Applied Organometallic Chemistry (1988) 2 9–15

0268–2605/88/02010009

Complexes in polymers II:* FT-IR spectra, iodine oxidation, and photochemistry of $[(\eta^5\text{-}C_5H)Fe(CO)_2]_2$, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ and $Mn_2(CO)_{10}$ in polystyrene, poly(methyl methacrylate) and polystyrene–polyacrylonitrile copolymer

Alan Shaver,[†] Jian Ping Gao and Ian S Butler[†]
Department of Chemistry, McGill University, 801 Sherbrooke St West, Montreal, Quebec, Canada, H3A 2K6

Received 14 September 1987 Accepted 16 November 1987

The infrared spectra of $[CpFe(CO)_2]_2$, $[CpMo(CO)_3]_2$ and $Mn_2(CO)_{10}$ ($Cp = \eta\text{-}C_5H_5$) embedded in films of polystyrene (PS), poly(methyl methacrylate) (PMMA), and polystyrene–polyacrylonitrile (PS–AN), are comparable with those of the dimers in toluene, ethyl acetate and acetonitrile, respectively. Irradiation of the embedded dimers with UV light led to decomposition in PS and PMMA, while in PS–AN the complexes $Cp_2Fe_2(CO)_3$PS–AN and $Mn_2(CO)_9$PS–AN were formed, wherein a pendant nitrile group is coordinated to one of the metal atoms. Exposure of the embedded dimers to iodine vapour gave $CpFe(CO)_2I$, $CpMo(CO)_3I$ and $Mn(CO)_5I$ with the reaction being much slower in PMMA than in PS.

Keywords: Organometallic compounds, polymers, FT-IR spectroscopy, photochemistry, oxidation, films

INTRODUCTION

Recently there has been growing interest in the properties of organometallic compounds embedded in polymers.[1] Such materials are potentially useful commercially[2] and have also been used as matrices for spectroscopic studies of metal carbonyls[3] and for investigating the mechanical spectra of organometallic complexes.[4] Earlier,[1] we described a general method for generating films of polystyrene (PS), poly(methyl methacrylate) (PMMA) and polystyrene–polyacrylonitrile (PS–AN) copolymer containing an organometallic complex. The infrared spectra in the ν(CO) stretching region for a number of monomeric metal carbonyl complexes in these films were investigated as well as their photochemistry.[1] In the present paper we report the infrared spectra in the ν(CO) region of the complexes $[CpFe(CO)_2]_2$, $[CpMo(CO)_3]_2$ and $Mn_2(CO)_{10}$ embedded in PS, PMMA and PS–AN, where $Cp = \eta^5\text{-}C_5H_5$, and their photochemistry. In addition the oxidation of the dimers in the films by iodine has been monitored by infrared spectroscopy and is highly dependent on the polymer.

EXPERIMENTAL

The dimers $[CpFe(CO)_2]_2$, $[CpMo(CO)_3]_2$ and $Mn_2(CO)_{10}$ were purchased from Strem Chemicals while the polymers PS, PMMA and PS–AN (75%:25%) were supplied by Polysciences. Films containing the embedded dimers were prepared as described previously.[1] Briefly, the polymer (1 g) and the complex (about 0.05 g) were dissolved in benzene under a nitrogen atmosphere and then the solvent was removed by freeze-drying. The fluffy residue was pressed (3000 psi; 21×10^3 k Pa) at 120°C for 30 min. to give the films upon cooling. FT-IR spectra were recorded on a Nicolet model 6000 spectrometer

---

*For Part I, see Ref. 1.

[†] Authors to whom correspondence should be addressed.

at 1 cm^{-1} resolution using a liquid-nitrogen cooled mercury–cadmium–telluride detector.

The iodine oxidation reactions were performed at ambient temperature on thin films of comparable thickness (usually about 0.05 mm); thick films (0.11 mm) were also employed for the iron dimer. The films were attached to plastic IR mounts by means of 'Scotch' tape and then placed in screwtop jars (280 cm^3 capacity) containing 4.6 g of pulverized iodine. The oxidations were monitored daily by FT-IR spectroscopy over a 10-day period.

The photochemical studies were conducted using a medium-pressure quartz mercury immersion lamp (Hanovia 450 W) in a water-cooled quartz photochemical immersion cell. The film samples, attached to IR-spectrometer sample holders, were clamped about 5 cm from the lamp and cooled by means of a jet of nitrogen gas. Irradiation with wavelengths above 310 nm only was achieved using a Pyrex filter.

RESULTS AND DISCUSSION

IR spectra

The infrared spectra of the polymers reveal an IR-window in the region where metal-carbonyl ν(CO) bands are observed. Even the strong band due to PMMA centered at 1720–1750 cm^{-1} did not interfere with the bands due to the bridging CO ligands in $[CpFe(CO)_2]_2$. Table 1 lists the observed peak positions for the ν(CO) bands of the dimers in the three polymer films and also in three organic solvents selected because of their similarity to one of the polymers.

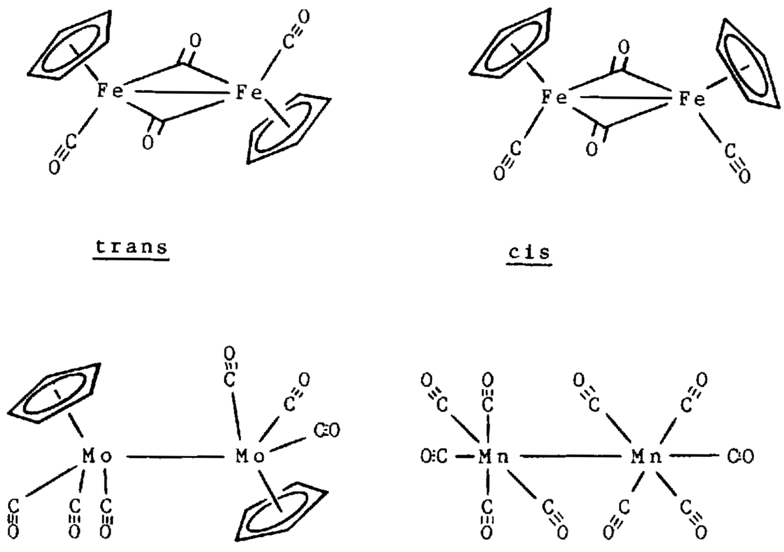
$[CpFe(CO)_2]_2$ exists in solution at room temperature as an equilibrium mixture of *cis* (C_{2v}) and *trans* (C_{2h}) isomers (Scheme 1); the barrier to interconversion is in the order of 40 kJ mol^{-1}.[5] Polar solvents favour the *cis* geometry. The *trans* stereochemistry of our sample was confirmed by its IR spectrum in KBr[6] which gave two wide bands at 1950 and 1770 cm^{-1}, both split into two peaks. The spectra in the polymers show two terminal ν(CO) bands; one around 1990 cm^{-1} due to the a_1 mode of the *cis* isomer, the other around 1950 cm^{-1} due to the b_u mode of the *trans* isomer, together with a bridging ν(CO) band at 1774 cm^{-1} (Fig. 1). This is consistent with the existence of both *cis* and *trans* isomers as observed in solution. Similarly the *cis*/*trans* ratio increased in the order PS < PMMA < PS–AN, consistent with the increasing polarity of these films.

$[CpMo(CO)_3]_2$ has C_{2h} symmetry (staggered *trans*, Scheme 1) for which three IR-active ν(CO) modes ($a_u + 2b_u$) are predicted,[7] although usually only two bands (II, III) are observed in solution with the lower-energy band (III) being broad and resolvable into two components in hydrocarbon solvents and nujol. In polar solvents another band (I) at higher energy is observed which has been attributed to the presence of non-centrosymmetric rotamers.[8] In the polymer films two strong bands (II, III) are observed together with band I. Band III is broad in PMMA and PS–

Table 1 Observed carbonyl stretching modes of $[CpFe(CO)_2]_2$, $[CpMo(CO)_3]_2$ and $Mn_2(CO)_{10}$ in different media (cm^{-1})

	Medium						
	PS	Toluene	PMMA	Ethyl acetate	PS–AN	Acetonitrile	Assignment
$[CpFe(CO)_2]_2$	1996(s)	1997(s)	1993(s)	1995(s)	1992(s)	1992(s)	a_1 (*cis*)
	1953(m)	1953(s)	1952(m)	1954(m)	1950(m)	1952(w)	b_u (trans)
	1782(vs)	1783(vs)	1782(s)	1783(s)	1777(s)	1775(s)	a_u, b_1 (bridging)
$[CpMo(CO)_3]_2$	2013(vw)	2015(vw)	2011(m)	2013(w)	2010(m)	2011(m)	I[a]
	1955(s)	1956(s)	1956(s)	1958(s)	1957(s)	1957(s)	II[a]
	1903(s)	1912(s)	1911(s)	1914(s)	1910(s)	1911(s)	III[a]
	1888(s)						
$Mn_2(CO)_{10}$	2044(s)	2046(m)	2043(s)	2047(m)	2044(m)	2047(m)	b_2
	2008(vs, br)	2010(s)	2010(sh)	2011(s)	2008(vs, br)	2011(s)	e_1
	1981(m)	1981(w)	2000(vs, br)	1982(w)	1983(w)	1981(w)	b_2

[a] No vibrational assignments have been proposed for these peaks.



Scheme 1

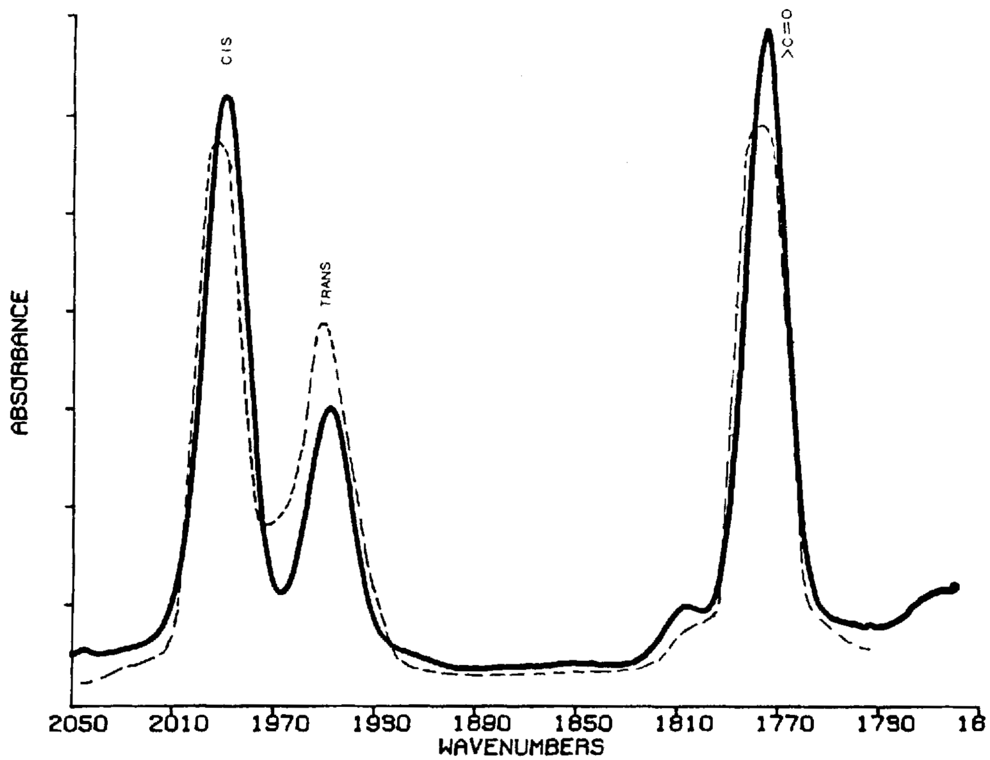


Figure 1 The infrared spectrum in the ν(CO) region of $[CpFe(CO)_2]_2$ in PS (---) and in PS–AN (——) showing the effect of the polymer on the relative amounts of the *cis* and *trans* isomers (absorbance on an arbitrary scale).

AN, and split into a doublet in PS. The intensity of the highest energy band (I) decreases in the order PS–AN > PMMA > PS, consistent with the solution studies.

The molecular symmetry of $Mn_2(CO)_{10}$ is D_{4d}[9] (Scheme 1) and three IR-active $\nu(CO)$ modes $(2b_2 + e_1)$ are expected. The peak positions in the three polymer films and the solvents show little variation except for the band at 2010–2000 cm^{-1} in PMMA which is quite broad, consistent with significant polymer–solute interaction.

Photochemistry

The UV spectra of the pure polymer films gave no significant absorption above 300 nm. The IR spectra of the pure PS–AN film was unchanged following UV irradiation (Pyrex filter) for 30 min. The dimer-containing films were also irradiated and their IR spectra monitored. The peaks due to the dimers in PS and PMMA gradually decreased in intensity and no new $\nu(CO)$ bands were detected. The bands due to the *cis* and *trans* isomers of $[CpFe(CO)_2]_2$ and their bridging carbonyl ligands all appeared to decrease in intensity at approximately the same rate. The decrease in intensity was much slower in PMMA than in PS for all three dimers (Table 2). The peaks due to $[CpMo(CO)_3]_2$ in PS–AN gradually diminished with no significant new peaks appearing. However, strong new peaks were observed for both $[CpFe(CO)_2]_2$ and $Mn_2(CO)_{10}$ in PS–AN (Fig. 2 and Fig. 3, respectively). In the case of the iron dimer these appeared at 1935 and 1744 cm^{-1}. A parallel experiment in acetonitrile (CH_3CN) gave similar spectral changes, consistent with the formulation of the new species in PS–AN as the monosubstituted dimer,[10] $Cp_2Fe_2(CO)_3$PS–AN, wherein a pendant nitrile ligand coordinates to one of the iron atoms. The irradiated PS–AN film containing $Mn_2(CO)_{10}$ was dissolved in toluene and precipitated with ethanol. The IR spectrum (Fig. 3) of the precipitated polymer was free of peaks due to $Mn_2(CO)_{10}$, which permitted the observation of the new bands at 2090(w), 2023(s), 1990–1981(s, br) and 1957–1944(s, br) cm^{-1}. These agree reasonably well with those reported[11] for eq-$Mn_2(CO)_9NCCH_3$ and are thus assigned to its PS–AN analog. A similar attempt to isolate $Cp_2Fe_2(CO)_3$PS–AN gave precipitated polymer with no $\nu(CO)$ bands in its IR spectrum, presumably due to instability of the complex.

The photochemistry of the iron,[12] molybdenum[13] and manganese[14] dimers has been studied intensively. There are two major processes: reversible metal–metal bond scission and reversible CO dissociation. In PS, photogenerated CO would diffuse out of the film[1] leaving coordinatively-unsaturated intermediates which would be expected to be unstable under the reaction conditions (room temperature, continued irradiation) and in the absence of stabilizing donors. Such a process would lead to the gradual decrease in intensity observed.

Table 2 Consumption of metal carbonyl starting material (as percentage) by photoreaction and iodine oxidation as a function of polymer and film thickness (mm)

		Photoreaction[a]		Iodine oxidation[b]	
Complex	Polymer	Thickness (mm)	Reaction (%)	Thickness (mm)	Reaction (%)
$[CpFe(CO)_2]_2$	PS	0.06	70	0.05	100
		0.11	25–35	0.11	20–30
	PMMA	0.06	10	0.05	0–5
	PS–AN	0.10	10	0.09	20–30
$[CpMo(CO)_3]_2$	PS	0.06	25	0.05	90–95
	PMMA	0.06	0–5	0.05	0–5
	PS–AN	0.06	30	0.08	20–30
$Mn_2(CO)_{10}$	PS	0.06	100	0.05	50–60
	PMMA	0.06	5–10	0.05	0–5
	PS–AN	0.07	70–80	0.06	20–30

[a] After irradiation for 30 min. [b] After exposure to iodine vapour for 10 days.

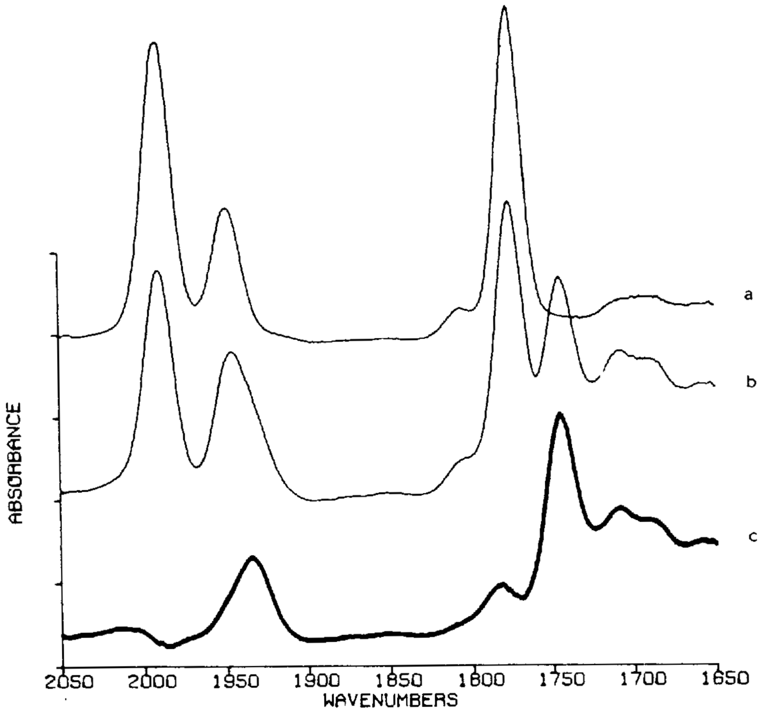


Figure 2 The infrared spectra in the ν(CO) region of $[\mathrm{CpFe(CO)_2}]_2$ in PS–AN: a, before irradiation; b, after irradiation for 4 h; c, spectrum a subtracted from spectrum b.

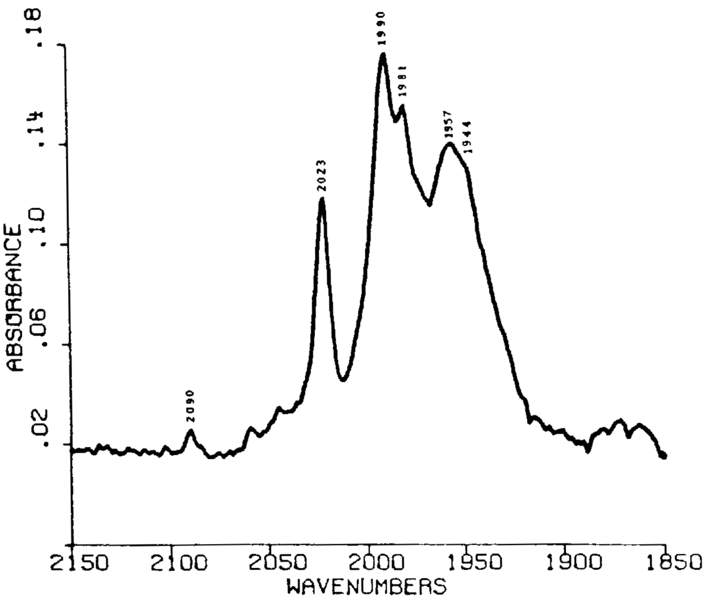


Figure 3 The infrared spectrum in the ν(CO) region of eq-$\mathrm{Mn_2(CO)_9}$PS–AN in PS–AN.

PMMA is much less permeable[15] than PS; thus the relatively slow photodecomposition of the dimers embedded in PMMA is consistent. The pendant nitrile groups in PS–AN can scavenge the photogenerated intermediates[1] leading to the observed products for the iron and manganese dimers. The failure to detect analogous products for the molybdenum case is of interest in view of the photochemical preparation of complexes such as $Cp_2Mo_2(CO)_5P(C_6H_5)_3$; however, the photochemistry of $[CpMo(CO)_3]_2$ is very sensitive to reaction conditions.[13a]

Oxidation by iodine

The pure polymer films and those containing the dimers were exposed to iodine vapour in sealed jars for 10 days and their IR spectra were monitored. No significant change in the spectra of the three pure polymer films was observed. $[CpFe(CO)_2]_2$ in PS reacted rapidly (one day) as evidenced by the appearance of a new ν(CO) band at 2030 cm^{-1} and an increase in intensity of the band at 1996 cm^{-1}, together with a concomitant decrease in intensities of the other bands due to the parent complex. After 10 days the spectrum of the deep brown coloured film gave only two bands (2044 and 2003 cm^{-1}) assigned[17] to $CpFe(CO)_2I$ (Eqn [1]).

$$[CpFe(CO)_2]_2 + I_2 \rightarrow 2CpFe(CO)_2I \quad [1]$$

$$[CpMo(CO)_3]_2 + I_2 \rightarrow 2CpMo(CO)_3I \quad [2]$$

$$Mn_2(CO)_{10} + I_2 \rightarrow 2Mn(CO)_5I \quad [3]$$

$[CpMo(CO)_3]_2$ behaves similarly in PS with a new peak appearing at 2038 cm^{-1} after one day, which reaches its maximum intensity after five days, during which time the peaks of the parent complex had greatly diminished revealing additional new peaks at 1961 and 1939 cm^{-1} consistent with the formation of $CpMo(CO)_3I$[17] (Eqn [2]). After 10 days' exposure, however, no ν(CO) peaks were detected, which suggests that further reaction occurred to give products containing no CO ligands. The final bands observed for $Mn_2(CO)_{10}$ in PS (2128(m), 2045(s) and 2008(s) cm^{-1}) are in excellent agreement for those of $Mn(CO)_5I$[18] (Eqn [3]).

The oxidation took place more slowly in thick PS films than in thin PS films and they were slower still in PS–AN (Table 2). However, virtually no oxidation occurred in the PMMA films during the 10-day period. Presumably these differences are related to the rate of diffusion of iodine in the films and illustrate the importance of the microstructure of the polymers.

CONCLUSIONS

The three polymers afford chemical environments similar to the appropriate solvents with respect to the ν(CO) bands of the three dimers in the infrared. PS–AN is capable of stabilizing photogenerated intermediates by means of coordination of a pendant nitrile group. The iodine reaction in PS demonstrates an additional method of transforming organometallic complexes embedded in a plastic substance. Finally the photochemical and oxidation reactions indicate that PMMA films offer a more protective environment for these dimers than PS or PS–AN.

The iodine reaction suggests that organometallics might be useful as indicators of gas permeability in various polymers. This is an important consideration in the food and drug industry as well as for soft contact lenses. Thus, a new method to measure gas permeability can be envisaged wherein a suitable complex, embedded in a plastic, would be exposed to an appropriate gas and the subsequent reaction monitored spectrophotometrically over time. Since the embedding process is conducted before final fabrication of the plastic, the effect of shape and thickness of the article on its gas permeability could easily be determined. The efficiency of barrier films could be determined by monitoring the rate of reaction of a complex embedded in a film of PS covered by the barrier material. Many organometallics undergo reversible thermal and photochemical reactions; therefore reversible indicators should be possible. Finally it should not escape notice that the electrical properties of conducting polymers can sometimes be modified by doping with gaseous iodine.[19]

Acknowledgements The authors acknowledge and thank Dr Adi Eisenberg for helpful discussion. This research was supported by operating and equipment grants from NSERC (Canada) and FCAR (Quebec). JPG thanks McGill University for the award of a Max Bindra graduate fellowship.

REFERENCES

1. Shaver, A, Butler, I S, Eisenberg, A, Gao, J P, Xu, Z H, Fong, B, Uhm, H and Klein, D *Appl. Organomet. Chem.*, 1987, 1: 383
2. Reference 1 and references therein
3. (a) De Paoli, M A *J. Macromol. Sci.—Chem.*, 1981, A16: 251; (b) Hitam, R B, Hooker, R H, Mahmoud, K A, Narayanaswamy, R and Rest, A J *J. Organomet. Chem.*, 1981, 222: C9; (c) Hooker, R H and Rest, A J *J. Organomet. Chem.*, 1983, 249: 137
4. (a) Eisenberg, A, Shaver, A and Tsutsui, T *J. Am. Chem. Soc.* 1980, 102: 1416; (b) Shaver, A, Eisenberg, A, Yamada, K, Clark, A J F and Farrokyzad, S *Inorg. Chem.*, 1983, 22: 4154
5. Bullitt, J G, Cotton, F A and Marks, T J *Inorg. Chem.*, 1972, 11: 671 and references therein
6. Manning, A R *J. Chem. Soc. (A)*, 1968, 1319
7. Fischer, R D and Noack, K *J. Organometal. Chem.* 1969, 16: 125
8. Braterman, P S *Metal Carbonyl Spectra*, Academic Press, New York, 1975, p 85
9. Parker, D J and Stiddard, M H B *J. Chem. Soc. (A)*, 1966, 695
10. Haines, R J and DuPreez, A L *Inorg. Chem.*, 1969, 8: 1459
11. Ziegler, M L, Haas, H and Sheline, R K *J. Inorg. Nucl. Chem.*, 1962, 24: 1172; (b) Koelle, U *J. Organomet. Chem.*, 1978, 155: 53
12. (a) Goldman, A S and Tyler, D R *Inorg. Chem.*, 1987, 26: 253; (b) Blaha, J P, Bursten, B E, Dewan, J C, Frankel, R B, Randolf, C L, Wilson, B A and Wrighton, M S *J. Am. Chem. Soc.*, 1985, 107: 4561; (c) Hepp, A F, Blaha, J P, Lewis, C and Wrighton, M S *Organometallics*, 1984, 3: 174; (d) Tyler, D R, Schmidt, M A and Gray, H B *J. Am. Chem. Soc.*, 1983, 105: 6018; (e) Hooker, R H, Mahmoud, K A and Rest, A J *J. Chem. Soc., Chem. Commun.*, 1983, 1022; (f) Caspar, J V and Meyer, T J *J. Am. Chem. Soc.*, 1980, 102: 7794; (g) Abrahamson, H B, Palazzolto, M C, Reichel, C L and Wrighton, M S, *J. Am. Chem. Soc.*, 1979, 101: 4123
13. (a) Philbin, C E, Goldmand, A S and Tyler, D R *Inorg. Chem.*, 1986, 25: 4434; (b) Hooker, R H, Mahmoud, K A and Rest, A J *J. Organomet. Chem.*, 1983, 254: C25; (c) Wrighton, M S and Ginley, D S *J. Am. Chem. Soc.*, 1975, 97: 4246
14. (a) Hepp, A F and Wrighton, M S *J. Am. Chem. Soc.*, 1983, 105: 5934; (b) Rothberg, L J, Cooper, N J, Peters, K S and Vaida, V *J. Am. Chem. Soc.*, 1982, 104: 3536; (c) Wegman, R W, Olsen, R J, Gard, D R, Faulkner, L R and Brown, T L *J. Am. Chem. Soc.*, 1981, 103: 6089; (d) Fox, A and Poë, A *J. Am. Chem. Soc.*, 1980, 102: 2497; (e) Wrighton, M S and Ginley, D S *J. Am. Chem. Soc.*, 1975, 97: 2065
15. (a) Lee, W M *Organic Coatings and Plastics Chemistry, ACS Adv. Chem. Ser.*, 1978, 39: 341; (b) Salame, M *Polymer Prepr. (Am. Chem. Soc. Div. Polym. Chem.)*, 1967, 8: 137
16. Steigman, A E and Tyler, D R *J. Am. Chem. Soc.*, 1982, 104: 2944
17. Sloan, T E and Wojcicki, A *Inorg. Chem.*, 1968, 7: 1268
18. Kaesz, H D, Bau, R, Hendrickson, D and Smith, J M *J. Am. Chem. Soc.*, 1967, 89: 2844
19. (a) Chiang, C K, Fincher, C R, Jr, Par, Y W and Heeger, A J *Phys. Rev. Lett.*, 1977, 39: 1098; (b) Lerner, N R *Polymer*, 1983, 24: 800