3396 *Organometallics* **1994,** *13,* 3396–3398

Living Polymerization of (*o*-(Trimethylsilyl)phenyl)acetylene Using "Small Alkoxide" Molybdenum(VI) Initiators

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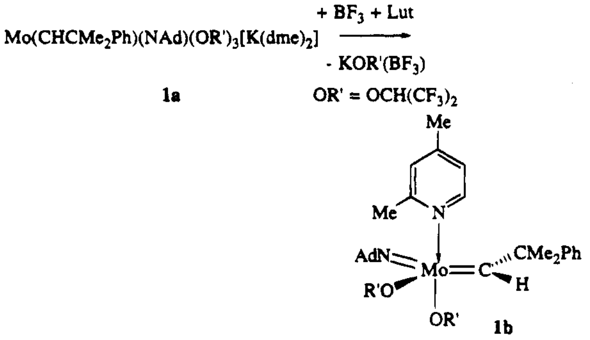
Received June 20, 1994®

Summary: (o-(Trimethylsilyl)phenyl)acetylene (o-TMSPA) is polymerized in a living manner by the new "small alkoxide" initiators $Mo(CHCMe_2Ph)(N\text{-}1\text{-}adamantyl)[OCH(CF_3)_2]_2(2,4\text{-}lutidine)$ *(**1b**) and* $Mo(CHCMe_2Ph)(NAr')(OC_6F_5)_2(quinuclidine)$ *(**2**; Ar′ =* $2,6\text{-}C_6H_3Me_2$*) to give low-polydispersity polyenes containing up to 100 equiv of o-TMSPA. The thermodynamically most stable form of poly(o-TMSPA) that contains <25 double bonds is air-sensitive and has a significantly red-shifted* λ_{max}*.*

Polyenes prepared from certain substituted phenylacetylenes (e.g., (*o*-(trimethylsilyl)phenyl)acetylene = *o*-TMSPA) are potentially of great interest for nonlinear optical studies since they are highly delocalized and are soluble.[1–5] There is good evidence that alkynes can be polymerized via an "alkylidene mechanism"[6–10] and that such processes can be living.[5–8,11–13] We report here that complexes of the type $Mo(CHCMe_2Ph)(NR)(OR')_2$(base), in which OR′ is a relatively small electron-withdrawing alkoxide (OC_6F_5 or $OCH(CF_3)_2$), are successful initiators for the controlled (low-PDI) living polymerization of *o*-TMSPA.

Addition of 3 equiv of $KOCH(CF_3)_2$ to $Mo(CHCMe_2Ph)(NAd)(OTf)_2(dme)$[14] (NAd = 1-adamantylimido, OTf = triflate, dme = 1,2-dimethoxyethane) in diethyl ether leads to a pentane-soluble yellow oil quantitatively whose NMR spectra are consistent with it having the composition $Mo(CHCMe_2Ph)(NAd)[OCH(CF_3)_2]_3[K(dme)_2]$ (**1a**).[15] The reaction is more complex when less than 3 equiv of $OCH(CF_3)_2$ is employed, in part because a significant amount of the apparent "ate" complex (**1a**) still forms, and because $Mo(CHCMe_2Ph)(NAd)[OCH(CF_3)_2]_2$ is likely to be unstable with respect to bimolecular decomposition.[16] Addition of $BF_3\cdot OEt_2$ to **1a** in the presence of 2,4-lutidine (Lut) yields nearly colorless $Mo(CHCMe_2Ph)(NAd)[OCH(CF_3)_2]_2(Lut)$ (**1b**) in high yield (eq 1).[17] All data are consistent with **1b** being a syn rotamer and having 2,4-lutidine bound to the CNO face. Although bound 2,4-lutidine in **1b** does not exchange rapidly on the NMR time scale with free 2,4-lutidine at 25 °C, **1b** reacts readily with *o*-TMSPA. **1b** is consumed completely upon addition of 3 equiv of *o*-TMSPA to **1b** to give a mixture of first-insertion and higher insertion products. When the amount of *o*-TMSPA is varied, resonances for H_β (doublet at 8.87 ppm) and H_γ (doublet at 4.96 ppm) in a single type of first-insertion product can be identified (eq 2; CHR_i = initial alkylidene); their chemical shifts are similar to those found in other Mo(VI) vinylalkylidene complexes of this general type that arise via "α-addition" of the alkyne[7,18] and to those of the first-insertion product from the reaction between $Mo(NAd)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ and *o*-TMSPA (see below). The first-insertion



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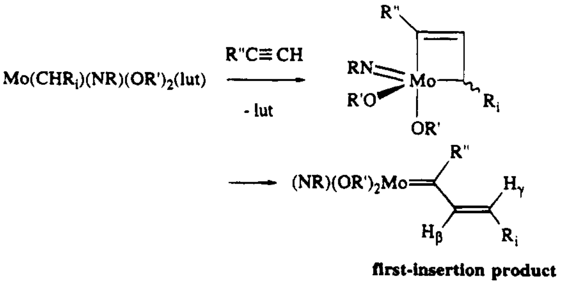

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® Abstract published in *Advance ACS Abstracts,* August 1, 1994.

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[15] ^1H NMR (C_6D_6): δ 12.51 (s, 1, $CHCMe_2Ph$). ^{19}F NMR (C_6D_6): δ −74.38, −75.13, −75.47 (1:1:1 ratio). ^{13}C NMR (C_6D_6): δ 296.6 (J_{CH} = 119 Hz, $CHCMe_2Ph$).

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[17] ^1H NMR (C_6D_6): δ 13.76 (s, 1, $CHCMe_2Ph$). ^{19}F NMR (C_6D_6): δ −74.99, −74.63, −74.54 (1:2:1 ratio). ^{13}C NMR (C_6D_6): δ 297.8 (J_{CH} = 121 Hz, $CHCMe_2Ph$).

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Table 1. Poly(*o*-TMSPA) Prepared with 1b or 2 in Toluene

initiator	amt of *o*-TMSPA (equiv)	λ_{max} (nm)[a]	M_n[c]	PDI
1b	10	460	1410	1.07
1b	20	502	2680	1.07
1b	30	518	4400	1.05
1b	40	526	5750	1.05
1b	50	534	6930	1.06
1b	60	536	8810	1.04
1b	70	536	9940	1.05
1b	80	540	11600	1.05
1b	90	540	12500	1.04
1b	100	540	13900	1.04
2	10	522[b]	1920	1.20
2	20	516[b]	3220	1.17
2	30	518[a]	4890	1.11
2	50	526[b]	7900	1.07
2	80	536[b]	12100	1.07
2	100	534[b]	15500	1.05

[a] Low-energy transition only; experimental error ~±2 nm. [b] In THF in the absence of air. [c] By GPC versus polystyrene standards.

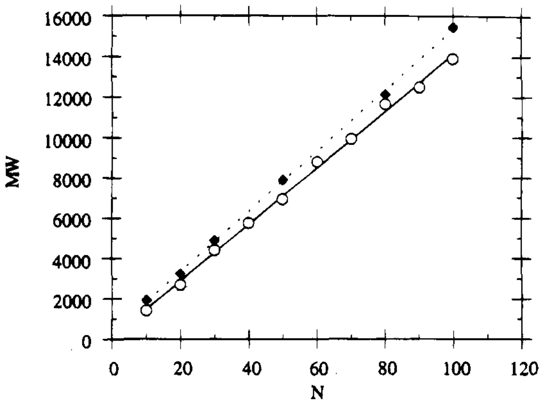

Figure 1. Plot of molecular weight (by GPC vs polystyrene) for poly(*o*-TMSPA) prepared from *N* equiv of *o*-TMSPA and **1b** (○) or **2** (◆) as the initiator in toluene. (See Supplementary Material for details.)

product is believed to be *base-free*, presumably for steric reasons, as judged by the appearance of resonances characteristic of free 2,4-lutidine as **1b** is consumed. (Mo(N-2,6-C_6H_3-*i*-Pr_2)[C(Me)Ph][OCMe(CF_3)$_2$]$_2$ was also shown to be stable as a base-free complex.[10]) The observed value for $J_{H_\beta H_\gamma}$ (15.6 Hz) in the first-insertion product is consistent with the C=C bond being trans. Interestingly, the first-insertion product does not react readily with several equivalents of benzaldehyde at concentrations of ~10 mM in Mo, even though it is base-free and even though **1b** reacts relatively readily with benzaldehyde.

o-TMSPA is polymerized smoothly in toluene using **1b** as an initiator[19] to give low-polydispersity poly(*o*-TMSPA) (Table 1) that presumably contains one *o*-(trimethylsilyl)phenyl group on every other carbon atom. The molecular weight of poly(*o*-TMSPA) (by GPC vs polystyrene standards) is proportional to the number of equivalents of *o*-TMSPA added (Figure 1). Both are consistent with a living polymerization that proceeds via a single type of chain growth and with a rate of initiation that approximately equals the rate of propagation. Polymerization of *o*-TMSPA using **1a** gave a polymer having a multimodal distribution by GPC, while Mo($CHCMe_2Ph$)(NAd)[OCH(CF_3)$_2$]$_2$(pyridine) is impractically slow as an initiator at 25 °C.

Another small-alkoxide initiator can be prepared that contains the (2,6-dimethylphenyl)imido and pentafluorophenoxide ligands. Addition of 2 equiv of KOC_6F_5 to Mo($CHCMe_2Ph$)(NAr′)(triflate)$_2$(1,2-dimethoxyethane) (NAr′ = N-2,6-$C_6H_3Me_2$)[14] in THF followed by 1 equiv of quinuclidine yields a complex with the composition Mo($CHCMe_2Ph$)(NAr′)(OC_6F_5)$_2$(quin) (**2**) as a mixture of two isomers (believed to be anti and syn) having alkylidene proton resonances at 14.16 and 13.02 ppm, respectively. Polymerizations of *o*-TMSPA using **2** as an initiator proceed smoothly,[20] but more slowly than polymerizations employing **1b**, to give low-polydispersity poly(*o*-TMSPA) that is essentially identical with poly(*o*-TMSPA) prepared employing **1b** (Table 1). In this case also the relationship between M_n and the number of equivalents of *o*-TMSPA employed is linear (Figure 1).

It is important to note that a variety of four-coordinate Mo alkylidene initiators of this type which are successful catalysts for living ROMP of norbornadienes and norbornenes,[21,22] all of which contain relatively bulky alkoxide ligands, do *not* polymerize *o*-TMSPA satisfactorily. Mo($CHCMe_2Ph$)(NAr)(O-*t*-Bu)$_2$ does not react readily with *o*-TMSPA at 25 °C. Mo($CHCMe_2Ph$)(NAr)-[OCMe(CF_3)$_2$]$_2$[23] reacts only very slowly with *o*-TMSPA, and the GPC of poly(*o*-TMSPA) prepared with this initiator is multimodal.[24a] The GPC of poly(*o*-TMSPA) prepared with Mo($CHCMe_2Ph$)(NAd)[OCMe(CF_3)$_2$]$_2$[14,25] is unimodal, but polydispersities range between 1.2 and 1.4 for polymers containing between 5 and 80 equiv of *o*-TMSPA, in spite of the fact that Mo($CHCMe_2Ph$)(NAd)[OCMe(CF_3)$_2$]$_2$ is converted virtually completely to two isomers of a single type of "α-addition first-insertion product" upon addition of a slight excess of *o*-TMSPA (cf. eq 2).[24b]

A potentially important finding is that the poly(*o*-TMSPA) samples prepared here have two forms, a "blue-

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(19) Bulk toluene solutions were prepared for both **1b** (13.9 mM) and *o*-TMSPA (0.23 M). The polymerization reactions were carried out under dinitrogen in a drybox by quickly adding the *o*-TMSPA solution to a vigorously stirred solution of **1b** at room temperature. In a typical experiment, 0.24 mL of the *o*-TMSPA solution (55.2 μmol) was quickly injected into a toluene solution of **1b** (50 μL bulk solution diluted to ~3 mL). The solution turned purple within $^{1}/_{2}$ h, and the color did not change significantly thereafter. Therefore, we believe the reaction to be complete in several hours, at the most. After 82 h, the reaction was brought into the air and methanol was added to the polymerization solution to induce precipitation of poly(*o*-TMSPA) as a dark purple solid. The polymer was collected by filtration, washed with methanol, and dried in vacuo; yield 9.0 mg (93%).

(20) Stock solutions of the monomer (1.05 M in toluene) and the catalyst (0.04 M in toluene) were prepared. The catalyst was added to 5 mL of toluene. A 0.5-mL amount of the monomer solution was added rapidly to the stirred catalyst solution. The solutions turned immediately deep red and after 3 h turned purple. After 36 h 10 equiv of benzaldehyde was added. After an additional 12 h the purple solution was passed through alumina and the solvent was removed in vacuo, affording the polymer as a purple film (88–92 mg; 96–100%). All operations were carried out under dinitrogen.

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(24) (a) Fox, H. H. Ph.D. Thesis, Massachusetts Institute of Technology, 1993. (b) The isomers were initially postulated to be rotamers, but the possibility that they are actually analogous compounds that contain two different alkylidenes, i.e., *trans*-Mo=C($Me_3SiC_6H_4$)CH=$CHCMe_2Ph$ and *trans*-Mo=C(CMe_2Ph)CH=CH($Me_3SiC_6H_4$) cannot be excluded.

(25) In a typical polymerization the initiator (5 mg, 7 μmol) was dissolved in 1 mL of toluene. *o*-TMSPA (94 mg, 0.541 mmol) was dissolved in 1 mL of toluene, and the solution was added to the stirring catalyst solution. After 19 h, benzaldehyde (4 μL) was added and the solution was stirred for 8 h. The polymer was precipitated in acetonitrile, collected by filtration, and redissolved in THF. The THF was removed in vacuo, affording the polymer as a purple film (90 mg, 95%). All operations were carried out under dinitrogen.

shifted λ_{max}" form, similar to what has been reported in the literature,[5,26] and a "red-shifted λ_{max}" form. The difference in λ_{max} for the two forms is 50 nm or greater. The shorter polymers (<25 double bonds) are obtained initially as a mixture of the two forms but isomerize over a period of hours at 25 °C to give largely the red-shifted λ_{max} form. The longer polyenes (>50 double bonds) appear to be an equilibrium mixture of the two forms, largely the blue-shifted λ_{max} form. One possibility is that the red-shifted λ_{max} form has the trans,s-trans structure and the blue-shifted λ_{max} form contains a high percentage of some cis form.[27] Cis and trans forms of classically prepared polyacetylene are well-known, and cis to trans isomerization has also been observed for polyacetylenes prepared from substituted cyclooctatetraenes.[28] From a practical point of view it should be noted that the red-shifted λ_{max} form is air-sensitive, especially in solution. Forms having red-shifted λ_{max} values have not been noted in the literature, perhaps because high molecular weight polyenes contain little of this form, or because these polyenes are typically isolated in air.

The results reported here are consistent with "α-addition" of the alkyne to the CNO face of one rotamer[18,29] of a pseudotetrahedral $Mo(CHR_i)(NR)(OR')_2$ complex (eq 2) to give an α,α'-disubstituted molybdacyclobutene intermediate, a reaction that we propose is a consequence of the relatively small size of R' in the alkoxide in combination with the large size of the (disubstituted) alkylidene. Interestingly, although only base adducts (or "ate" complexes) of $Mo(CHR_i)(NR)(OR')_2$ species are stable toward bimolecular decomposition reactions, chain-propagating species that contain disubstituted alkylidenes appear to be relatively stable in the *absence* of a base, yet are still reactive enough, at least toward *terminal* alkynes, to be intermediates in the polymerization reaction.

Acknowledgment. R.R.S. thanks the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy (Contract No. DE-FG02-86ER13564) and the National Science Foundation (Grant No. CHE 91 22827) for support. N.C.Z. thanks the Schweizerischer Nationalfonds for a postdoctoral fellowship.

Supplementary Material Available: Text giving experimental details for the syntheses and characterization data for **1a,b** and **2** (2 pages). Ordering information is given on any current masthead page.

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