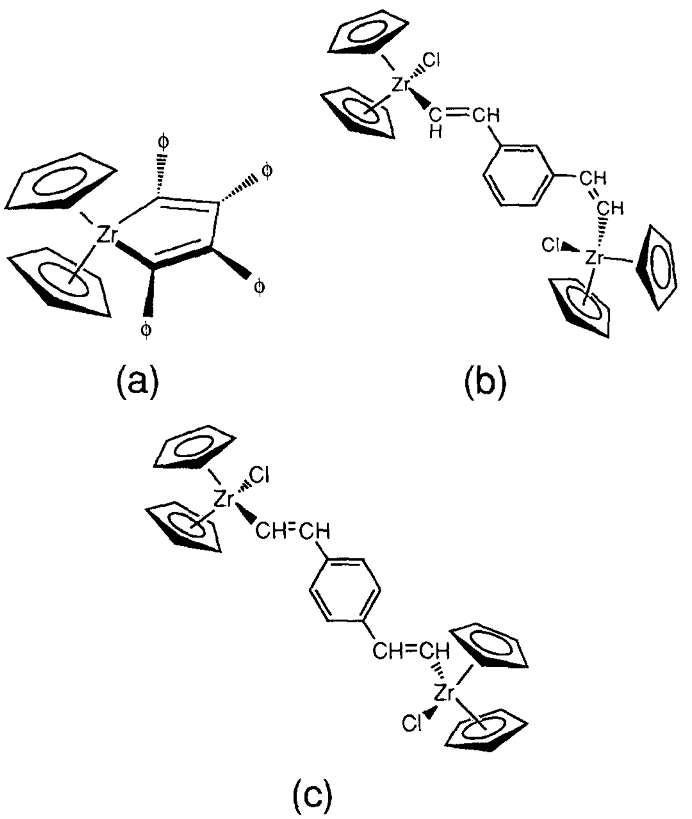

Fig. 2. (a) $Cp_2Zr(C_4\phi_4)$, (b) *meta*-Zr dimer, (c) *para*-Zr dimer.

the LMCT is changed significantly by variation of the halide (I < Br < Cl < F) or the metal (Ti < Zr < Hf). Therefore, we were interested in studying the NLO properties of the metallocene halides for two important reasons: (1) to determine the effect of changing the halide and the metal on the NLO properties, and (2) to determine a baseline value of γ for the "Cp_2M" portion of these compounds to compare to the metallocene acetylide and alkenylzirconocene compounds.

The third order NLO properties of these compounds were measured by third harmonic generation (THG), using the cell design of Kazjar and Messier.[17] In this technique, γ is obtained by determining the efficiency of the material at frequency tripling the light of an incident laser beam ($\omega \rightarrow 3\omega$). A Raman shifted Nd : YAG laser with a fundamental of 1.907 μm ($3\omega = 636$ nm) was used for the THG experiment. All of the compounds measured are transparent at both the fundamental and the third harmonic wavelengths, minimizing the chances of resonant enhancement of the measured γ values. The measurements are carried out in solution, with a series of different dilutions for each compound. The THG experiment is described in detail in the experimental section. The third order properties of the metallocene halides are listed in Table 1.

As shown in Table 1, the γ values for the group 4 metallocene halide complexes are reported as upper limits. This is due to the low solubility and small γ of these complexes. The solutions we used were on the order of 0.1 M or less, depending upon the particular halide. The concentration of solvent is on the order of 10 M. If the γ of the solute is comparable to the solvent, the signal from the solute will be swamped by the solvent. This is the case in these compounds and is the reason for the upper limit on γ. What is clear from these measurements is that the "Cp_2M" portion of the molecule does not have a large third order nonlinearity. Unfortunately, the low solubility prevented the determination of the effect that halide substitution has on the NLO properties of these complexes. The complexes could be made substantially more soluble by substituting Cp with Cp* (Me_5C_5), but we chose not to pursue this due to the low γ for the metallocene halides.

The reason for studying group 4 metallocene complexes was that orbital interaction between metal *d* orbitals and filled ligand orbitals may lead to a polarizable π electron system leading to good

Table 1. Third order NLO properties of group 4 metallocene halides[a] and related molecules

Compound	Solvent	λ_{max} (nm)	Technique	$\gamma \times 10^{36}$ esu[b,e]
Cp'_2TiF_2[c]	$CHCl_3$	414	THG[d]	<3
Cp'_2TiCl_2	$CHCl_3$	518, 388	THG	<5
Cp'_2TiBr_2	$CHCl_3$	568	THG	<5
Cp_2ZrCl_2	$CHCl_3$	334	THG	<5
Cp_2HfCl_2	$CHCl_3$	306	THG	<5
$CHCl_3$[17b]	neat	<250	THG	3
benzene[17b]	neat	204	THG	4
n-butyl ferrocene	neat	440	THG	25
ferrocene[7a]	THF	440	DFWM[f]	16
ferrocene[7g]	molten	440	S-F[g]	64000

[a] γ values of compounds reported in this work were measured using a Nd : YAG laser shifted to 1.907 μm ($3\omega = 636$ nm). Compounds are transparent at these wavelengths.

[b] Error bars are $\pm 15\%$.

[c] $Cp' = MeC_5H_4$.

[d] THG = third harmonic generation.

[e] "<" indicates that the number listed is an upper limit due to low solubility.

[f] DFWM = degenerate four wave mixing.

[g] S-F = self focussing.

NLO properties. The LUMO of group 4 metallocene acetylides is very similar to that found for other group 4 metallocenes (Fig. 1b).[18] The cylindrical symmetry of the π system of the acetylide ligands make them ideal for interaction with this metal based LUMO. Moreover, acetylide ligands and *d* orbitals of the metal are often of similar energy.[9] This type of ligand/metal interaction may allow the two organic substituents to be in electronic communication with one another through the metal.

Spectroscopic evidence suggests ligand/metal interactions may be important in these acetylide complexes. Pertinent IR and NMR data are given in the experimental section. The $\nu_{C\equiv C}$ frequency observed for the group 4 metallocene complexes are lowered relative to that of the free acetylene compound, as would be expected if electron density is drawn away from the π bonding orbitals. This is also seen in the group 10 complexes[19] where metal/ligand interactions are important, but must involve donation from the metal based orbitals into the π^* orbitals of the acetylide. The ^{13}C NMR spectra of the group 4 acetylides show that the *sp* carbons are very deshielded ($\delta = 142$–152 ppm). They fall in the region where sp^2 carbons are generally located. This shows that the electron density around the acetylene is highly perturbed.[20]

Evidence from the crystal structure of $Cp_2Zr(C{\equiv}CMe)_2$ seems to conflict with the spectroscopic evidence.[21] The bond lengths of the Zr—C and C≡C bonds are 2.249 and 1.206 Å respectively. The C≡C bond length in propyne is 1.207 Å, so there is not the expected lengthening of this bond. Also the Zr—C bond is not very much shorter than a Zr—sp^2 C or Zr—sp^3 C bond. However, this is also the case in crystal structures of group 10 acetylides.[22] It is not clear then, from previous evidence the importance ligand/metal interactions in the metallocene acetylides.

For comparison, we have therefore examined some of our titanocene acetylides by X-ray diffraction and report herein the molecular structure of one of them, i.e. $Cp'_2Ti(C{\equiv}C\phi)_2$. The compound crystallizes from toluene in the monoclinic space group $P2_1/c$ (No. 14) with $Z = 12$. The three crystallographically independent molecules observed are depicted in Fig. 3. The average Ti—Cp′ distance, Cp′—Ti—Cp′ angle (i.e. metal—centroid and centroid—metal—centroid) and acetylide—Ti—acetylide angle are 2.05 Å, 134.2° and 95.7°, respectively. All of these are within the expected ranges of values observed for bent metallocene complexes.[23] In all three molecules, one phenyl group is oriented essentially perpendicular to the acetylide—Ti—acetylide plane; the phenyls being rotated 85.0, 85.9 and 84.8°, respectively, out of the acetylide—Ti—acetylide plane of the complex. In contrast, the remaining phenyl rings are rotated over a wider range of angular values,

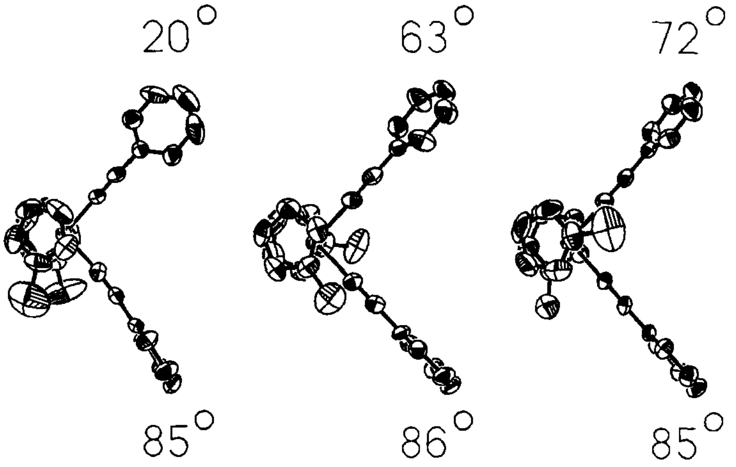

Fig. 3. Structures of the three molecules which make up the asymmetric unit of $Cp'_2Ti(C{\equiv}C\phi)_2$. The number next to each phenyl ring is the angle between the plane of that ring and the $M(C{\equiv}C—)_2$ plane.

i.e. 19.7, 62.8 and 71.6°, respectively. The average Ti—acetylide distances are 2.086(10) Å in the former case (i.e. with the phenyl perpendicular) and 2.105(20) Å in the latter, and are comparable to the Ti—acetylide value of 2.070 Å previously reported for related Ti^{IV} bis(cyclopentadienyl) complexes.[24] This body of evidence is in contrast to the Zr example above and shows that Ti—acetylide bonds are in general shorter than Ti—alkyl bonds. As such, the possibility of a *dπ–pπ* interaction between empty Ti *d* orbitals and filled acetylide *π* orbitals cannot be discounted crystallographically.

The NLO properties of several acetylide complexes were measured by THG. In order to insure the complexes did not decompose during the experiment, the solutions were prepared in the glove box and loaded into the THG cell (the Ti complexes were prepared in the air). The UV–vis spectrum was recorded before and after the THG experiment. This was accomplished by mounting the THG cell directly in the UV–vis spectrometer. The UV–vis spectra are very sensitive to decomposition of the complexes. No decomposition was observed over the time period of the THG experiment. The γ for the metallocene acetylides and other organometallic and organic compounds are reported in Table 2.

Several points can be drawn from the measured γ values for the Ti, Zr and Hf acetylide complexes. The γ of group 4 metallocenes are comparable to other conjugated organometallic compounds, and are larger than the sum of the Cp_2M fragment and phenylacetylene. The γ varies depending on the metal atom with Ti > Zr > Hf.

The γ reported for the 1,1′-distyrylferrocene compound is slightly larger than the group 4 acetylide complexes. However, the styrylferrocene compounds were measured using a 602 nm laser, which is close to the absorption edge of the molecule. Therefore, these numbers may be resonantly enhanced, although an imaginary γ was not reported.[7a] The large γ reported for group 10 acetylide complexes are, in most cases, resonantly enhanced. These compounds and their related polymers show strong two photon absorptions.[6b] The γ in these compounds is dominated by the imaginary part. The γ values of the metallocene acetylide complexes are most likely not resonantly enhanced, as discussed above.

Assuming real γ values, with no resonant enhancement, there are several other explanations for the enhancement of γ of the metallocene acetylide complexes compared to the sum of the Cp_2M fragment and the organic acetylenes. One explanation is that the Cp_2M moiety is acting as an electron accepting group for the phenylacetylene ligand. Acceptor substituted organic compounds have increased third order susceptibilities over their unsubstituted analogs. For example, β-nitrostyrene has a γ of 29×10^{-36} esu,[4c] compared to 17×10^{-36} esu for styrene itself.[7a] If the Cp_2M unit is acting as a simple electron accepting group, the γ value for $Cp_2Ti(Cl)C{\equiv}C\phi$ would be expected to be at least half of that observed for $Cp_2Ti(C{\equiv}C\phi)_2$. The measured γ of $Cp_2Ti(C{\equiv}C\phi)Cl$ is approximately one third that of $Cp_2Ti(C{\equiv}C\phi)_2$, demonstrating that another electronic process is most likely contributing to the third order properties.

In Table 2, one can see that the γ for all the metal compounds are greater than that of diphenylbutadiyne. This suggests that if the process which is leading to the NLO properties involves electronic

Table 2. Third order NLO properties of group 4 metallocene acetylides[a] and related molecules

Compound	Solvent	λ_{max} (nm)	Technique	$\gamma \times 10^{36}$ esu
$Cp_2Ti(C{\equiv}C\phi)_2$	THF	416	THG[a]	92
$Cp_2Zr(C{\equiv}C\phi)_2$	THF	370	THG	58
$Cp_2Hf(C{\equiv}C\phi)_2$	THF	358	THG	51
$Cp_2Ti(C{\equiv}C\phi)(Cl)$	THF	402, 510 (sh)	THG	31
$Cp_2Ti(C{\equiv}C\text{-butyl})_2$[b]	$CHCl_3$	390	THG	12
$\phi\text{-}C{\equiv}C{-}H$	neat	284, 350 (sh)	THG	6
$\phi\text{-}C{\equiv}C{-}C{\equiv}C\text{-}\phi$[6f]	THF	—	THG	45
butyl-$C{\equiv}C{-}H$	neat	≈250	THG	3
1,1′ styrylferrocene[7a]	THF	461	DFWM[c]	270
$(PBu_3)_2Pd(C{\equiv}C\phi)_2$[6b]	THF	—	DFWM	110
$(PBu_3)_2Pt(C{\equiv}C\phi CCH)_2$[6e]	THF	338	DFWM	53[d]
$Cp_2Zr[C_4(\phi_4)]$	THF	474, 370	THG	47
$Cp_2Zr(Cl)(C{=}C\phi\text{-}Me)$	THF	356	THG	24
meta-Zr dimer	THF	356	THG	68
para-Zr dimer	THF	380	THG	154
$(Cp_2ZrCl)_2O$	THF	282	THG	10

[a] THG = third harmonic generation. γ was measured with a fundamental wavelength at 1.907 μm, which is tripled to 636 nm (all compounds are transparent at these frequencies). Error bars are ±15%.

[b] This complex is light-sensitive in $CDCl_3$, therefore some decomposition may have occurred. A UV–vis spectrum taken after the experiment showed it was not significant.

[c] DFWM = degenerate four wave mixing.

[d] Only the real part of γ, does not include the imaginary part.

communication of the acetylide ligands mediated by the metal, the addition of the metal enhances the γ over directly conjugated phenylacetylenes. Comparing the increase of the $Cp_2Ti(C{\equiv}C\phi)Cl$ to $Cp_2Ti(C{\equiv}C\phi)_2$, we can see the γ gets 3 times larger. But the data of phenylacetylene compared to diphenylbutadiyne increases by 7 times, which is typical for conjugated organic polymers. One of the reasons for a smaller increase may be that our metallocene complexes do not have a linear π system (C—Ti—C angle is *ca* 100°), whereas linear π systems are common in organic polymers.

A ligand/metal orbital interaction may be contributing to the measured γ values, which was the original hypothesis for studying the metallocene acetylides. Interaction between filled π acetylide orbitals and metal *d* orbitals would allow the two phenylacetylene ligands to be in electronic communication with one another, leading to a polarizable system. The decreasing trend in γ values with variation of the metal ($Ti > Zr \sim Hf$) is rationalized by assuming that there is more significant mixing between the alkynyl π orbitals and the *d* orbitals for the Ti complexes as compared to the Zr or Hf complexes. The smaller energy gap between the metal and organic ligand orbitals seen in the absorption spectra (Ti is red shifted relative to Zr and Hf) support a closer energy match for Ti than for Zr or Hf.

An alternate ligand/metal orbital interaction involves the acetylide π orbitals which are perpendicular to the plane between the Cp rings. A theoretical calculation of the electronic structure of $Cp_2Ti(C{\equiv}CR)_2$ shows significant orbital mixing between filled Cp—Ti bonding orbitals and filled $C{\equiv}C$ π orbitals in the ground state.[19] Similar mixing is observed in related metallocene complexes.[25] This suggests that a polarizable network may be arising from Cp, metal and acetylide π orbital mixing in our complexes. The two different types of ligand/metal interaction proposed here involve different sets of acetylide π orbitals. An interaction between the metal based LUMO and the acetylide would involve acetylide orbitals in the plane of the wedge, while the interaction between the Cp—metal bonding orbitals and the acetylide would involve acetylide π orbitals that are perpendicular to the wedge, as shown in Fig. 4.

In an attempt to determine which type of ligand/metal interaction is most important in enhancing the NLO properties, we measured γ for $Cp_2Zr(C_4\phi_4)$ ($Cp_2Zr{-}C\phi{=}C\phi{-}C\phi{=}C\phi$, Fig. 2). The titanium analog would have been the better one to compare to our acetylides, however, it has a

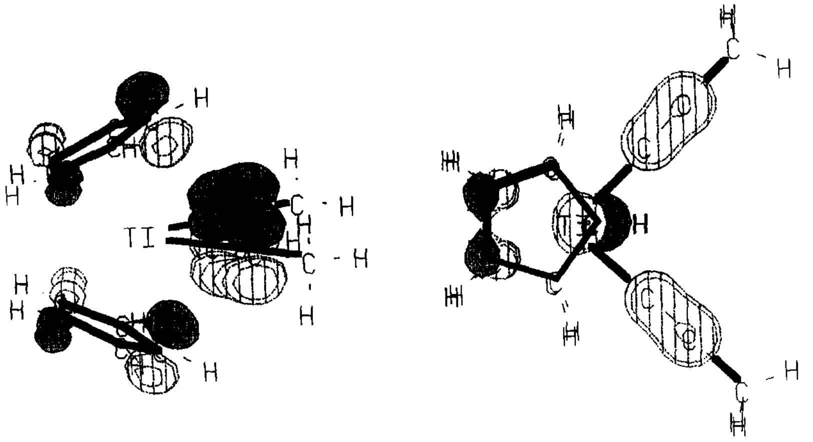

Fig. 4. Two views of the HOMO of $Cp_2Ti(C{\equiv}CCH_3)_2$.[19]

maximum in its absorption spectrum at 600 nm, which is very close to our third harmonic signal. The logic in choosing a metallocyclopenatadiene complex is that if the ligand/metal interaction involves the LUMO, there should be very little enhancement of the NLO properties, since the metallocyclopentadienyl ($C_4\phi_4$) π orbitals are orthogonal to this orbital. The metallocyclopentadienyl π orbitals are well situated, however, to interact with the Cp—metal bonding orbitals, such that if this interaction is important there should be a large enhancement of the NLO properties of the complex relative to the individual components that make up the complex (i.e. zirconacene and tetraphenylbutadiene). The measured γ for $Cp_2Zr(C_4\phi_4)$ is 47×10^{-36} esu; the most closely related free organic compound, *trans*-1,4-diphenyl-1,3-butadiene (DPB), has a γ of 36×10^{-36} esu. Compared to the difference in the γ of $Cp_2Zr(C{\equiv}C\phi)_2$ and phenylacetylene, complexing tetraphenylbutadiene to the Cp_2M moiety does not increase the third order properties to a large extent. Moreover, based on the red shifted UV-vis band in $Cp_2Zr(C_4\phi_4)$ compared to DPB, one may have expected an increase in γ due to resonant processes contributing to the nonlinearity.

A reason that may explain a smaller than expected increase in γ is that the butadiene ligand of $Cp_2Zr(C_4\phi_4)$ is in a *cis* orientation in the metallocene compound, rather than the *trans* conformation of DPB. What we feel is more likely, however, is that the ligand/metal interactions between the ligand π orbitals and the Cp_2M bonding orbitals, described above for $Cp_2M(C{\equiv}CR)_2$ complexes, may not be very strong in $Cp_2Zr(C_4\phi_4)$. Theoretical studies of the related titanium complex, $Cp_2\overline{Ti{-}CH{=}CH{-}C}{=}CH$, indicate that while the metallobutadiene ligand has good overlap between the π orbitals of the ligand and the like symmetry orbitals of the metallocene fragment, the energy match between the ligand and metallocene orbitals is very poor, leading to very little interaction.[19] The principal difference between the butadiene and bisacetylide ligand set is the energy difference between in the in phase and out of phase combinations of the ligand π orbitals. If the metallocene fragment is not amplifying the nonlinearity of $Cp_2Zr(C_4\phi_4)$ at all, one would expect the observed γ value should be similar to that of DPB, as observed.

In order to explore further the origin of the NLO response in these organometallic complexes a set of zirconacene vinyl complexes were examined. These zirconacene vinyl complexes are $Cp_2Zr(Cl)CH{=}CH{-}Ar{-}CH{=}CH(Cl)ZrCp_2$, Ar = 1,4-phenyl, 1,3-phenyl), which are abbreviated *para*-Zr dimer and *meta*-Zr dimer, respectively. In these complexes the most stable conformation will have the vinyl group in the plane between the Cp ligands, due to steric interactions between the Cp rings and the vinyl group. This conformation puts the vinyl π orbitals perpendicular to the wedge. The pertinent orbital overlaps are similar to those described for the metallocylcopentadienyl complexes. If the ligand/metal interaction involves the LUMO, there should be very little enhancement of the NLO properties, since the vinyl π orbital is orthogonal to this orbital. The vinyl π orbital is well situated, however, to interact with the Cp—metal bonding orbitals. The measured γ value for *para*-Zr dimer is 154×10^{-36} esu, compared to a γ of 58×10^{-36} esu for $Cp_2Zr(C{\equiv}C\phi)_2$. This increase is not due to the bridging organic group (i.e. *p*-divinylbenzene),[26] but must involve an extended network, involving the metallocene and divinylbenzene groups. The significant decrease in γ observed for *meta*-Zr dimer ($\gamma = 68 \times 10^{-36}$ esu) is consistent with the fact that the *meta* linkage at the phenyl group should significantly decrease the extent of mixing between the two metallocene units. The γ value observed for this *meta* derivative is close to two times larger than that of $Cp_2Zr(Cl)(CH{=}CHC_6H_4CH_3)$. This doubling of γ is expected, since the *meta* linkage through the central phenyl group will prevent conjugation of the two metallocene fragments. The two metallocene-styrenyl units of the *meta* derivative should act independently, as demonstrated by the doubling of γ. The *para* substituted derivative, however, has good conjugation through the central phenyl group, leading to a significant increase in γ relative to $Cp_2Zr(Cl)(CH{=}CHC_6H_4CH_3)$.

CONCLUSION

The third order nonlinear optical properties of a number of group 4 metallocene complexes were examined. It was found that the metallocene halide complexes do not have measurable optical nonlinearities. Acetylide and vinyl complexes, however, have reasonably large nonlinear optical coefficients, with the largest nonlinearity observed for $Cp_2Zr(Cl)CH{=}CH$-1, 4-phenyl-$CH{=}CH(Cl)ZrCp_2$. The origin of this optical nonlinearity is most likely due to a conjugated π system, which involves the Cp—metal bonding network and like symmetry orbitals of the vinyl and acetylide ligands.

The large third order NLO coefficient observed for $Cp_2Zr(Cl)CH{=}CH$ - 1,4-phenyl - $CH{=}CH(Cl)ZrCp_2$ is very encouraging. Moreover, the fact that only a small red shift is observed between this complex and $Cp_2Zr(Cl)(CH{=}CHC_6H_4CH_3)$ suggests that building extended networks of these materials may lead to materials with good optical transparency and large optical nonlinearity. Unfortunately, for these types of Zr compounds, it is not possible to add additional Cp_2M moieties by substitution of the Cl ligand. Previous work by Bercaw *et al.*[27] shows that bis-substituted alkenyl zirconocenes [i.e. $Cp_2Zr(CH{=}CHR)_2$] are not stable. They rearrange at room temperature to zirconacylopentenes. The Hf analogs were found to be stable, however. Although no progress was made in synthesizing these compounds to date, the data obtained for the zirconium complexes suggest that the hafnium compounds may have good NLO properties as well.

EXPERIMENTAL

General considerations

Cp'_2TiCl_2 ($Cp' = C_5H_4CH_3$) was purchased from Pressure Chemical. Cp_2ZrCl_2 was purchased from Strem Chemical. *meta*-Diethynyl benzene was purchased from Lancaster Chemical Co. The remaining metallocene halide complexes were prepared by literature procedures.[28] Metallocene acetylides[29] and vinyl[30] complexes, as well as the zirconacene μ-oxo dimer[31] were also prepared by literature procedures. Solvents were dried from the appropriate desiccants under Ar: THF, ethyl ether, toluene, benzene, hexane and pentane over Na-benzophenone, methylene chloride over CaH_2. Benzene-d_6, $CDCl_3$, and CD_2Cl_2 were stored over molecular sieves and THF-d_8 was stored over Na-benzophenone and vacuum transferred. Air sensitive manipulations were carried out using Schlenk techniques, or were done in a dry box. Sodium acetylides were prepared by stirring Na sand in an excess of the appropriate acetylene. UV–vis spectra were measured on a Hewlett–Packard 8452A diode array spectrophotometer. NMR spectra were obtained on a General Electric QE 300 MHz spectrometer operating at 75 MHz for ^{13}C or a JEOL 270MHz GSX spectrometer operating at 67.9 MHz for ^{13}C spectroscopy. The pulse delay for the coupled ^{13}C spectra were typically 8–10 s, due to the slow relaxing acetylenic carbons. IR spectra were determined using a Nicolet 730 FT-IR spectrometer. Mass spectra were determined by Dr Dorothy Little at Princeton University using a Kratos MS-9 spectrometer. Elemental analysis were determined on a in house Carla Erba 1106 CHN analyzer.

THG experiment

The data for the THG experiment were collected using a Raman shifted Continuum YG660 Nd: YAG laser (fundamental—1907 nm) with 5–10 ns pulses. The measurement technique was the standard wedge cell technique.[17] Translation of the cell in a direction perpendicular to the incoming laser beam allows the laser to penetrate through varying pathlengths of the solution. This leads to the formation of wedge fringe patterns of the third harmonic intensity. The data was analyzed by the following method. The THG was measured for a set of dilutions (typically four or five) for a compound as well as the pure solvent. This data was fit to a modification of the equation described previously.[17,32] The fitting is done using the Simusolv®[33] software package. This software allows fitting of all the parameters of the equation. The solvent reference is fit first to determine several experimental conditions: wedge angle of the cell, the path length, the power and cross-sectional area of the laser and the baseline for the electronics. This data determined from the reference is used to fit the other data sets. The absorption coefficients of the solutions at 636 and 1907 nm are measured with a Shimadzu UV3101 spectrometer. The index of refraction of solutions is estimated from a modified Abbe refractometer.[32] The $\chi^{(3)}$ is determined from the fit of this data. A normalized $\chi^{(3)}$ is obtained by dividing by the Lorentz local field factors. A linear fit of the χ^3 vs concentration leads to the γ.

$Cp_2Ti(C{\equiv}C\phi)_2$

NMR (C_6D_6, ppm) δ 6.12 (s, 5H, Cp-H), 6.94–7.05 (m, 3H, phenyl-H, *meta* and *para*), 7.43 (d, $^3J_{H-H}$ 6.93 Hz, 2H, phenyl-H, *ortho*). ^{13}C NMR (CD_2Cl_2, ppm) δ 113.9 (Cp), 125.6 (*ipso* phenyl carbon, $^3J_{C-H}$ 6.96 Hz, the $^2J_{C-H}$ was too small to be resolved), 127.4 (*para* phenyl carbon $^1J_{C-H}$ 161.04, $^3J_{C-H}$ 6.96 Hz), 128.5 (*meta* phenyl carbon $^1J_{C-H}$ 160.0 Hz, $^3J_{C-H}$ 6.96 Hz), 130.7 (β acetylenic carbon, $^3J_{C-H}$ 6.0 Hz), 131.1 (*ortho* phenyl carbon, $^1J_{C-H}$ 162 Hz, $^3J_{C-H}$ 5.96 Hz), 151.6 (α acetylenic carbon, no coupling). IR (KBr, cm^{-1}) 2064, $C{\equiv}C$ stretch. UV–vis (toluene, nm) 490 (sh), 418, 358 (sh), 312 (sh), 284. MS (*m/z*) found, 380.1, 278.0, 202.0, 178.0, 102.0, calc. 380.1, (M^+).

$Cp_2Zr(C{\equiv}C\phi)_2$

NMR (C_6D_6, ppm) δ 6.09 (s, 5H, Cp-H), 6.89–6.98 (m, 3H, *meta* and *para* phenyl protons), 7.45 (d, 2H, *ortho* phenyl protons). ^{13}C NMR (C_6D_6, ppm) δ 111.3 (Cp), 125.0 (β acetylenic carbon), 125.7 (*ipso* phenyl carbon), 127.4 (*para* phenyl carbon), 128.4 (*meta* phenyl carbon), 131.5 (*ortho* phenyl carbon), 142.8 (α acetylenic carbon). IR (Nujol, cm^{-1}) 2072 ($C{\equiv}C$ stretch). UV–vis (toluene, nm) 370 (sh), 292.

$Cp_2Hf(C{\equiv}C\phi)_2$

NMR (C_6D_6, ppm) δ 6.02 (s, 5 H, Cp-H), 6.92–6.95 (m, 3H, *meta* and *para* phenyl protons), 7.45 (d, 2H, *ortho* phenyl protons). ^{13}C NMR (C_6D_6, ppm) δ 110.5 (Cp), 126.0 (*ipso* phenyl carbon), 127.5 (β acetylenic carbon), 127.6 (*para* phenyl carbon), 128.7 (*meta* phenyl carbon), 131.7 (*ortho* phenyl carbon), 152.1 (α acetylenic carbon). IR (Nujol, cm^{-1}) 2083 ($C{\equiv}C$ stretch). UV–vis (toluene, nm) 358 (sh), 322, 286.

Preparation of $Cp_2Ti(C{\equiv}C\phi)Cl$

The first attempt at preparation of this complex involved treating Cp_2TiCl_2 with one equivalent of sodium phenylacetylide. This procedure led to mixtures of the dichloride, the monoacetylide and the diacetylide. The second attempt employed a reaction reported by Erker[21] for mono-substituted Zr acetylide complexes. In this method, 1 equivalent of the Cp_2TiCl_2 and 1 equivalent of the $Cp_2Ti(C{\equiv}C\phi)_2$ were stirred together in diethyl ether for several hours. Only starting materials were isolated from the reaction mixture.

$Cp_2Ti(C{\equiv}C\phi)Cl$ was successfully prepared by first dissolving $Cp_2Ti(C{\equiv}C\phi)_2$ (0.26 g, 0.69 mmol) in a minimum amount of THF (*ca* 15 cm^3). HCl (1 M in diethyl ether, 0.7 cm^3) was diluted in THF and slowly dropped into the flask of the Ti complex at 0°C over 15 min. This solution was stirred for 1/2 h at 0°C, and then the THF was removed. The red solid was then dissolved in toluene. Hexane was layered on top and allowed to slowly diffuse into the toluene solution. Crystals began to form slowly. This flask was cooled to −15°C to try to obtain more crystals. The solution was filtered and the red crystals were dried. The compound was obtained in 70% yield. This compound does not retain toluene upon crystallization. NMR (C_6D_6, ppm) δ 5.94 (s, 10H, Cp-H), 6.92–7.03 (m, 3H, *meta* and *para* phenyl protons), 7.41 (d, $^3J_{H-H}$ 7.43 Hz, 2H, *ortho* phenyl protons). ^{13}C NMR (CD_2Cl_2, ppm) δ 117.0 (Cp), 125.9 (*ipso* phenyl carbon), 127.7 (*para* phenyl carbon), 128.8 (*meta* phenyl carbon), 130.9 (α acetylenic carbon), 131.2 (*ortho* phenyl carbon), 147.9 (β acetylenic carbon). IR (KBr, cm^{-1}) 2068 ($C{\equiv}C$ stretch). UV–vis (toluene, nm) 506, 434 (sh), 404, 334 (sh), 282. MS (*m/z*) found 314.0, 278.0, 248.0, 213.0, 183.0, 148.0, 102.0, calc. 314.0 (M^+).

$Cp_2Ti(C{\equiv}Cbutyl)_2$

Cp_2TiCl_2 (1.25 g, 5 mmol) and sodium butylacetylide (1.1 g, 10.5 mmol) were stirred in 40 cm^3 ethyl ether for 5 h. This solution was filtered and concentrated. Pentane was added and cooled to −78°C. An orange solid formed. This solid was redissolved in 30 cm^3 ethyl ether and 20 cm^3 pentane and recrystallized at −78°C. An orange solid was collected in 50% yield. NMR (C_6D_6, ppm) δ 0.81 (t, 3H, CH_3), 1.33–1.39 (m, 4H, CH_2-CH_2-methyl), 2.27 (t, 2H, $C{\equiv}CCH_2$-propyl), 6.06 (s, 10H, Cp-H). IR (KBr, cm^{-1}) 2083 ($C{\equiv}C$ stretch), 3083, 2929, 1442, 1020, 816. This compound decomposes upon standing in an inert atmosphere to a green compound in the dark and also upon photolysis.

Preparation of $Cp_2Zr(CH{=}CH\text{-}4\text{-}CH_3\text{-}C_6H_4)Cl$

NMR (C_6D_6, ppm) δ 7.76 (d, $^3J_{H-H}$ 18.81 Hz, 1H, α-vinyl proton), 7.34, 7.07 (d, 4H, phenyl protons), 6.94 (d, 1H, β-vinyl proton), 5.83 (s, 10H, Cp-H), (s, 3H, CH_3 ϕ). ^{13}C NMR (C_6D_6, ppm) δ 176.7

(α-vinyl carbon, $^1J_{C-H}$ 122.3 Hz), 141.2 (β-vinyl carbon, $^1J_{C-H}$ 151.1 Hz), 137.5 (*ipso* phenyl carbon), 136.4 (*para* phenyl carbon), 129.6 (*meta* phenyl carbon), 126.4 (*ortho* phenyl carbon), 113.0 (Cp carbons), 21.2 (methyl carbon). UV–vis (toluene, nm) 356, 286.

Preparation of $Cp_2(Cl)ZrCH{=}CH\text{-}1,4C_6H_4CH{=}CHZr(Cl)Cp_2$, *para-*Zr *dimer*

NMR (C_6D_6, ppm) δ 7.79 (d, $^3J_{H-H}$ 18.2 Hz, 1H, α-vinyl protons), 7.43 (s, 2H, phenyl protons), δ 6.95 (d, $3J_{H-H}$ 18.2 Hz, 1H, β-vinyl protons), 5.77 (s, 10H, Cp protons). ^{13}C NMR (THF-d_8, ppm) δ 178.4 (α-vinyl carbon), 141.6 (β-vinyl carbon), 138.7 (*ipso* phenyl carbon), 126.6 (*ortho* phenyl carbon), 114.0 (Cp carbon). This compound was not soluble enough to obtain a ^{13}C coupled spectrum. UV–vis (toluene, nm) 380, 304.

Preparation of $Cp_2(Cl)ZrCH{=}CH\text{-}1,3\text{-}C_6H_4CH{=}CHZr(Cl)Cp_2$, *meta-*Zr *dimer*

NMR (C_6D_6, ppm) δ 7.88 (d, $^3J_{H-H}$ 19.1 Hz, 2H, α-vinyl protons), 7.70, 7.32 (2s, one is broad, 4H, phenyl protons), 7.05 (d, 2H, β-vinyl protons), 5.83 (s, 20H, Cp-H). ^{13}C NMR (CD_2Cl_2, ppm) δ 178.3 (α-vinyl carbon, $^1J_{C-H}$ 123.3 Hz), 141.5 (β-vinyl carbon, $^1J_{C-H}$ 150.1 Hz), 140.5 (*ipso* phenyl carbon), 128.8, 124.7, 124.5 (phenyl carbons), 114.0 (Cp carbons). UV–vis (toluene, nm) 356, 296.

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Supplementary Materials for Third Order Nonlinear Optical Properties of Group 4 *Metallocenes*—Description of data collection and refinement, tables of crystallographic data, three figures indicating atom numbering scheme, tables of atom positions, bond lengths and pertinent bond angles for $Cp'_2Ti(C{\equiv}C\phi)_2$ (16 pages).

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