is readily explained by a two-step process with formation of $\mathbf{B}^{2,6}$ as the rate-determining step. d) The existence of an intermediate is the only rationalization for the nonstereospecific hydrogen transfer in the reaction of **1e**. e) The lack of solvent effects on the rates of the formal ene and Diels–Alder reactions supports the proposed biradical and excludes a zwitterionic intermediate.

In summary, a novel thermal $C^2-C^6$ cyclization of substituted enyne allenes has been established for substrates in which an aryl group is affixed to the alkyne terminus. Apparently, aryl substitution raises the barrier for the Myers cycloaromatization and lowers the barrier for the biradical $C^2-C^6$ cyclization, rendering the latter one the exclusive pathway.[17] Further mechanistic work on this intriguing reaction and its synthetic applications is currently in progess in our group.

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[1] a) R. G. Bergman, R. R. Jones, *J. Am. Chem. Soc.* **1972**, *94*, 660–661; b) A. G. Myers, *Tetrahedron Lett.* **1987**, *28*, 4493–4496; c) A. G. Myers, E. Y. Kuo, N. S. Finney, *J. Am. Chem. Soc.* **1989**, *111*, 8057–8059; d) R. Nagata, H. Yamanaka, E. Okazaki, I. Saito, *Tetrahedron Lett.* **1989**, *30*, 4995–4998; e) R. Nagata, H. Yamanaka, E. Murahashi, I. Saito, *ibid.* **1990**, *31*, 2907–2910.

[2] a) M. E. Maier, *Synlett* **1995**, 13–26; b) K. C. Nicolaou, P. Maligres, J. Shin, E. de Leon, D. Rideout, *J. Am. Chem. Soc.* **1990**, *112*, 7825–7826; c) K. C. Nicolaou, G. Skokotas, P. Maligres, G. Zuccarello, E. J. Schweiger, K. Toshima, S. Wendeborn, *Angew. Chem.* **1989**, *101*, 1255–1257; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1272–1275; d) K. C. Nicolaou, W. M. Dai, *ibid.* **1991**, *103*, 1453–1481 and **1991**, *30*, 1387–1416.

[3] a) Y. W. Andemichael, Y. G. Gu, K. K. Wang, *J. Org. Chem.* **1992**, *57*, 794–796; b) J. W. Grissom, B. J. Slattery, *Tetrahedron Lett.* **1994**, *35*, 5137–5410; c) J. W. Grissom, D. Huang, *J. Org. Chem.* **1994**, *59*, 5114–5116; d) *Angew. Chem.* **1995**, *107*, 2196–2198; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2037–2039.

[4] Even enyne ketenes undergo a reaction analogous to the Myers–Saito cyclization: a) K. Nakatani, S. Isoe, S. Maekawa, I. Saito, *Tetrahedron Lett.* **1994**, *35*, 605–608; b) H. Xia, H. W. Moore, *J. Org. Chem.* **1992**, *57*, 3765–3766; c) A. Padwa, D. J. Austin, U. Chiacchio, J. M. Kassir, A. Rescifina, S. L. Xu, *Tetrahedron Lett.* **1991**, *32*, 5923–5926.

[5] M. Schmittel, M. Strittmatter, S. Kiau, *Tetrahedron Lett.* **1995**, *36*, 4975–4979.

[6] M. Schmittel, M. Strittmatter, K. Vollmann, S. Kiau, *Tetrahedron Lett.* **1996**, *37*, 999–1002.

[7] J. E. Bennett, J. A. Howard, *Chem. Phys. Lett.* **1971**, *9*, 460–462.

[8] The $C^1-C^6$ and $C^2-C^6$ distances determined by AM1 calculations (cf. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909) for **1a** in the s-*cis* conformation are 3.47 and 2.98 Å, respectively.

[9] W. Carruthers, *Cycloaddition Reactions in Organic Synthesis*, Pergamon, Oxford **1990**.

[10] a) R. Brückner, R. Huisgen, J. Schmid, *Tetrahedron Lett.* **1990**, *31*, 7129–7132; b) J. Sauer, R. Sustmann, *Angew. Chem.* **1980**, *92*, 773–801; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 779–807.

[11] a) M. Schmittel, C. Rüchardt, *J. Am. Chem. Soc.* **1987**, *109*, 2750–2759; b) M. A. Flamm-ter Meer, H.-D. Beckhaus, K. Peters, H.-G. von Schnering, C. Rüchardt, *Chem. Ber.* **1985**, *118*, 4665–4673.

[12] All enyne allenes described in this paper were prepared from the corresponding propargyl alcohols by rearrangement in the presence of chlorodiphenylphosphane. All starting materials and products were isolated as pure compounds and fully characterized by $^1H$, $^{13}C$, and $^{31}P$ NMR spectroscopy, mass spectrometry, and IR spectroscopy (see Table 2).

[13] R. Hollis, L. Hughes, V. W. Bowry, K. U. Ingold, *J. Org. Chem.* **1992**, *57*, 4284–4287.

[14] The relative configuration is determined by the three contiguous stereogenic units: the stereogenic axis of the allene and the stereogenic centers in the cyclopropyl ring, C*H and C*HPh.

[15] a) J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 209–221; b) *J. Comput. Aided Mol. Design* **1990**, *4*, 1–105.

[16] D. P. Curran, W. Shen, *J. Am. Chem. Soc.* **1993**, *115*, 6051–6059.

[17] a) Since our first report on a $C^2-C^6$ cyclization two other papers have been published [17b,c] that report on a similar reaction leading to benzofulvene derivatives. However, in these cases owing to the substitution patterns a zwitterionic intermediate seems to be more plausible than a biradical. b) T. Gillmann, T. Hülsen, W. Massa, S. Wocadlo, *Synlett* **1995**, 1257–1259; c) J. G. Garcia, B. Ramos, L. M. Pratt, A. Rodriguez, *Tetrahedron Lett.* **1995**, *36*, 7391–7394.

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# Photoinduced Ring-Opening Metathesis Polymerization (PROMP) with Photochemically Generated Schrock-Type Catalysts

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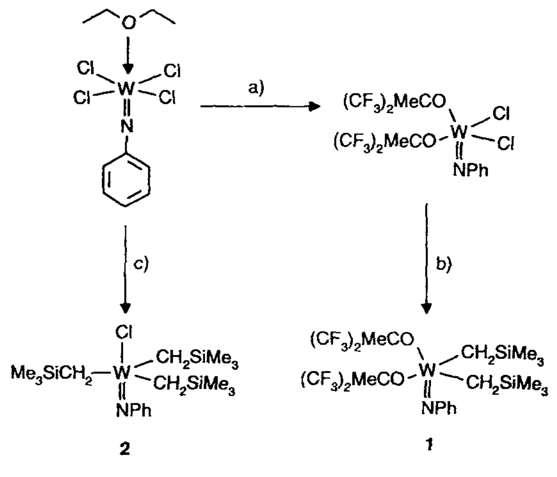
Ring-opening metathesis polymerization (ROMP) is a versatile tool for the preparation of a wide variety of polymers.[1] Since the postulated mechanism by Herisson and Chauvin in 1970[2] that metal alkylidenes[3] are the active species in this type of reaction and the discovery by Schrock et al. in 1974 that these are generated by an α-H abstraction reaction between two alkyl substituents,[4] a tremendous amount of effort has been directed, successfully, to the design of well-defined one-component ROMP initiators. To date, a broad range of initiators is known with a versatile range of applications. The best studied initiators are those based on early transition metals, in particular molybdenum and tungsten complexes developed by Schrock et al.[5] These compounds are excellent initiators for a wide variety of monomers, but their main disadvantage is their lack of latency (thermal stability) in the presence of pure monomers. Although there are indications that alkyl complexes of early transition metals can be light-sensitive and even that irradiation can accelerate α-H abstraction reactions,[6] no examples are known, besides our own work on $Ru^{II}$ complexes, using the principle of photoinduced ring-opening metathesis polymerization (PROMP) with well-defined, one-component metal complexes.[7,8] This is even more surprising when one considers that photoprocesses are known for almost all other polymerization reactions and employed in numerous commercial applications.[9] We report here the first results in the field of photoinduced ROMP (PROMP) reactions using simple alkyl tungsten complexes *and* light for the in situ generation of active ROMP initiators.[10]

Complexes **1** and **2** are easily prepared by standard transmetalation procedures (Scheme 1). Both **1** and **2** are mois-

$[W(=NPh)(CH_2SiMe_3)_2\{OCMe(CF_3)_2\}_2]$ **1**

$[W(=NPh)(CH_2SiMe_3)_3Cl]$ **2**



Scheme 1. Synthesis of the complexes **1** and **2**: a) 2 equiv $LiOCMe(CF_3)_2$ in $Et_2O$ at 0 °C, b) $NEt_4Cl$ and $Zn(CH_2SiMe_3)_2$ in $CH_2Cl_2$ at 0 °C, c) $NEt_4Cl$ and 1.5 equiv $Zn(CH_2SiMe_3)_2$ in $CH_2Cl_2$ at 0 °C.

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ture-sensitive compounds; **1**, as a crystalline material, can be handled in air for short periods. Both complexes are thermally very stable. Solutions in [D$_8$]toluene can be heated at 80 °C for at least one day without decomposition products apparent by $^1$H NMR spectroscopy. The $^1$H NMR data (see Experimental Procedure) suggest that in both complexes the alkyl groups are *cis* positioned. For direct proof of the stereochemistry an X-ray structural determination of **1** was carried out (Fig. 1).[11]

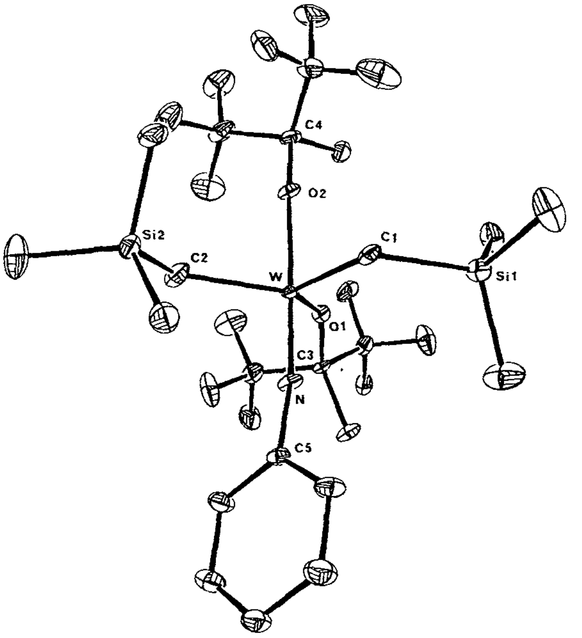
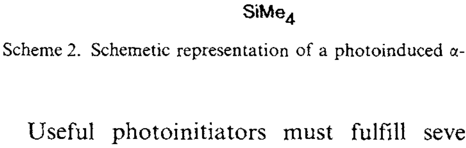


Fig. 1. Molecular structure of **1** (hydrogen atoms are ommited for clarity). Selected bond lengths [Å] and angles [°]: W-C1 2.11(1), W-C2 2.09(1), W-O1 1.919(7), W-O2 1.982(6), W-N 1.753(7); W-C1-Si1 121.7(7), W-C2-Si2 117.2(5), W-O1-C3 137.3(6), W-O2-C4 161.5(7), W-N-C5 171.2(7).

The crystal structure of **1** shows clearly that the two trimethylsilylmethyl groups have a *cis* relationship, as desired for an α-H abstraction reaction. To prove that Schrock-type initiators are formed during irradiation, solutions of **1** and **2** in $C_6D_6$ were irradiated with UV light and $^1$H NMR spectra were recorded (Scheme 2). Unfortunately, only decomposition products were observed. However, the in situ formation of an alkylidene metal complex could be proven indirectly by trapping reactions with an aldehyde.[12]



Scheme 2. Schemetic representation of a photoinduced α-H abstraction reaction.

Useful photoinitiators must fulfill several requirements. Firstly, they should, of course, be photoactive, and secondly, they should be latent, that is thermally stable, in the presence of the monomer and initiate the polymerization reaction only when activated with light.

UV irradiation of **1** and **2** in the presence of norbornene or dicyclopentadiene (DCPD) yielded the ring-opening metathesis polymers quantitatively.[13] The photoactivity was demonstrated as well by photo-DSC (DSC = differential scanning calorimetry) experiments and viscosity measurements during UV irradiation of solutions of **1** or **2** in DCPD. The results of the photo-DSC experiments for solutions of 1% of **1** and **2** in DCPD are given in Figure 2. As soon as the light beam is switch on the polymerization is initiated. Whereas the polymerization reaction with **2** is complete after 30 seconds of irradiation, the polymerization reaction with **1** continues when the light is switched off after 3 minutes of irradiation.

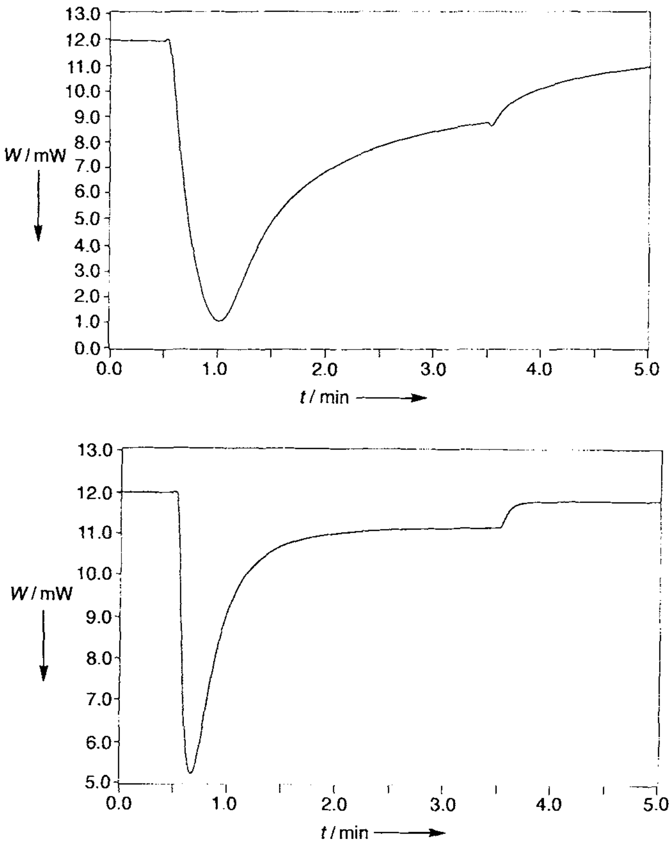


Fig. 2. Results of photo-DSC experiments of **1** (top) and **2** (bottom) in DCPD. *W* = heat flow.

The latency of complexes **1** and **2** in DCPD was tested by using a viscosity apparatus. During these experiments the samples could be either heated or irradiated with a UV lamp. The viscosity of the samples (1% initiator in DCPD containing 5% octane) was determined every minute. The results of the experiments for **1** and **2** are given in Figure 3. Complex **1** slowly polymerizes DCPD at 60 °C in the dark (Fig. 3 top). After 2 h the DCPD starts to gel and after 3 h it is fully polymerized. When the same solution at room temperature is irradiated with a UV lamp, polymerization starts directly and within 15 min the reaction is complete. Surprisingly, complex **2** in DCPD is even more latent (Fig. 3 bottom). Again, irradiation leads to a fast DCPD polymerization. However, when the solution is heated to 80 °C in the absence of light, no polymerization takes place. Moreover, this solution can be stored for days at room temperature without an increase of viscosity, and, even more importantly, without loss of photoactivity.

To our knowledge, these are the first examples of photo-induced ROMP reactions with well-defined early transition metal complexes. With these experiments we showed that simple alkyl tungsten complexes can act as one-component photo-ROMP initiators, and that their photoactivity as well as latency is very

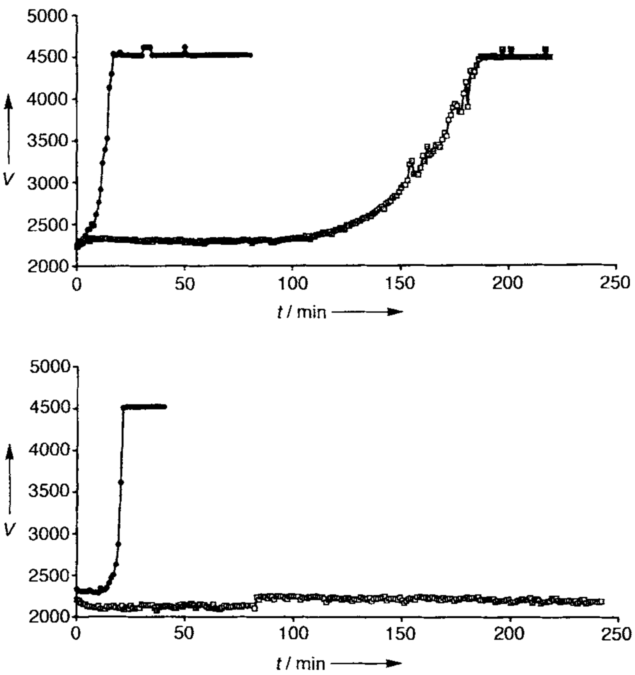


Fig. 3. Plots of real-time viscosimetric measurements of **1** (top) and **2** (bottom) in DCPD, showing the latency of the initiators in the dark. V = viscosity (arbitrary units). Top: ▨: 60 °C, in the dark; ●: 30 °C, UV irradiation. Bottom: ▨: 80 °C, in the dark; ●: 30 °C, UV irradiation.

high. In further studies on these and related complexes we are examining their reactivity with other cyclic olefins as well as the kinetics and quantum yields of these reactions. Applications of this new photopolymerization principle are also being studied.

## *Experimental Procedure*

**1**: A green solution of [W(=NPh)$Cl_4$·$OEt_2$] (11.58 g, 23.59 mmol) in $Et_2O$ (50 mL) at −78 °C was treated with a solution of [LiOCMe$(CF_3)_2$] (8.87 g, 47.18 mmol) in $Et_2O$ (50 mL). The brownish reaction mixture was warmed to room temperature, stirred for 30 min, and centrifuged. The orange solution was decanted from a white precipitate (LiCl). Volatiles were removed in vacuo leaving a red solid. The crude product was extracted with hexane (2 × 80 mL). The hexane fractions were combined and dried in vacuo leaving [W(=NPh){OCMe$(CF_3)_2$}$_2$$Cl_2$] as a red powder; yield 16.54 g (90%). To a solution of [W(=NPh){OCMe$(CF_3)_2$}$_2$$Cl_2$] (16.54 g, 21.15 mmol) in $CH_2Cl_2$ (50 mL) was added $NEt_4Cl$ (4.00 g, 24.14mmol) as a solid. After 10 min the resulting dark red suspension was cooled to 0 °C and a solution of Zn$(CH_2SiMe_3)_2$ (5.08 g, 21.24 mmol) in $CH_2Cl_2$ (20 mL) was added within 5 min. Upon addition the color of the reaction mixture turned yellow/orange and a precipitate formed. The reaction mixture was then warmed to room temperature and stirred for an additional hour. Volatiles were evaporated in vacuo leaving a light-yellow solid, which was extracted with hexane (80 and 50 mL). The combined hexane fractions were concentrated to ca. 70 mL and stored at −30 °C. The pure product was obtained, in two crops, as yellow crystalline needles; yield 12.57 g (73.2%). C, H, N analysis: found C 32.61, H 3.89, N 1.79%; calcd C 32.56, H 4.10, N 1.73%; $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ = 7.22 (d, 2H, *o*-H, NPh), 7.10 (t, 2H, *m*-H, NPh), 6.76 (t, 1H, *p*-H NPh), 2.57 (d, 2H, $^2J(H_a,H_b)$ = 7.5 Hz, $^2J(W,H)$ = 5.1 Hz, $CH_aH_bSi$), 2.28 (d, 2H, $^2J(H_a,H_b)$ = 7.5 Hz, $^2J(W,H)$ = 5.0 Hz, $CH_aH_bSi$), 1.87 and 1.37 (2s, 6H, 2 × OCMe), 0.09 (s, 18, $SiMe_3$).

**2**: A green solution of [W(=NPh)$Cl_4$·$OEt_2$] (8.98 g, 18.29 mmol) in $CH_2Cl_2$ (60 mL) was treated with powdered $NEt_4Cl$ (3.20 g, 19.31 mmol) and stirred for 30 min. The resulting green suspension was cooled to 0 °C, and a solution of [Zn$(CH_2SiMe_3)_2$] (6.58 g, 27.44 mmol) in $CH_2Cl_2$ (25 mL) was added dropwise within 15 min. Upon addition the color of the reaction mixture changed immediately to light brown. The reaction mixture was then stirred for an additional hour. The volatiles were removed in vacuo leaving a sticky light-brown solid. The crude product was extracted with pentane (2 × 60 mL). The combined pentane fractions were concentrated to ca. 50 mL and stored at −30 °C. The pure product was obtained as off-white crystals in 85% yield. C,H,N analysis: found C 37.91, H 6.80, N 2.40%; calcd C 37.79, H 6.70, N 2.45%; $^1$H NMR (250 MHz, $C_6D_6$): $\delta$ = 7.43 (d, 2H, *o*-H, NPh), 7.09 (t, 2H, *m*-H, NPh), 6.89 (t, 1H, *p*-H, NPh), 2.17 (s, 6H, $^2J(W,H)$ = 4.3 Hz, $CH_2Si$), 0.20 (s, 27H, $SiMe_3$).

Photo-DSC experiments were carried out at room temperature using a Perkin-Elmer DSC-7 equipped with a Perkin-Elmer DPA-7 light unit. The light source was a 200 W Hg/Xe lamp with 2.5 mW$cm^{-2}$ power. Samples of 1% **1** or **2** in DCPD containing 5% octane were transferred in a sapphire cell under a flow of argon.

Viscosity measurements were performed with a real-time viscosity apparatus of our own construction. Samples of 1% **1** or **2** in DCPD containing 5% octane were heated or irradiated in a pyrex or quartz test tube under a flow of argon while the viscosity was measured every minute. Irradiation was carried out using a 200 W Hg lamp.

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[1] a) R. H. Grubbs in *Comprehensive Organometallic Chemistry, Vol. 8* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, New York, **1982**. b) K. J. Ivin, *Olefin Metathesis*, Academic, London, **1983**. c) R. R. Schrock, *Acc. Chem. Res.* **1990**, *23*, 158.

[2] J. L. Herisson, Y. Chauvin, *Makromol. Chem.* **1970**, *141*, 161.

[3] The term "alkylidene complex" is commonly used for a complex distinguished by a double bond between a high-valent metal and carbon; according to IUPAC nomeclature these complexes are "metallaolefins".

[4] R. R. Schrock, *J. Am. Chem. Soc.* **1974**, *96*, 6796.

[5] J. Feldman, R. R. Schrock, *Prog. Inorg. Chem.* **1991**, *39*, 1.

[6] a) C. D. Wood, S. J. McLain, R. R. Schrock, *J. Am. Chem. Soc.* **1979**, *101*, 3210. b) L. R. Chamberlain, A. P. Rothwell, I. P. Rothwell, *ibid.* **1984**, *106*, 1847. c) M. D. Fryzuk, P. A. MacNeil, S. R. Rettig, *ibid.* **1985**, *107*, 6708. d) M. D. Fryzuk, X. Gao, K. Joshi, P. A. MacNeil, R. L. Massey, *ibid.* **1993**, *115*, 10581. e) J. Kress, M. Wesolek, J.-P. Le Ny, J. Osborn, *J. Chem. Soc. Chem. Commun.* **1981**, 1039. f) D. B. Pourreau, G. L. Geoffroy, *Adv. Organomet. Chem.* **1985**, *24*, 249. g) L. R. Chamberlain, I. P. Rothwell, *J. Chem. Soc. Dalton Trans.* **1987**, 155; *ibid.* **1987**, 163.

[7] A few examples of polymerization reactions are described in which solutions of [Mo$(CO)_6$] or [W$(CO)_6$] salts in $CCl_4$ are irradiated to initiate polymerization reactions: a) B. Gita, G. Sundararajan, *Tetrahedron Lett.* **1993**, *34*, 6123. b) K. Tamura, T. Masuda, T. Higashimura, *Polym. Bull.* **1994**, *32*, 289.

[8] Our initial work in the field of photo-ROMP was based on the photosolvation of bis(arene)$Ru^{II}$ salts to form the active $[Ru(H_2O)_6]^{2+}$ catalyst: T. Karlen, A. Ludi, A. Mühlebach, P. Bernard, C. Pharisa, *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 1665; A. Mühlebach, P. Bernard, A. Hafner, T. Karlen, A. Ludi, WO-P 95 07,310 [*Chem. Abstr.* **1993**, *123*, 287151].

[9] N. Bühler, D. Belluš, *Pure Appl. Chem.* **1995**, *67*, 25.

[10] A. Hafner, P. A. Van der Schaaf, A. Mühlebach, WO-P 95 14,051 [*Chem. Abstr.* **1993**, *123*, 314873].

[11] Crystals were grown by cooling a saturated hexane solution to −30 °C; crystal size 0.7 × 0.4 × 0.2 mm; monoclinic, space group $P2_1/c$; $Z = 4$; $a = 9.913(3)$, $b = 16.956(5)$, $c = 18.755(6)$ Å, $\beta = 102.34(2)°$; $V = 3082.9$ Å$^3$, $\rho_{calcd} = 1.748$ g$cm^{-3}$; $2\theta = 6-130°$ ($Cu_{K\alpha}$, $\lambda = 1.5418$ Å, graphite monochromator, $2\theta-\theta$ scan, $T = 188$ K); 5768 reflections measured, 4885 observed $[F > 3\sigma > (F)]$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-82. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

[12] An example: irradiation of **1** in the presence of 3,4-dimethoxybenzaldehyde yielded trimethyl[2-(3,4-dimethoxyphenyl)ethenyl]silane (the product of a Wittig-like reaction) in 84% yield with an *E*/*Z* ratio of 1. A complete study on this subject will be published.

[13] Reaction with 100 equivalents of norbornene with **1** and **2** yielded ring-opened polynorbornene quantitatively with 85 and 50% *cis*-configurated double bonds, respectively. Polymerization of a 1% solution of **1** in neat DCPD gave a material with properties typical of metathesis-polymerized DCPD. $T_g$: 130 °C (after postcure at 120 °C for 30 min), E-modulus: 1920 MPa, crosslink density (from swelling in toluene): ca. 0.4%, weight loss (TGA, 10 °C$min^{-1}$, 20–300 °C): 3.0%).