4450 *Macromolecules* **1999,** *32,* 4450−4453

Photochemical Synthesis of Organometallic Oligomers of Defined Composition and Length

Helen A. Cruse and Nicholas E. Leadbeater*

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW

Received January 6, 1999

Revised Manuscript Received April 14, 1999

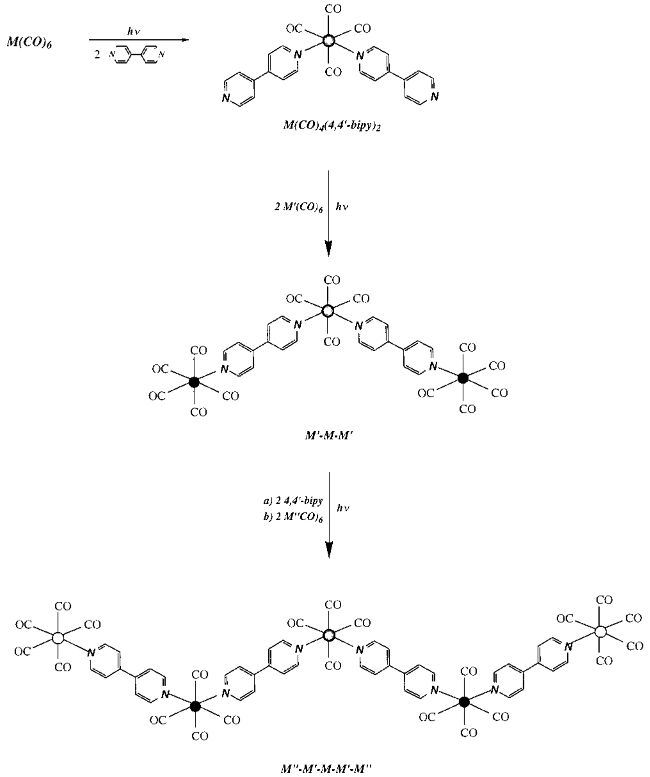
Introduction

The preparation and physical studies of conjugated organometallic complexes and polymers have been the subject of significant research recently because of the possible applications of these compounds to the materials industry.[1−3] Although a number of methodologies have been developed for the synthesis of organometallic oligomers and polymers,[4,5] there is still a need for a way of generating complexes of defined lengths and metal content in systems where ring-opening polymerization techniques are not appropriate.[6] In this note, we show how photochemistry can be used to prepare a number of conjugated organometallic oligomers, selectively, efficiently, and in high yield. Photochemistry offers a simple, and often highly selective, route to organometallic compounds, overcoming large enthalpy barriers. As a consequence, it is often possible to prepare complexes that are otherwise inaccessible by conventional thermochemical routes.[7] In addition, in many cases known complexes can be prepared far more efficiently and rapidly using photochemistry as compared to thermochemistry.[8] We report here the synthesis and characterization of a series of novel oligomeric organometallic complexes of the chromium triad.

Results and Discussion

Irradiation of a dichloromethane solution of $[\mathrm{M(CO)_6}]$ (M = Cr, Mo, W) and the ditopic, nonchelating ligand 4,4′-bipyridine (4,4′-bipy) in a 1:2 ratio leads to the cis-disubstituted complex $[\mathrm{M(CO)_4(4,4'\text{-}bipy)_2}]$ (**1**) (M = Cr, Mo, W) in 95% yield. Subsequent photolysis of $[\mathrm{M'(CO)_6}]$ (M′ = Cr, Mo, W) and **1** in a 2:1 ratio leads to the formation of the homometallic or heterometallic trimetallic complexes $[\mathrm{(CO)_5M'(4,4'\text{-}bipy)M(CO)_4(4,4'\text{-}bipy)M'(CO)_5}]$ (**2**), denoted as M′−M−M′, in between 75 and 85% yield. The organometallic chains can be extended by irradiating **2** with 4,4′-bipy in a 1:2 ratio and then with 2 equiv of $[\mathrm{M''(CO)_6}]$ (M″ = Cr, Mo, W) to yield the pentametallic species $[\mathrm{(CO)_5M''(4,4'\text{-}bipy)(CO)_4M'(4,4'\text{-}bipy)M(CO)_4(4,4'\text{-}bipy)M'(CO)_4(4,4'\text{-}bipy)M''(CO)_5}]$ (**3**) denoted as M″−M′−M−M′−M″. The synthesis of these complexes is shown in Scheme 1. This methodology leads to symmetrically substituted oligomers with an odd number of metal atoms. To prepare oligomers containing even numbers of metal atoms, it is necessary to start from either $[\mathrm{M(CO)_5(4,4'\text{-}bipy)}]$ or $([\mathrm{CO)_5M(4,4'\text{-}bipy)M(CO)_5}]$, both of which can be prepared photochemically by irradiation of a dichloromethane solution of $[\mathrm{M(CO)_6}]$ and 4,4′-bipy in either a 1:1 or 2:1 ratio, respectively. The photolysis of these complexes with further equivalents of metal and ligand then leads tothe formation of either symmetrical or asymmetrical oligomers containing up to four metal atoms such as $[\mathrm{(CO)_5M(4,4'\text{-}bipy)M'(CO)_4(4,4'\text{-}bipy)M(CO)_4(4,4'\text{-}bipy)M'(CO)_5}]$, denoted as M−M′−M−M′, and $[\mathrm{(CO)_5M(4,4'\text{-}bipy)M'(CO)_4(4,4'\text{-}bipy)M'(CO)_4(4,4'\text{-}bipy)M(CO)_5}]$, denoted as M−M′−M′−M. The synthesis of these complexes is shown in Schemes 2 and 3.

Scheme 1

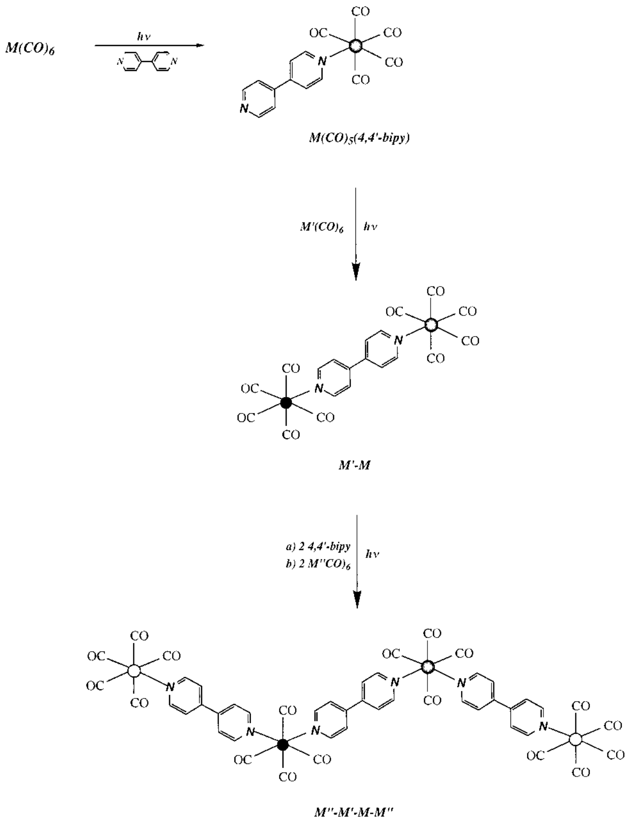


The significant advantages of using photochemistry over other methods are that the oligomers can be generated selectively and are of known composition. This means that future studies on their photophysics properties and applications can be undertaken more easily. Also, the electronic properties of the oligomers can be tuned more easily when they are constructed in the block-by-block approach that is possible using photochemical synthesis.

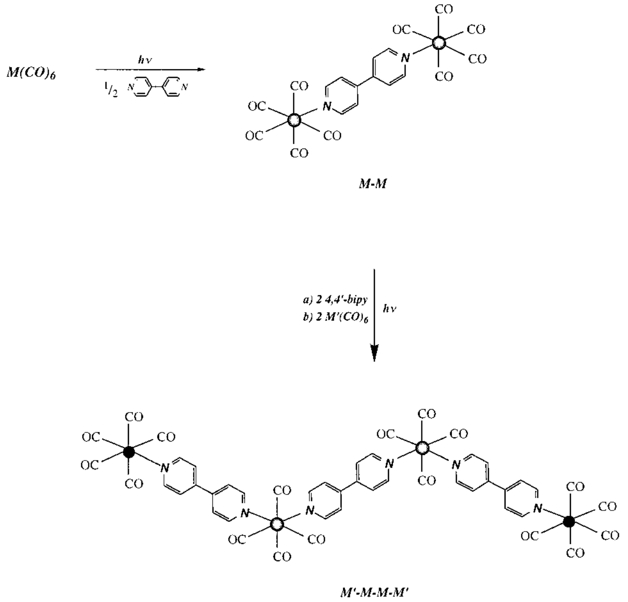
The oligomers have been characterized by IR, UV, and ^{1}H NMR spectroscopy and, in the case of some of the tungsten-containing systems, mass spectroscopy. It is possible to monitor the formation of the oligomers using IR spectroscopy, focusing on the ν_{CO} region. This can be illustrated by taking the example of the pentametallic complex [Mo−Mo−Mo−Mo−Mo]. On photolysis of $[\mathrm{Mo(CO)_6}]$ with 2 equiv of 4,4′-bipy, signals due to $[\mathrm{Mo(CO)_4(4,4'\text{-}bipy)_2}]$ grow in and those due to the parent hexacarbonyl grow out of the IR spectrum. On addition of 2 equiv of $[\mathrm{Mo(CO)_6}]$ to the photolysis mixture, signals due to this and to $[\mathrm{Mo(CO)_4(4,4'\text{-}bipy)_2}]$ are seen in the spectrum. As the photolysis takes place, the signals due to $[\mathrm{Mo(CO)_4(4,4'\text{-}bipy)_2}]$ remain while those due to $[\mathrm{Mo(CO)_6}]$ are seen to decrease. At the same time, signals due to a monosubstituted metal center appear, this due to formation of $[\mathrm{(CO)_5Mo(4,4'\text{-}bipy)Mo(CO)_4(4,4'\text{-}bipy)}]$ and the $[\mathrm{(CO)_5Mo(4,4'\text{-}bipy)Mo(CO)_4(4,4'\text{-}bipy)Mo(CO)_5}]$.

10.1021/ma990010o CCC: $18.00

Scheme 2



Scheme 3



As time passes, the signals for the monosubstituted species increase and those due to [Mo(CO)$_6$] disappear entirely, signifying complete formation of the trimetallic species. Addition of 2 equiv of 4,4′-bipy to the reaction mixture then leads to formation of [Mo−Mo−Mo] as exemplified by the decrease in the IR spectrum of signals corresponding to monosubstituted metal centers and growth of those corresponding to bis-substituted centers. Addition of a further 2 equiv of [Mo(CO)$_6$] once again leads to signals for mono- and bis-substituted metal centers signifying formation of the pentametallic oligomer, this being confirmed by the complementary spectroscopic techniques. The synthesis of the other homometallic and heterometallic complexes can be followed in a similar manner.

As the oligomers stick to silica, they could not be purified by column or thin-layer chromatography. Instead, they were purified using preferential solvation. The starting materials are soluble in hexane, but the oligomers are soluble only in dichloromethane. Hence, washing the solid product mixture with hexane and then with dichloromethane leads to an effective purification of the oligomers. IR and NMR analysis of the oligomers shows that the reaction is highly selective, producing only the desired product since no peaks due to byproducts are observed. The fact that only one product is formed in the reaction shows the highly systematic manner in which the oligomers can be prepared. Unlike other synthetic methods where a range of oligomeric products are formed encompassing a range of chain lengths and molecular weights, using the photochemical approach it is possible to prepare a single oligomer selectively and in high yield and purity. Although internal cyclization would be an option, the controlled manner in which the oligomers are formed and the fact that the stoichiometric addition of reagents is controlled avoid the formation of cyclization products. If the stoichiometry of the reaction is changed, it is possible to generate a range of molecular square complexes as reported by us elsewhere.[9]

The solubility of the oligomers, as expected, decreases with length. The complexes containing one to four metal atoms are soluble in dichloromethane, but for those containing five a more polar solvent such as ethyl acetate or acetone is required. Extension of the oligomer chain to a greater length than five metal atoms is not possible due to the lack of solubility of the products in common organic solvents.

The stability of the oligomers is dependent on the metals present, on whether they are stored in solution or as a solid, and, in the case of the former, in which solvent they are dissolved. The oligomers containing chromium are all air, moisture, and solvent sensitive at room temperature; the greater the proportion of chromium, the greater the thermal decomposition. In the absence of scavenging ligands, the chromium-containing oligomers decompose irreversibly into M(CO)$_4$(4,4′-bipy)$_2$ and undefined insoluble metal-containing products. However, if 4,4′-bipyridine is added to the solution of the polymer, M(CO)$_4$(4,4′-bipy)$_2$ is formed in greater amounts. The molybdenum- and tungsten-containing oligomers are more stable and can be exposed to the air. However, they are slightly solvent sensitive, decomposition occurring over time in polar solvents such as acetone. This is not a problem for the oligomers of type **2** but, once formed, the oligomers of type **3** must be stored as solids and, if they are to be studied in solution, this must be done as rapidly as possible. The observation that, in some cases, group 6 metal carbonyl−polypyridine complexes are prone to decomposition is not totally unexpected, having been discussed on a number of occasions previously.[9]

The electronic spectra of the oligomers have been investigated. The lowest energy transition in the electronic absorption spectra of M(CO)$_5$(4,4′-bipy), M(CO)$_4$(4,4′-bipy)$_2$ is substantially red-shifted by formation of the oligomers, consistent with the assignment of this feature as a metal-to-ligand charge-transfer transition (MLCT). The fact that the transition moves significantly on formation of the oligomers suggests that the energy of the π^*-acceptor orbitals on the 4,4′-bipy ligand are effectively lowered on association of the monomers to form oligomers. The peaks observed in the oligomers at between 395 and 415 nm are attributed to ligand field transitions. These are not shifted significantly from those observed in the monomers. The $\pi-\pi^*$ ligand−ligand transitions of 4,4′-bipy, observed at ca. 245 nm in the monomers, are essentially unaffected by formation of the oligomers.

In conclusion, photochemistry has been used as a synthetic method to prepare organometallic oligomers of known composition and length. The potential and versatility of this work are exciting, and attempts are now being made to extend the area and prepare other oligomeric and polymeric materials and to study their electrochemistry and assess their photophysical properties.

Experimental Section

All syntheses were performed under an inert atmosphere of dry nitrogen. All photochemical reactions were performed in a specially designed glass reaction vessel fitted with a nitrogen bubbler and reflux condenser. A 125 W mercury arc broad-band UV immersion lamp was used as the irradiation source. Infrared (IR) spectra were recorded using a Perkin-Elmer PE 1710 Fourier transform infrared spectrometer, solution spectra in NaCl solution cells (path length 0.5 mm), and solid-state spectra in compressed KBr pellets. All values quoted are in wavenumbers (cm^{-1}). UV−vis spectra were recorded on a Perkin-Elmer 5523 UV−vis spectrophotometer stabilized at 20 °C. All values quoted are in nanometers. The ^1H NMR spectra were recorded using a Bruker AM400 or WM250 Fourier transform NMR spectrometer, and data reported using the chemical shift scale in units of ppm relative to $SiMe_4$ ($\delta = 0$). Mass spectra were recorded using a KRATOS MS-50 spectrometer, with either 3-nitrobenzyl alcohol or thioglycerol as a matrix and CsI as calibrant. All reagents were purchased from commercial sources and used as received unless noted otherwise.

Representative Synthesis of a Trimetallic Oligomer. Synthesis of [Cr−Cr−Cr]: A dichloromethane solution (250 mL) of $Cr(CO)_6$ (30 mg, 0.136 mmol) and 4,4′-bipyridine (42.5 mg, 0.272 mmol) was irradiated for 10 min, producing (4,4′-bipy)$Cr(CO)_4$(4,4′-bipy) in 95% yield (by IR). To the photolysis mixture was added $Cr(CO)_6$ (60 mg, 0.272 mmol), and the photolysis continued for a further 12 min. Removal of the solvent in vacuo and washing the residue with cold hexane several times removed any unreacted starting materials. The addition of dichloromethane to the resultant solid and subsequent removal of the deep purple solution were repeated several times until the dichloromethane was no longer colored on shaking with the remnant solid. Removal of the dichloromethane from the collected washings led to the recovery of a deep maroon solid, characterized as the trimetallic oligomer in a yield of 80% based on the quantities of the starting materials. IR and NMR analyses show that the pentametallic oligomer is the only species present in solution as no other peaks are observed. IR (CH_2Cl_2): $\nu_{CO} = 2067$ (m), 2008 (m), 1934 (s), 1922 (m), 1888 (vs), 1876 (s, sh), 1837 cm^{-1} (s). UV/vis (CH_2Cl_2): $\lambda_{max} = 245$ ($\lambda_{\pi-\pi^*}$), 403 (λ_{LF}), 435 nm (λ_{MLCT}) . ^1H NMR (250 MHz, 25 °C, $CDCl_3$): $\delta = 8.91$ (d), 8.87 (d), 7.56 (d), 7.51 ppm (d).

Representative Synthesis of a Tetrametallic Oligomer. Synthesis of [W−Mo−Mo−W]: A dichloromethane solution (250 mL) of $Mo(CO)_6$ (45.7 mg, 0.272 mmol) and 4,4′-bipyridine (42.5, 0.136 mmol) was irradiated for 10 min, producing $(CO)_5Mo$(4,4′-bipy)$Mo(CO)_5$ in 95% yield (by IR). Addition of 4,4′-bipyridine (85 mg,0.272 mmol), 10 min further photolysis and then addition of $W(CO)_6$ (70 mg,0.272 mmol), and a further 250 mL of solvent followed by 15 min photolysis resulted in the formation of a deep maroon product solution. Removal of the solvent in vacuo and washing the residue with cold hexane and then cold 5:1 hexane/dichloromethane several times removed any unreacted starting materials. The addition of dichloromethane to the resultant solid and subsequent removal of the deep purple solution were repeated several times until the dichloromethane was no longer colored on shaking with the remnant solid. Removal of the dichloromethane from the collected washings led to the recovery of a deep maroon solid, characterized as the pentametallic oligomer in a yield of 70% based on the quantities of the starting materials. IR and NMR analyses show that the tetrametallic oligomer is the only species present in solution as no other peaks are observed. IR (CH_2Cl_2): $\nu_{CO} = 2068$ (m), 2011 (m), 1934 (s), 1922 (m), 1895 (vs), 1878 (s, sh), 1836 cm^{-1} (s). UV/vis (CH_2Cl_2): $\lambda_{max} = 245$ ($\lambda_{\pi-\pi^*}$), 404 (λ_{LF}), 450 nm (λ_{MLCT}). ^1H NMR (400 MHz, 25 °C, $CDCl_3$): $\delta = 8.94$ (d), 8.86 (d) 8.84 (d), 8.83 (d), 7.56 (d), 7.52 (d), 7.51 (d, 2H), 7.49 ppm (d). Mass spectrum: $m/z = 1535$ (calcd 1532).

Representative Synthesis of a Pentametallic Oligomer. Synthesis of [Mo−Mo−Mo−Mo−Mo]: A dichloromethane solution (250 mL) of $Mo(CO)_6$ (30 mg, 0.113 mmol) and 4,4′-bipyridine (35.3 mg, 0.226 mmol) was irradiated for 10 min, producing (4,4′-bipy)$W(CO)_4$(4,4′-bipy) in 90% yield (by IR). To the photolysis mixture was added $Mo(CO)_6$ (60 mg, 0.226 mmol), and the photolysis continued for a further 12 min. Addition of 4,4′-bipyridine (35.3 mg, 0.226 mmol), 10 min further photolysis and then addition of $Mo(CO)_6$ (60 mg, 0.226 mmol), and a further 250 mL of solvent followed by 15 min photolysis resulted in the formation of a very deep maroon product solution. Purification in an identical manner to that used for the tetrametallic complexes led to the recovery of a deep maroon solid, characterized as the pentametallic oligomer in a yield of 65% based on the quantities of the starting materials. IR and NMR analyses show that the pentametallic oligomer is the only species present in solution as no other peaks are observed. IR (CH_2Cl_2): $\nu_{CO} = 2071$ (m), 2010 (m), 1943 (s), 1924 (m), 1893 (vs), 1879 (s, sh), 1835 cm^{-1} (s). UV/vis (CH_2Cl_2): $\lambda_{max} = 243$ ($\lambda_{\pi-\pi^*}$), 407 (λ_{LF}), 459 nm (λ_{MLCT}). ^1H NMR (250 MHz, 25 °C, $CDCl_3$): $\delta = 8.98$ (d), 8.93 (d) 8.89 (d), 8.86 (d) 7.59 (d), 7.57 (d), 7.55 (d, 2H), 7.531 ppm (d). Mass spectrum: $m/z = 1628$ (calcd 1624).

Acknowledgment. Girton College is thanked for a Research Fellowship (N.E.L.) and the Nuffield Foundation thanked for an Undergraduate Research Bursary (H.A.C.). The financial support of BP plc and Johnson Matthey plc is greatly appreciated.

Supporting Information Available: Spectroscopic data for the complexes prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Bruce, D. W., O'Hare, D., Eds. *Inorganic Materials*; Wiley: Chichester, 1992. (b) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21. (c) Frazier, C. C.; Harvey, M. A.; Cockerham, M. P.; Hand, H. M.; Chauchard, E. A.; Lee, C. H. *J. Phys. Chem.* **1986**, *90*, 5703.

(2) (a) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1603. (b) Blau, W. J.; Byrne, H. J.; Cardin, D. J.; Davey, A. P. *J. Mater. Chem.* **1991**, *1*, 245. (c) Cheng, L.-T.; Tam, W.; Meredith, G. R.; Marder, S. R. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 137.

(3) (a) Hogarth, G.; Norman, T. *Polyhedron* **1996**, *15*, 2859. (b) Handa, M.; Mikuriya, M.; Nukada, R.; Matsumoto, H.; Kasuga, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3125. (c) Connor, J. A.; Overton, C. *J. Organomet. Chem.* **1983**, *249*, 165.

(4) Harriman, A.; Zeissel, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1707.

(5) Lewis, J.; Khan, M. S.; Khakkar, A. K.; Johnson, B. F. G.; Marder, T. B.; Fyfe, H. B.; Wittmann, F.; Friend, R. H.; Day, A. E. *J. Organomet. Chem.* **1992**, *425*, 165.

(6) Manners, I. *Chem. Br.* **1996**, *32*, 46.

(7) Leadbeater, N. E.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1997**, *543*, 251.

(8) Hay, C. M.; Leadbeater, N. E.; Lewis, J.; Raithby, P. R.; Burgess, K. *New J. Chem.* **1998**, 787.

(9) (a) Leadbeater, N. E.; Cruse, H. A. *Inorg. Chem. Commun.* **1999**, *2*, 93. (b) Leadbeater, N. E.; Cruse, H. A. *Inorg. Chem.*, in press.

(10) (a) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 1139. (b) Lees, A. J.; Forbare, J. M.; Mattimore, E. F. *Inorg. Chem.* **1984**, *23*, 2709. (c) Ernhoffer, R.; Shepherd, R. E. *J. Chem. Soc., Chem. Commun.* **1978**, 859.

MA990010O