New organometallic solids

Malcolm L.H. Green[*], Jingui Qin[+], Dermot O'Hare, Heather E. Bunting,
Mark E. Thompson[s], Seth R. Marder[&], and Kalyan Chatakondu.

Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, U.K.

<u>Abstract</u> A series of salts of stoichiometry $[C_n^{x+}][A_m^{x-}]$, where A and C represent redox-active cluster cations and anions have been prepared. These compounds which we call "soft salts", have been studied with a long term view of obtaining examples in which the charge x is non-integral. The synthesis and bulk properties of new organometallic intercalation compounds such as $[MoO_3\{Fe_4(\eta\text{-}C_5H_5)_4(\mu\text{-}S)_4\}_{0.15}]$ are reported. Finally, the synthesis of organometallic compounds with large non-linear optical properties will be described. The compound {(cis)-[1-ferrocenyl-2-(4-nitrophenyl)ethylene]} has been shown to have the ability for second harmonic generation (S.H.G.) which is 62 times that of urea.

INTRODUCTION

The last twenty years have witnessed many often unexpected discoveries of new materials with interesting and potentially useful properties. For example the metallic properties of $(SN)_x$ (ref. 1), the second harmonic generation and waveguiding properties of $KTiOPO_4$ (KTP) (ref. 2), the classic organic metal [TTF][TCNQ] (ref. 3), (TTF = tetrathiofulvalene; TCNQ = tetracyano-quinodimethane), and $[TMTSF]_2ClO_4$ (TMTSF=tetramethyltetraselena-fulvalene) the first zero-pressure organic superconductor (ref. 4).

During this period, organotransition metal chemistry has been one of the fastest developing areas of chemistry. There has been, however, relatively little study of the solid state properties of organometallic compounds.

ORGANOMETALLIC CHARGE-TRANSFER SALTS

Many organometallic cluster compounds can undergo multiple and reversible redox reactions forming stable cations or anions. For example, the compound $[Fe_4(NO)_4(\mu^3\text{-}S)_4]^n$, can add up to two electrons giving anions where n = -1 or -2, whilst the compounds $[M_4(\eta\text{-}C_5H_4R)_4(\mu^3\text{-}S)_4]^n$, n = 0, can form cations where n = +1 or +2 for M = Cr, Mo.

Charge transfer salts formed by reaction of these cubane clusters with organic poly-cyano acceptors have been prepared. Table 1 summarises the physical data obtained for these materials. The conductivity of these materials all show activated semiconductor behavior.

TABLE 1. Conductivity and magnetic data on some charge transfer salts.

Compound	$\sigma_{300}/\Omega^{-1}\,cm^{-1}$	μ_{eff}	Θ
$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}S)_4][TCNQ]_2$	2.3×10^{-6}	2.53	-2.26
$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}S)_4][TCNE]$	5.5×10^{-6}	2.57	-3.8
$[Fe_4(\eta\text{-}C_5H_5)_4(\mu^3\text{-}S)_4][TCNQ]$	4.4×10^{-5}	---	---
$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu^3\text{-}S)_4]_2[TCNQ]$	4.9×10^{-8}	2.79	-8.0
$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}Se)_4][TCNQ]$	-----	2.15	-1.33

[*] To whom correspondence should be addressed.

[+] Present address: Department of Chemistry, Wuhan University, Wuhan, Hubei, People's Republic of China.

[s] Present address: Department of Chemistry, Princeton University, Princeton, New Jersey, 08544,USA.

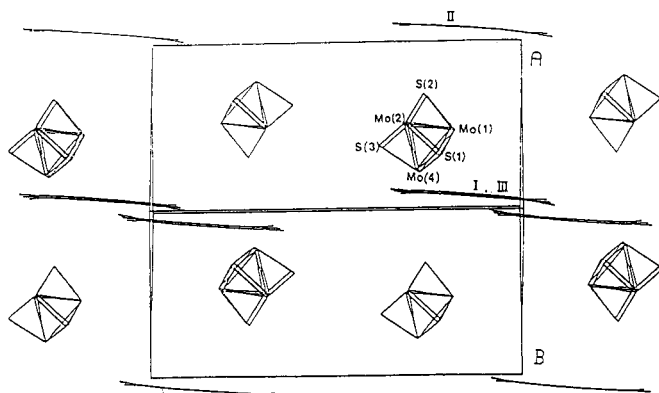[&] Present address: Department of Chemistry, California Institute of Technology, Pasadena, California, 91125, USA.

Fig. 1. Molecular packing of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu^3\text{-}S_4)]^+[TCNQ]^-$. The iso-propyl-cyclopentadienyl ligands have been omitted for clarity.

In particular the X-ray structure of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu^3\text{-}S_4)]^+$ $[TCNQ]^-$ (Fig. 1) shows the TCNQ molecules to be arranged in ribbons, separated by cluster cations.

The high magnetic susceptibility shows the salt to be paramagnetic and corresponds to two independent unpaired electrons per formula unit. The material also shows weak antiferromagnetic behaviour with T_{Neel} *ca.* 12 K, suggesting there is a direct exchange interaction between the electrons on the TCNQ anion and cluster cation.

Also, we were interested to prepare and study the solid state properties of simple organometallic salts of the general formula $[C_n^{x+}][A_m^{x-}]$, where C indicates a cluster cation and A represents a cluster anion. We were interested, to discover whether the structures of such salts were well-described by simple electrostatic considerations and, given the availability of multiple redox states to both C and A, there is the interesting possibility that x could be non-integral.

The new cluster $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu^3\text{-}Se)_4]$ was prepared by treatment of $[Mo(\eta\text{-}C_5H_4Pr^i)(\mu\text{-}Cl)_2]_2$ with LiHSe. Further, we found convenient high yield routes to the synthesis of compounds $[Cr_4(\eta\text{-}C_5H_4R)_4(\mu^3\text{-}Se)_4]$, R = H, and Me, by treatment of the corresponding chromocene compounds in toluene with H_2Se. Soft salts were prepared by mixing equimolar toluene solutions of the neutral clusters. The reactions were immediate and the resulting precipitates were recrystallised from acetone. The new salts are detailed in Table 2 together with their physical properties. The characterising data indicate that these materials are best described as simple charge transfer salts. Magnetic susceptibility measurements show simple Curie-Weiss paramagnetism, and electrical conductivity measurements indicate semiconductor behaviour with activation energies <u>ca.</u> 0.5 eV (ref.21).

ORGANOMETALLIC INTERCALATION COMPOUNDS

Many layered solids including metal chalcogenides, oxides and phosphates may act as host lattices and react with a variety of guest atoms or molecules to give intercalation compounds in which the guest is inserted between the host layers. In a true intercalation compound, this insertion should be reversible and the host lattice should retain its structural integrity (ref. 6). The readily reversible formation of intercalation compounds and the modifications of the physical properties of the host on intercalation have made them natural candidates for electrochemical   d e v i c e s   a n d heterogeneous catalysts (ref. 7).

The cubane clusters $[M_4Cp'_4S_4]$ [Cp' = $(\eta\text{-}C_5H_4Me)$, M = Fe, Mo] have been inserted into oxidising hosts such as MoO_3 or FeOCl by direct thermal reaction (Fig. 3) (ref. 8). A representation of the structure of a <u>cluster bronze</u> is shown in Figure 3. Crystals of $[MoO_3\{Fe_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}S)_4\}_{0.15}]$ exhibit substantial conductivity of 0.6 $\overset{+}{-}$ Ω^{-1} cm^{-1} along the crystal axis, while the conductivity along the shortest axis (interlayer direction) is lower by two orders of magnitude.

Ferrocene will intercalate into the oxidising host FeOCl; (ref. 9) however, it will not intercalate into 1T TaS_2 or MoO_3. However, intercalation of organoamines and ammonia into layered compounds such as 2H TaS_2 and MoO_3 is well known (ref. 10). We correspondingly found that the amino-ferrocenes readily intercalate into MoO_3. The monoamino-ferrocenes form bi-layers, as indicated by the stoicheiometry and the large inter-layer separations (Fig. 4) (ref. 8).
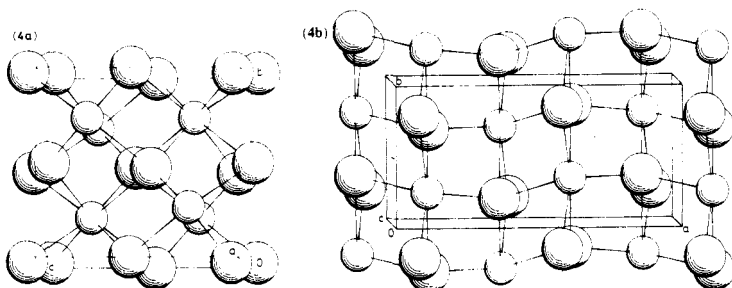
Fig. 2. Molecular packing of the "soft salt" $[Mo_4(\eta-C_5H_4Pr^i)_4(\mu^3-S)_4]^+_2[Os_6(CO)_{18}]^{2-}$ in its two alternative monoclinic forms (4a) and (4b). The larger spheres represent cations and the smaller anions.

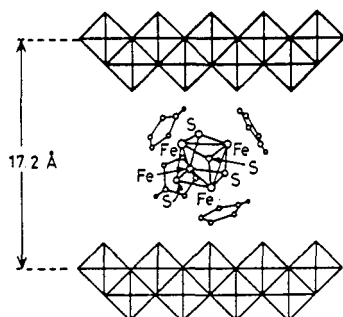Fig. 4. Representation of the intercalate $[MoO_3\{Fe(\eta-C_5H_4CH_2CH_2NH_2)(\eta-C_5H_5)\}_{0.65}]$

Fig. 3. Representation of the cluster bronze $[MoO_3\{Fe_4(\eta-C_5H_4Me)_4(\mu^3-S)_4\}_{0.13}]$

TABLE 2. Conductivity and Magnetic Data on some Soft Salts.

Compound	$\sigma_{300}/$ $\Omega^{-1}\,cm^{-1}$	μ_{eff}	Θ
$[Mo_4(\eta-C_5H_4Pr^i)_4(\mu^3-S)_4][Fe_4(NO)_4(\mu^3-S)_4]$	7.6×10^{-9}	2.48	-0.67
$[Fe_4(\eta-C_5H_5)_4(\mu^3-S)_4][Fe_4(NO)_4(\mu^3-S)_4]$	4.7×10^{-9}	--	--
$[Mo_4(\eta-C_5H_4Pr^i)_4(\mu^3-S)_4]_2[Os_6(CO)_{18}]$	---	2.73	-0.97
$[Cr_4(\eta-C_5H_4Me)_4(\mu^3-S)_4][Fe_4(NO)_4(\mu^3-S)_4]$	5.4×10^{-9}	--	--

We have found that ultrasound can greatly enhance the rate of many intercalation reactions, for example, the chemical synthesis of $[ZrS_2\{CoCp_2\}_{0.25}]$ requires 50 hours at 20 °C thermally whereas sonochemically it only requires 2 hours at 20 °C (ref. 11). Rate enhancements of up to 200 fold have been observed and may be associated with an increase of the host surface area. For example, when host solid suspensions are irradiated in an inert solvent and subsequently treated with the guest without any further sonication, the rate of intercalation is significantly enhanced compared with unsonicated host.

ORGANOMETALLIC NONLINEAR OPTICAL MATERIALS (NLO)

The development of new materials with large optical nonlinearities is an exciting discipline with applications in telecommunications, optical information processing and optical computering (ref. 12). Two important manifestations of light interacting with a nonlinear medium are the process of second harmonic generation (SHG) which is relevant to new laser technology, and the electro-optic effect which has applications in telecommunications and in integrated optics.

In comparison to the large effort focussed on the synthesis of organic compounds with large SHG efficiencies, little attention has been paid to organometallic compounds. Until recently, there have been only a few reports of organometallic compounds exhibiting second-order optical nonlinearities and the SHG efficiencies have been modest (ref. 13). The diversity of oxidation states as well as ligand environments of organometallic and coordination complexes can impart excellent acceptor or donor properties upon the metal centre. Further, the ligand sphere of organometallic and coordination complexes can often be easily varied in a systematic manner to give specific properties to the complex which may improve the electronic or crystallographic factors leading to very large coefficients of $X^{(2)}$. On this basis, we initiated an exploratory synthesis programme to prepare organometallic complexes exhibiting large second-order nonlinearities. Here we present results which suggest that complexes incorporating the well studied ferrocenyl moiety can undergo very efficient second harmonic generation as evidenced by the Kurtz powder test.

Deprotonation of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4)CH_2P(C_6H_5)_3)]^+$ I^-, (ref. 14) **1**, with n-butyllithium, followed by addition of 4-nitrobenzaldehyde, yielded dark purple crystals of (Z) - [1-ferrocenyl-2-(4-nitrophenyl)ethylene], (ref. 15) **2**, and the previously reported (E)-[1-ferrocenyl-2-(4-nitrophenyl)ethylene], **3**. Compound **2** was characterized by microanalysis and n.m.r. spectra which indicated the structure shown in Figure 5(a). The UV-visible spectrum of **2** was markedly affected by solvent. In heptane there were three absorptions at 320, 406, and 466nm, whereas in N,N-dimethylformamide there were only two absorptions at 340 and 492nm.

In view of this solvatochromic behaviour, (Z)-[1-ferrocenyl-2-(4-nitrophenyl)ethylene], **2**, was screened for SHG efficiencies using the Kurtz powder technique on unsized particles, using 1.907 µm light (ref. 16). This resulted in frequency doubled light at 0.953 µm which had an intensity 62 times that of the urea reference standard. The origin of this large nonlinearity may largely be due to disparate contributions of both canonical forms of (Z)-[1-ferrocenyl-2-(4-nitrophenyl)ethylene], **2**, shown in figure 5, to the ground and excited states of the molecule, leading to a large $\Delta(\mu_{gs} - \mu_{es})$, which is consistent with the observed solvatochromic behavior (Fig. 5).
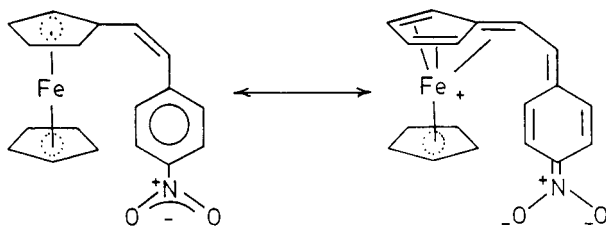

Fig. 5. Two canonical forms of (Z)-[1-ferrocenyl-2-(4-nitrophenyl)ethylene].

A single crystal X-ray diffraction study of **2** was performed on a crystal obtained from slow evaporation of a saturated solution of 2-propanol. Crystals of **2** obtained in this manner crystallize in the non-centrosymmetric space group F2dd. From the molecular packing diagram shown in Figure 6, it is clear that the molecular dipole of **2** will be preserved to a substantial extent in the crystalline material.
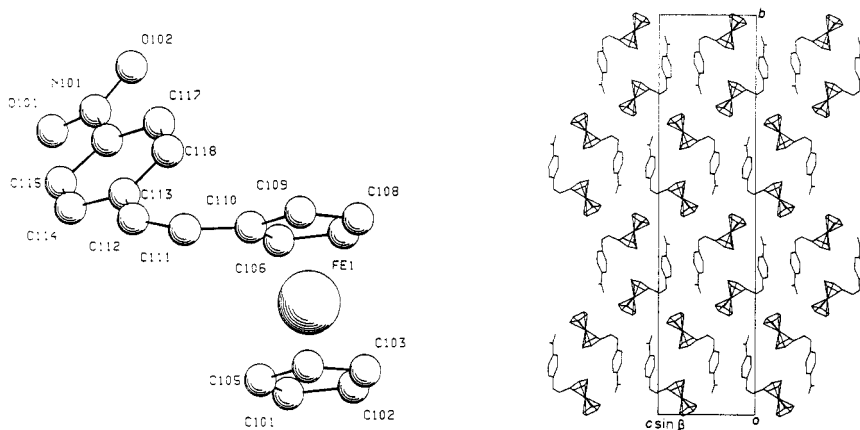

Fig. 6. Molecular structure of **2** with hydrogen atoms omitted for clarity.

To gain insight into the scope ferrocene complexes as nonlinear optical materials, we set out to synthesize a series of substituted ferrocenyl ethylene complexes. The complexes were prepared analogously to compound **2** via the route described by Pauson (Fig. 7) (ref. 14). As can be seen from Table 3, a variety of complexes can be prepared (ref. 17). Using a similar procedure, Toma et al. have prepared compounds **5** and **7** (ref. 17).

These compounds were also screened for SHG efficiencies by the Kurtz powder test and the results are summarized in Table 3. Although none of the complexes show SHG efficiencies of the order of **2**, several had efficiencies comparable to urea. Furthermore, over half of the compounds gave non-zero efficiencies. This result is encouraging in that it implies that this general class of compounds does not have an overriding propensity to crystallize in centrosymmetric space groups.

TABLE 3. The synthesis and SHG efficiencies of compounds of the form

$$Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4)CH=CHR.$$

R	Compound	Isomer	SHG [a,b]
-(p)-C$_6$H$_4$-NO$_2$	2	Z	62
-(p)-C$_6$H$_4$-NO$_2$	3	E	0
-(p)-C$_6$H$_4$-CN	4	Z	0.95
-(p)-C$_6$H$_4$-CN	5	E	0.87
-(p)-C$_6$H$_4$-CHO	6	Z	0
-(p)-C$_6$H$_4$-CHO	7	E	0.72
-(E)-CH=CH-(p)-C$_6$H$_4$-NO$_2$	8	Z	0
-(E)-CH=CH-(p)-C$_6$H$_4$-NO$_2$	9	E	0.04
-C=CH-CH=(NO$_2$)O	10	E	0.03

a All measurements were performed at 1.907 μm.
b The SHG signal is the magnitude of the signal at 0.953 μm for the compound of interest relative to a urea reference standard measured under the same conditions.

TABLE 4. The synthesis and SHG efficiencies of compounds of the form

$$(\underline{s})\text{-}Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_3CH_3)CH=CHR$$
$$(\ 82\%\ \underline{ee}\ of\ \text{"}\underline{s}\text{"}\ isomer).[14]$$

R	Compound	Isomer	SHG [a,b]
-(p)-C$_6$H$_4$-NO$_2$	13	E	8.0
-(p)-C$_6$H$_4$-CN	14	E	1.2
-(p)-C$_6$H$_4$-CHO	15	E	2.5
-(E)-CH=CH-(p)-C$_6$H$_4$-NO$_2$	16	E	6.4
-C=CH-CH=(NO$_2$)O	17	E	17.0

a All measurements were performed at 1.907 μm.
b The SHG signal is the magnitude of the signal at 0.953 μm for the compound of interest relative to a urea reference standard measured under the same conditions.
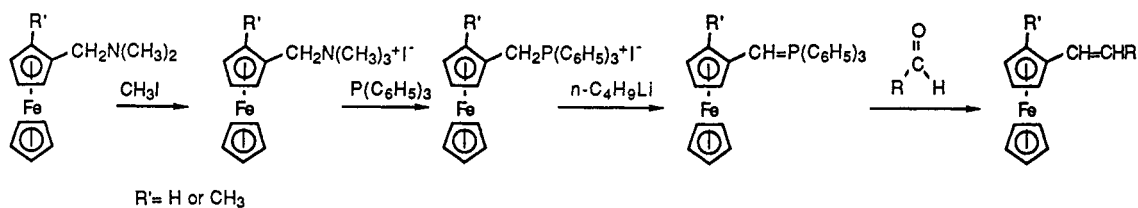

R'= H or CH$_3$

Fig. 7. General synthesis of ferrocenyl ethylene complexes.

We decided to introduce asymmetry and   optical activity in the molecules by substituting the cyclopentadienyl ring which contains the acceptor moiety with an additional methyl group.   It was our hope that by analogy to approaches used in organic systems, this would lead to a more desirable alignment of the molecular dipole in the crystal lattice.   Using a procedure developed by Sokolov, the compound (s)-Fe(η-C$_5$H$_5$)(η-C$_5$H$_3$CH$_3$)CH$_2$N(CH$_3$)$_2$, (ref. 18) **12**, was synthesized and carried on to a series of ferrocenyl ethylene complexes as shown in Figure 7.   Compound **12** was isolated in 82% enantiomeric excess (ee) as determined by n.m.r. spectra recorded with chiral shift reagents. Thus the ferrocenyl ethylene complexes isolated were assumed to be isolated in   82% ee, as racemization was not expected in this system.   The Z isomers were formed in much lower yields in this series of compounds as compared to the series of compound shown in Table 3.   As a result, only the E isomers have been screened for SHG efficiencies.   The results which are shown in table 4 (ref. 19) are very encouraging.   Every compound exhibited larger efficiencies than the analogous compound in Table 3.   Compound **17** for example has an SHG efficiency of over 500 times that of compound **10**.   Thus in the compounds described here we have attempted to engineer into the molecules both the desired electronic and crystallographic properties desirable for second-order optical nonlinearities.

In these preliminary studies we have demonstrated that organometallic compounds can have large optical nonlinearities.   Clearly, further synthetic, crystallographic and optical studies are needed if we are to fully understand and exploit the large optical nonlinearities of organometallic compounds.

CONCLUSION

The study of the solid state properties of materials based on organometallic compounds is at a very early stage of development.   Nonetheless, it is clear from observations such as the non-linear optical properties of the ferrocene derivatives, and from the electrical properties of the   cluster bronzes that materials based on organometallic compounds can give rise to bulk properties of not only academic interest, but also there is clearly the potential for materials with useful applications.

REFERENCES

1.   V.V. Walatka, M.M. Labes, J.H. Perlstein, Phys. Rev. Lett., 31, 1139 (1973).
2.   F.C. Zumsteg, J.D. Bierlein, T.E. Gier, J. Appl. Phys., 47, 4980 (1976).
3a. J. Ferraris, D.O. Cowan, V. Walatka,Jr., J.H. Perlstein, J. Am. Chem. Soc., 95, 948 (1973),
 b   L.B. Coleman, M.J. Cohen, D.J. Sandman, F.G.Yamagishi, A.F. Garito, A.J. Heeger, Solid State Commun., 12, 1125 (1973).
4.   K. Bechgaard, K. Carneiro, C.S. Jacobsen, M. Olsen, F.B. Rasmussen G. Rindorf, Physica B + C., 108, 1193 (1981).
5.   M.L.H. Green, A. Hamnett, J. Qin, P. Baird, J.A. Bandy, K. Prout, E. Marseglia and S.D. Obertell, J. Chem. Soc., Chem Commun., 1811 (1987).
6.   Intercalation Chemistry, Ed. M.S. Whittingham, A.J. Jacobnson, Academic Press, New York, (1982).
7.   M.S. Whittingham, L.B. Ebert, in Intercalated Layered Materials, Ed. F. Levy, D. Reidel, Dodrecht, (1979), p.533.
8.   K. Chatakondu, M.L.H. Green, J Qin, M.E. Thompson, and P.J. Wiseman, J. Chem. Soc., Chem Commun., 223 (1988).
9a. T.R. Halbert and J. Scanlon, Mater. Res. Bull., 14, 415 (1979).
 b   H. Schafer-Stahl, and R. Abele, Angew Chem Int Ed Engl., 19, 477 (1980).
 c   H. Schafer-Stahl and R. Abele, Mater Res. Bull., 15, 1157, (1980).
10a. F.R. Gamble, J.M. Osieki, M. Cais, R. Pisharody, F. J. Disalio, and T.H. Geballe, Science, 174, 493 (1971).
  b P.G. Dickens and S.J. Hibble, Solid State Ionics., 22, 69, (1986).
11. K. Chatakondu, M.L.H. Green, M.E. Thompson, K.S. Suslick, J. Chem. Soc., Chem Commun, 900 (1987).
12a. D.J. Williams, Angew. Chem. Int. Ed. Engl., 23, 690 (1984).
  b D.J. Williams, Nonlinear Optical Properties of Organic and Polymeric Materials, ACS Symp. Ser., 233, American Chemical Society, Washington, 1983.
  c D.S. Chemla and J. Zyss, Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, Orlando, 1987, Volumes 1 and 2.
13a. C.C. Frazier, M.A. Harvey, M.P. Cockerham, E.A. Chauchard andC.H. Lee, J. Phys. Chem., 90, 5703 (1986).
  b D.F. Eaton, A.G. Anderson, W. Tam and Y. Yang, J. Amer. Chem.Soc., 109, 1886 (1987).
  c J.C. Calabrese and W. Tam, Chem. Phys. Letters, 133, 245 (1987).
14. P.L. Pauson and W.E. Watts, J. Chem. Soc., 2990 (1963).
15. M.L.H. Green, S.R. Marder, M.E. Thompson, J.A. Bandy, D. Bloor, P.V. Kolinsky and R.J. Jones, Nature, 330, 360 (1987).
16. S.K. Kurtz and T.T. Perry, J. Appl. Phys., 39, 3798 (1968).
17. M.L.H. Green, S.R. Marder, D. Bloor, M.E. Thompson, P.V.Kolinsky and R.J. Jones, J. Organomet. Chem., submitted for publication.
18. S. Toma, A. Gaplovsky and P. Elecko, Chem. Papers, 39, 115 (1985).
19. V.I. Sokolov, L.L. Troitskaya and O.A. Reutov, J. Organomet.Chem., 182, 537 (1979).
20. H.E. Bunting, M.L.H. Green, S.R. Marder, D. Bloor, P.V. Kolinsky and R.J. Jones, to be submitted to J. Chem. Soc., Chem. Commun, (1988).