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Preparation of Biscarboxylato Imido Alkylidene Complexes of Molybdenum and Cyclopolymerization of Diethyldipropargylmalonate To Give a Polyene Containing only Six-Membered Rings

Florian J. Schattenmann, Richard R. Schrock,* and
William M. Davis

Department of Chemistry 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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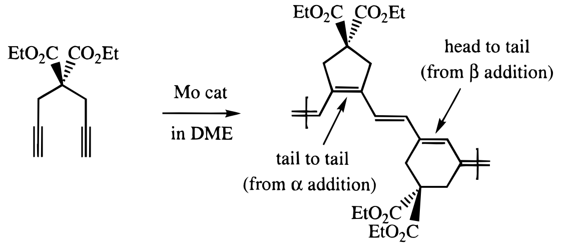
Soluble, conjugated organic polymers have potentially useful optical and electronic properties.[1−5] An important ultimate goal is to prepare polymers whose chain length, endgroup identity, and structure are known, to correlate these properties with an NLO property such as the third-order hyperpolarizability (γ), and to use this information to prepare polymers with optimal properties of some specific type. We recently reported[6] that 1,6-heptadiynes such as diethyldipropargylmalonate (DEDPM) could be cyclopolymerized[7,8] in a living manner by initiators of the type $Mo(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ ($Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$). However, the polyene backbone was found to contain a mixture of five- and six-membered rings as a consequence of the first terminal triple bond adding to an alkylidene to give either an α-substituted or a β-substituted metallacyclobutene intermediate (α or β addition, respectively; eq 1).



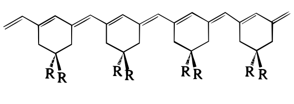
(1)

We wanted to prepare a catalyst that would yield polymers having exclusively one ring size and therefore began a search for new initiators containing "ancillary" ligands other than alkoxides. We report here that a new class of catalysts containing bulky carboxylate ligands can be prepared which encourage regioselective addition of the first triple bond to an alkylidene to give only a β-substituted metallacyclobutene and therefore polyenes that contain only six-membered rings in the polymer backbone as a consequence of specific head-to-tail cyclopolymerization.

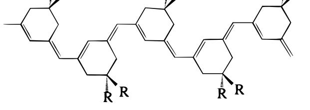
Addition of excess sodium triphenylacetate to $Mo(NAr')(CH\text{-}t\text{-}Bu)(OTf)_2(DME)$ ($Ar' =$ 2-*tert*-butylphenyl) gave yellow crystalline $Mo(NAr')(CH\text{-}t\text{-}Bu)(O_2CCPh_3)_2$ (**1a**) in 55% isolated yield. The proton and carbon NMR spectra of **1a** reveal that only one rotamer[9] is present which has an alkylidene H_α resonance at 13.76 ppm and an alkylidene C_α resonance at 313.4 ppm. Other carboxylate complexes that have been prepared by similar methods are listed in Table 1, along with NMR data that suggest that all are analogous. The relatively small alkylidene CH_α coupling constants (between 117 and 123 Hz) suggest that the alkylidene ligand has the *syn* orientation. Compounds containing the $N\text{-}2,6\text{-}Me_2C_6H_3$ ligand retained 1 equiv of loosely bound THF, but decomposed to form insoluble materials when the THF was removed in vacuo in the solid state or when the THF adduct was dissolved in solvents such as toluene.

An X-ray structural study of **1a** (Figure 1) showed it to be a monomeric species. The alkylidene ligand is *syn*, as suspected on the basis of the magnitude of $J_{CH\alpha}$. Neither the Mo−C(7) distance (1.884 Å) nor the Mo−C(7)−C(9) angle (145.8°) is unusual. The imido ligand is bent slightly (Mo−N(6)−C(12) = 164.4°), and the plane of the phenyl ring is oriented approximately perpendicular to the C(7)−Mo−N(6) plane. The carboxylate ligands are both bound to the molybdenum in a bidentate (η^2) fashion, although unsymmetrically; the longer Mo−O bonds (2.261 and 2.336 Å) are those that are in positions more transoid to the imido or alkylidene ligand, respectively (N(6)−Mo−O(4) = 155.4°; C(7)−Mo−O(5) = 151.9°). The other two Mo−O bonds are relatively short (2.136 and 2.090 Å). Therefore binding of the two carboxylate ligands can be said to be somewhere between η^1 and η^2. The steric bulk provided by the carboxylates is likely to prevent bimolecular decomposition of **1a**. The electron count in **1a** is 18 if the carboxylato ligands are counted as bidentate ligands and π electron donation from the imido ligand is included. Bending of the imido ligand as well as η^2 to η^1 conversion of the carboxylato ligands may be important features of **1a** as a catalyst.

Addition of diethyldipropargylmalonate to **1a** in toluene yields poly(DEDPM) with a polydispersity that ranges from 1.13 to 1.26 (see Table 2). The structure of these polymers can be determined by ^{13}C NMR, since the carbonyl carbon and the quaternary carbon are especially sensitive to the ring size. Carbon resonances at 172.0 ppm (carbonyl carbon) and 57−58 ppm (quaternary carbon) are characteristic of five-membered rings, while resonances at 170.8 and 54 ppm are characteristic of six-membered rings.[6] Since ^{13}C NMR spectra of poly(DEDPM)$_n$ samples reveal just one peak at 170.7 ppm for the carbonyl carbon and one at 54.4 ppm for the quaternary carbon, we conclude that they contain >99% six-membered rings. Four resonances between 131.7 and 134.3 ppm for the four sp^2 carbons and two resonances for the ring CH_2 groups make a complete assignment of resonances possible. Proton NMR spectra are also relatively simple and can be assigned completely. The cis/trans configuration of the exocyclic double bond or the s-cis/s-trans configuration of the backbone single bond cannot be determined. Two possible idealized planar conformational isomers (**A** and **B**; $R = CO_2Et$) are drawn below.



A



B

UV/vis spectra reveal that λ_{max} increases with increasing chain length. However, these λ_{max} values are lower by 20−30 nm for a given apparent chain length than those for the previously reported cyclopolymers that contain both five- and six-

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(1) Prasad, P. N. In *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum Press: New York, 1987; p 41.

(2) Prasad, P. N. *Polymer* **1991**, *32*, 1746.

(3) Lytel, R.; Lipscomb, G. F.; Thackara, J.; Altman, J.; Elizondo, P.; Stiller, M.; Sullivan, B. In *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum Press: New York, 1987; p 415.

(4) Zyss, J.; Chemla, D. S. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, FL, 1987; Vol. 1, p 23.

(5) *Conjugated Polymers*; Brédas, J. L., Silbey, R., Eds.; Kluwer: Boston, 1991.

(6) Fox, H. H.; Wolf, M. O.; O'Dell, R.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827.

(7) Choi, S. K. *Makromol. Chem., Macromol. Symp.* **1990**, *33*, 145.

(8) Ryoo, M. S.; Lee, W. C.; Choi, S. K. *Macromolecules* **1990**, *23*, 3029.

(9) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.

0002-7863/96/1518-3295$12.00/0

Table 1. NMR Data for Carboxylato Complexes, $Mo(CHR')(NR)(O_2CR'')_2$

R		R′	R″	δ H$_\alpha$	δ C$_\alpha$ (J_{CH})
2-*t*-BuC_6H_4	**1a**	CMe_3	CPh_3	13.76	313.4
2-*t*-BuC_6H_4	**1b**	CMe_2Ph	CPh_3	13.92	309.4 (123)
2,6-*i*-Pr_2-C_6H_3	**2**	CMe_2Ph	CPh_3	13.91	308.9 (122)
2,6-*i*-Pr_2-C_6H_3	**3**	CMe_2Ph	$CMePh_2$	13.96	308.5 (121)
1-adamantyl	**4a**	CMe_3	CPh_3	13.84	
1-adamantyl	**4b**	CMe_2Ph	CPh_3	13.89	305.5 (117)

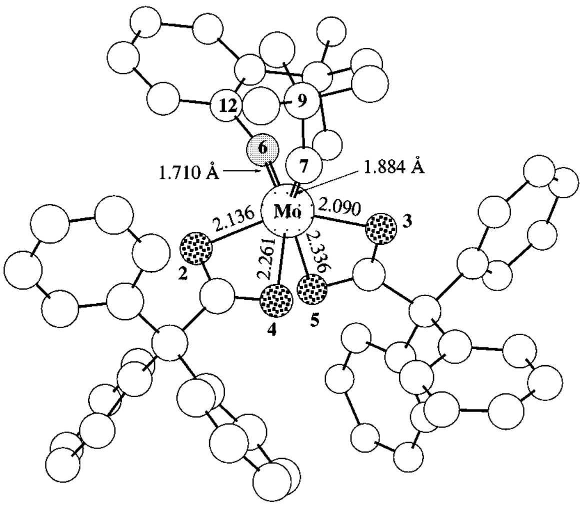


Figure 1. A Chem 3D drawing of the structure of Mo(N-2-*t*-BuC_6H_4)(CH-*t*-Bu)$(O_2CCPh_3)_2$ (**12**): Mo−N(6)−C(12) = 164.4°; Mo−C(7)−C(9) = 145.8°; N(6)−Mo−C(7) = 99.7°; N(6)−Mo−O(2) = 96.6°; N(6)−Mo−O(3) = 105.6°; N(6)−Mo−O(4) = 155.4°; N(6)−Mo−O(5) = 101.8°; C(7)−Mo−C(2) = 101.2°; C(7)−Mo−O(3) = 98.0°; C(7)−Mo−O(4) = 89.8°; C(7)−Mo−O(5) = 151.9°; O(2)−Mo−O(3) = 147.6°; O(4)−Mo−O(5) = 77.9°; O(2)−Mo−O(4) = 59.2°; O(3)−Mo−O(5) = 58.8°.

Table 2. GPC, Visible, and Yield Data for Poly(DEDPM)$_n$ Prepared Using **1a** in Toluene (6 h, 25 °C)

sample	M_{calc}	M_n[a]	M_n/M_w[a]	λ_{max} (nm)[b]	yield (%)
poly(DEDPM)$_5$	1403	6 847	1.18	470	96
poly(DEDPM)$_8$	2112	7 105	1.22	488	90
poly(DEDPM)$_{11}$	2821	9 452	1.26	494	97
poly(DEDPM)$_{15}$	3766	11 500	1.26	502	97
poly(DEDPM)$_{20}$	4947	13 590	1.26	500	91
poly(DEDPM)$_{40}$	9673	40 280	1.13	518	92
poly(DEDPM)$_{60}$	14398	45 690	1.13	526	91
poly(DEDPM)$_{80}$	19124	72 440	1.15	530	89
poly(DEDPM)$_{120}$	28574	99 470	1.15	534	92

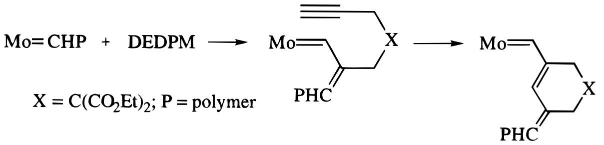
[a] Determined by GPC on-line viscometry versus a polystyrene universal calibration curve (Viscotek). [b] In CH_2Cl_2.

membered rings, consistent with a lower average degree of conjugation in this more regular polymer.

GPC data (viscometry versus a polystyrene calibration curve) reveal a linear dependence of the chain length on the amount of monomer added, consistent with a living polymerization. Although the molecular weights appear to be too high by a factor of 4, MALDI TOF mass spectrometry, a technique that only recently has been employed for characterization of synthetic polymers,[10−12] revealed that the molecular weights are actually close to those expected.[13] The systematic error can be ascribed to the different solution properties of the presumably more rigid conjugated polymers compared to those of polystyrene.

In contrast to **1a** and **1b**, **2** and **3** are impractically slow initiators for polymerization of DEDPM. Even after 24 h only ∼50% of the monomer had been consumed. The fact that **2** does not react with PMe_3 suggests that the monomer simply cannot access the metal if both coordination positions are blocked by isopropyl groups. In contrast, **4a** and **4b** are again good initiators for the polymerization of DEDPM. Samples of poly(DEDPM) prepared with **4a** and **4b** have slightly higher polydispersity and molecular weights, but also contain only six-membered rings in the backbone. **4a** forms a white PMe_3 adduct quantitatively (13.28 ppm), which is a poor initiator for polymerization of DEDPM.

We assume that the mechanism of polymerization consists of addition of the first triple bond to an alkylidene to give exclusively a β-substituted metallacyclobutene intermediate, i.e., α addition is sterically untenable. Opening of the metallacycle followed by intramolecular β addition (cyclization) leads to the propagating terminal alkylidene (eq 2). Intramolecular formation



(2)

of the six-membered ring must be fast relative to intermolecular addition of the second triple bond to a Mo=C bond, a reaction that would lead to cross-linking. None is observed.

Interestingly, **1a** and **1b** are *not* successful ROMP initiators. Even norbornene is not readily polymerized by **1a**. We presume that a disubstituted olefin, even one as reactive as norbornene, simply cannot coordinate to the metal in **1a** for steric reasons. **1a** also does not react readily with *ortho*-((trimethylsilyl)-phenyl)acetylene or even phenylacetylene itself. It will be interesting to exploit the "β selectivity" of these triphenylcarboxylato complexes, especially in view of the recently discovered "α selectivity" for addition of *ortho*-((trimethylsilyl)-phenyl)acetylene to catalysts that contain "small" alkoxides (e.g., $OCH(CF_3)_2$).[14]

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Supporting Information Available: Experimental details for syntheses and polymerizations, a detailed description of X-ray data collection and structure solution and refinement, labeled ORTEP diagram, tables of fractional coordinates, isotropic and anisotropic thermal parameters, and bond lengths and angles for **1a** (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(10) Danis, P. O.; Karr, D. E.; Simonsick, W. J., Jr.; Wu, D. T. *Macromolecules* **1995**, *28*, 1229.

(11) Maloney, D. R.; Hunt, K. H.; Lloyd, P. M.; Muir, A. V. G.; Richards, S. N.; Derrick, P. J.; Haddleton, D. M. *J. Chem. Soc., Chem. Commun.* **1995**, 561.

(12) Pasch, H.; Gores, F. *Polymer* **1995**, *36*, 1999.

(13) Köchling, H. J.; Biemann, K.; Schattenmann, F. J.; Schrock, R. R. To be published.

(14) Schrock, R. R.; Luo, S.; Zanetti, N.; Fox, H. H. *Organometallics* **1994**, *13*, 3396.