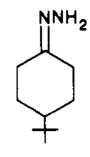

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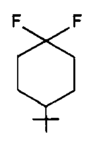

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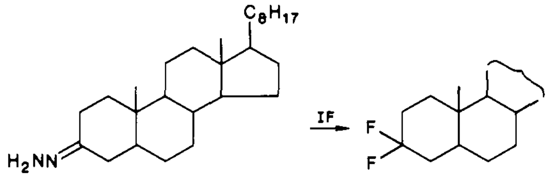

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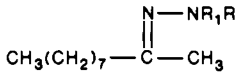


$CH_3(CH_2)_7C(=NNR_1R_2)CH_3$

9: $R_1 = R_2 = H$
13: $R_1 = H$; $R_2 = Me$
14: $R_1 = R_2 = Me$

$CH_3(CH_2)_7CF_2CH_3$
12

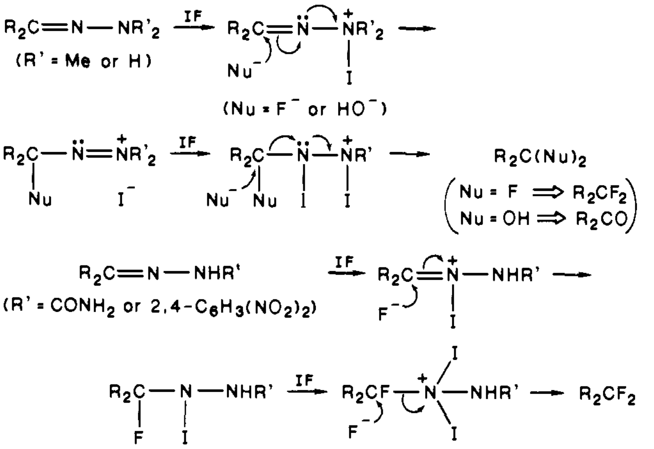
turned our attention to some stable crystalline derivatives such as semicarbazones and (2,4-dinitrophenyl)hydrazones (DNP). These derivatives of acetophenone (**15** and **16**) and of 2-decanone (**17** and **18**) were prepared in practically quantitative yields and

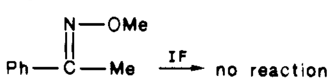
PhC(=NNHR)Me
15: R = $CONH_2$
16: R = 2,4-$C_6H_3(NO_2)_2$

$CH_3(CH_2)_7C(=NNHR)CH_3$
17: R = $CONH_2$
18: R = 2,4-$C_6H_3(NO_2)_2$

reacted with IF. No difluoro derivatives were detected at −78 °C, but after gradual warming and additional stirring for 3–4 h at room temperature the expected *gem*-difluoro products **6** and **12** were obtained, although in yields about 20% lower than the ones obtained with the corresponding unsubstituted hydrazones.

Unlike the mechanisms for the iodination[10] or fluorination[4b] of hydrazones which call for an attack on the NH_2 end of the hydrazone, such an attack would be unfavorable in the case of semicarbazones or DNP's and much slower for the *N*-alkyl ones. We propose the two following schemes for the two different types of hydrazones, based on the differences of the nitrogens' basicity. The key starting step should be the attack of the positive iodine on the more basic nitrogen.





19

In agreement with this mechanism, when a competing nucleophile such as water or alcohols is present, considerable amounts of the corresponding ketone are also formed. This scheme is also in agreement with the fact that when the second nitrogen is either more hindered (R′ = Me) or less basic (NHCOR′) than the imine one, the reaction is slower compared to the unsubstituted hydrazones. The initial reaction must be at low temperatures, at least −40 °C, since above this IF disproportionates mainly to IF_3 and IF_5. These reagents do not possess easily available electrophilic iodine as in IF, giving further support for the initial intervention of electrophilic iodine. Since, however, the slowest step should be the C–N bond cleavage assisted by the nucleophilic fluorine, the subsequent raising of the temperature can only facilitate the reaction. It is also worth noting that when the basicity is low as in the case of the oxime ether **19**, no reaction takes place even after 24 h at room temperature.

In conclusion, this general method can be a very good alternative to the conventional one based on SF_4, eliminating the need for the drastic reaction conditions which this expensive and toxic reagent requires.

Acknowledgment. We thank the Fund for Basic Research, administrated by the Israel Academy of Science and Humanities, for supporting this research.

Registry No. 1, 5350-57-2; **2**, 5171-96-0; **3**, 13466-30-3; **4**, 360-11-2; **5**, 350-62-9; **6**, 657-35-2; **7**, 62082-37-5; **8**, 106094-56-8; **9**, 105232-57-3; **10**, 19422-34-5; **11**, 16319-73-6; **12**, 106094-57-9; **13**, 106094-58-0; **14**, 106094-59-1; **15**, 2492-30-0; **16**, 1677-87-8; **17**, 3622-72-8; **18**, 2675-17-4; **19**, 3376-33-8; IF, 13873-84-2.

First Absolute Rate Constants for Some Hydrogen Atom Abstractions and Addition Reactions of an Aroyloxyl Radical: 4-Methoxybenzoyloxyl[1]

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Aroyloxyl radicals are the last major class of reactive organic free radicals for which there are no absolute rate data.[2] We were unsuccessful in a recent attempt to measure absolute rate constants for benzoyloxyl radicals by laser flash photolysis (LFP).[3] After our work was complete, an exciting report appeared[4] that LFP (308 nm) of certain diaroyl peroxides in CCl_4 solution yielded the corresponding aroyloxyl radicals which were detected by time-resolved EPR spectroscopy. Since 4-methoxybenzoyloxyl had the longest lifetime (1.6 μs) we decided to apply LFP (308 nm) to a 10^{-2} M solution of bis(4-methoxybenzoyl) peroxide in CCl_4 at 24 °C using optical detection. Three distinct transient species were observed (see Figure 1). The transient that possesses a broad, structureless absorption in the visible region with the intensity steadily increasing from 500 to 800 nm (monitored at 720 nm throughout this work) we identify as $4\text{-}CH_3OC_6H_4CO_2^\bullet$ for the following reasons:

(i) The 720-nm absorption is produced "instantaneously" (≤4 ns, the full width at half-height of the laser pulse); i.e., there is no observable "grow-in" of this signal.

(ii) The 720-nm absorption decays with (pseudo)-first-order kinetics, $k_{exp} = 6.8 \pm 0.2 \times 10^5\ s^{-1}$, and the lifetime of this transient ($\tau \approx 1.4$ μs) is the same in N_2-, air-, and O_2-saturated solutions.

(iii) The 720-nm absorption can be "quenched", i.e., decays more rapidly, in the presence of H-atom donors and compounds to which $4\text{-}CH_3OC_6H_4CO_2^\bullet$ might be expected to add. Bimolecular rate constants, *k*, for the overall reaction (i.e., abstraction and addition) of this radical with the added substrate (see Table I) can be calculated from these pseudo-first-order decays, i.e., k_{exp}

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[1] Issued as NRCC No. 26599.

[2] For a comprehensive survey of absolute kinetic data for organic radicals in solution, see: *Landolt-Börnstein. New Series. Radical Reaction Rates in Liquids*; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13, Parts a–e. See, in particular: Scaiano, J. C.; Howard, J. A., Part d, pp 127–141.

[3] Grossi, L.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1985**, *50*, 5882–5885.

[4] Yamauchi, S.; Hirota, N.; Takahara, S.; Sakuragi, H.; Tokumaru, K. *J. Am. Chem. Soc.* **1985**, *107*, 5021–5022.

0002-7863/87/1509-0897$01.50/0 Published 1987 by the American Chemical Society

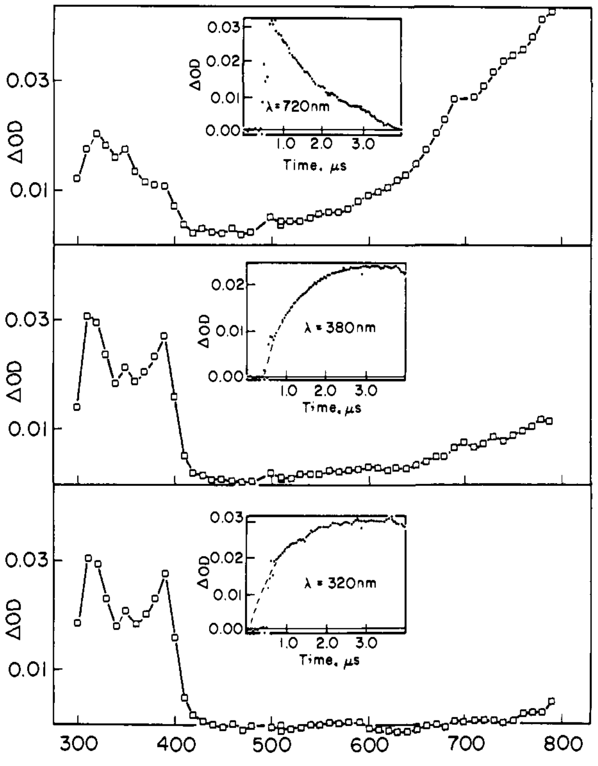

Figure 1. UV-visible time-resolved spectra obtained 80 (top), 2000 (middle), and 3200 ns (bottom) after 308-nm excitation of a 10^{-2} M solution of bis(4-methoxybenzoyl) peroxide in CCl_4. Inserts represent typical decay and growths of absorptions at 720, 380, and 320 nm, respectively.

Table I. Rate Constants for the Reactions of 4-Methoxybenzoyloxyl Radicals at 24 °C in CCl_4

source[a]	substrate	$k/M^{-1}\,s^{-1}$ [b]
PO	PO[a]	$(3.64 \pm 0.60) \times 10^7$
PO	cyclohexane	$(5.28 \pm 0.30) \times 10^5$
PE	cyclohexane	$(1.45 \pm 0.30) \times 10^6$
PO	cyclohexene	$(6.40 \pm 0.32) \times 10^7$
PE	cyclohexene	$(5.25 \pm 1.72) \times 10^7$
PO	1,3-cyclohexadiene	$(4.76 \pm 0.22) \times 10^8$
PE	1,3-cyclohexadiene	$(5.42 \pm 0.96) \times 10^8$
PO	1,4-cyclohexadiene	$(1.45 \pm 0.13) \times 10^8$
PE	1,4-cyclohexadiene	$(2.92 \pm 0.70) \times 10^8$
PO	triethylsilane	$(4.80 \pm 0.12) \times 10^6$
PE	triethylsilane	$(9.20 \pm 1.08) \times 10^6$
PO	benzene	$(2.32 \pm 0.17) \times 10^6$
PO	styrene	$(8.03 \pm 0.90) \times 10^7$

[a] PO = bis(4-methoxybenzoyl) peroxide; PE = *tert*-butyl perester of 4-methoxybenzoic acid. [b] Total rate constant for reaction, including all possible paths and sites of attack; errors represent 95% confidence limits.

$= k_0 + k$[substrate], where k_0 corresponds to all first-order and pseudo-first-order reactions of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ at zero substrate concentration.

(iv) The 720-nm absorption can also be "instantaneously" generated by LFP (308 nm) of a 10^{-2} M solution of $4\text{-}CH_3OC_6H_4CO_3C(CH_3)_3$ in CCl_4. At 24 °C, decay of this 720-nm transient occurs with $k_{exp} = (5.57 \pm 0.33) \times 10^5\ s^{-1}$ ($\tau = 1.76$ μs). Furthermore, this decay rate is not changed by oxygen saturation of the solution.

(v) Bimolecular rate constants calculated for a variety of substrates by monitoring the 720-nm band derived from the perester (PE) are equal within experimental error[5] to those derived from the diaroyl peroxide (PO) (see Table I).

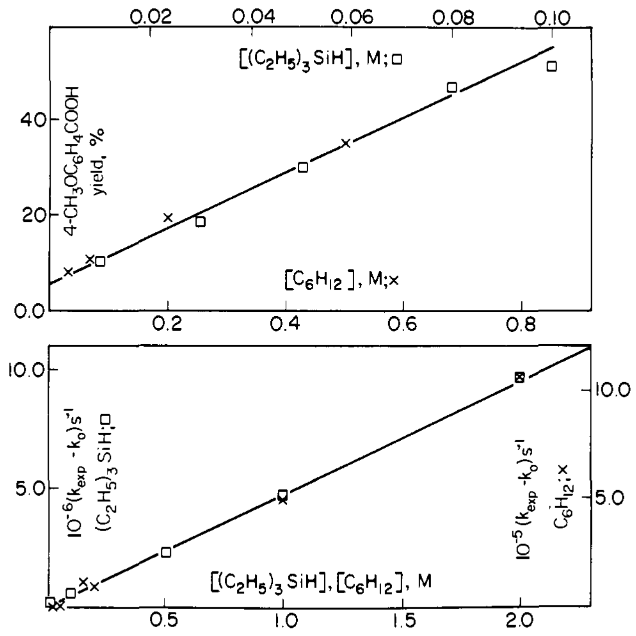

Figure 2. Relative reactivity of triethylsilane (□) and cyclohexane (×) toward the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ radical. Top: yields of $4\text{-}CH_3OC_6H_4CO_2H$ on photolysis to complete decomposition of 10^{-4} M $(4\text{-}CH_3C_6H_4CO_2)_2$ in CCl_4 with added H-donor (scaling factor = 8.5). Bottom: effect of H-donor concentration on $k_{exp} - k_0$ (scaling factor = 9.1).

(vi) Transient absorptions with very similar intensity patterns in the 500–800-nm region are also "instantaneously" generated by LFP (308 nm) of $(C_6H_5CO_2)_2$ and $(4\text{-}ClC_6H_4CO_2)_2$.[6] These absorptions are weaker than those produced by LFP of $(4\text{-}CH_3OC_6H_4CO_2)_2$ under comparable conditions. Nevertheless, we assign them to $C_6H_5CO_2^{\bullet}$ and $4\text{-}ClC_6H_4CO_2^{\bullet}$ because their lifetimes, using 10^{-2} M peroxide in nitrogen-saturated CCl_4 at 24 °C [which are 0.22 μs (cf. 0.25 μs[4]) and 0.64 μs (cf. 0.72 μs[4]), respectively], were unchanged when the solution was saturated with oxygen.

(vii) McBride et al.[7] have reported that irradiation of a crystal of acetyl benzoyl peroxide containing $C_6H_5CO_2^{\bullet}/CH_3^{\bullet}$ radical pairs at 67 K with an incandescent lamp causes quantitative conversion of this radical pair to the $C_6H_5^{\bullet}/CH_3^{\bullet}$ radical pair. The rate of this conversion was studied as a function of wavelength in the range 550–1300 nm and the efficiency per incident quantum was found to be maximal at 750 nm.

We conclude that a broad absorption in the 500–800-nm region is characteristic of aroyloxyls.

Further confirmation that we are actually monitoring reactions of the $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ was obtained by preparative photolysis of 10^{-4} M $(4\text{-}CH_3OC_6H_4CO_2)_2$ in CCl_4 containing either cyclohexane or triethylsilane.[8,9] To obtain the same yield of $4\text{-}CH_3OC_6H_4CO_2H$ required approximately 8.5 times higher concentration of cyclohexane than of triethylsilane (Figure 2, top). This ratio is in good agreement with the ratio of the absolute rate constants for reaction with triethylsilane and cyclohexane, viz., $(4.80 \times 10^6)/(5.28 \times 10^5) = 9.1$ (Figure 2, bottom).

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(5) Kinetic data with PE are less precise because 0.1 M PE is required to obtain a 720-nm band of reasonable strength. This shortens the transient's lifetime.

(6) Preliminary LFP experiments with peroxydicarbonates, $(ROCO_2)_2$, and *tert*-butyl peroxycarbonates, $ROCO_3CMe_3$, suggest that $ROCO_2^{\bullet}$ radicals exhibit generally similar spectroscopic (broad absorption, $\lambda_{max} \sim 600\text{–}700$ nm) and kinetic properties.

(7) Karch, N. J.; Koh, E. T.; Whitsel, B. L.; McBride, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 6729–6743. See also: McBride, J. M.; Merrill, R. A. *Ibid.* **1980**, *102*, 1723–1725. Whitsel, B. L. *Diss. Abstr. Int. B* **1978**, *38*, 3203-B.

(8) At higher peroxide concentrations $4\text{-}CH_3OC_6H_4CO_2H$ is formed by reaction of $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ with the starting peroxide and its decomposition products.

(9) The choice of H-atom donors for this experiment was limited because $4\text{-}CH_3OC_6H_4CO_2^{\bullet}$ adds readily to C=C double bonds. Addition competes with H-atom abstraction even with such good H-donors as cyclohexene and 1,4-cyclohexadiene.

The two additional transient absorptions at 320 and 380 nm are derived from 4-$CH_3OC_6H_4CO_2^\bullet$ since they "grow-in" after the laser pulse at the same rate at which the 720-nm absorption decays. They can therefore be used as "probes"[10] to measure the rate constants for reactions of 4-$CH_3OC_6H_4CO_2^\bullet$, though it is generally simpler to monitor the decay of the 720-nm band. The nature of the radicals responsible for these two transients will be discussed in the full paper.

Measurements of the rate of decay of 4-$CH_3OC_6H_4CO_2^\bullet$ at different $(4\text{-}CH_3OC_6H_4CO_2)_2$ concentrations yields both k[PO] and k_0. Any contributions to k_0 from pseudo-first-order reactions is, of course, due to reactions with impurities in the solvent. We obtained values for k_0 of $3.4 \pm 0.1 \times 10^5$ s^{-1} in Aldrich gold-label CCl_4 and ca. 4.4×10^5 s^{-1} in $CF_2ClCFCl_2$. (The latter value is less reliable because of the lower solubility of the peroxide in Freon.) We identify these k_0 values with the decarboxylation process

$$4\text{-}CH_3OC_6H_4CO_2^\bullet \rightarrow 4\text{-}CH_3OC_6H_4^\bullet + CO_2 \qquad (1)$$

Our "best" value for k_1 of 3.4×10^5 s^{-1} at 24 °C is in excellent agreement with a value of 2.7×10^5 s^{-1} at the same temperature which can be calculated from our absolute rate constant for reaction with styrene (Table I) and data given by Bevington et al.[11] for the competition between reaction 1 and the addition of 4-$CH_3OC_6H_4CO_2^\bullet$ to styrene. This agreement provides further confirmation that we have correctly identifed the 4-methoxybenzoyloxyl radical.

We are currently attempting to measure absolute rate constants for reactions of $C_6H_5CO_2^\bullet$ and other aroyloxyl radicals.

Acknowledgment. We thank Dr. J. C. Scaiano for helpful discussions and for the use of his LFP equipment.

Registry No. H_2, 1333-74-0; 4-methoxybenzoyloxyl, 33574-06-0; cyclohexane, 110-82-7; cyclohexene, 110-83-8; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; triethylsilane, 617-86-7; benzene, 71-43-2; styrene, 100-42-5.

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(10) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

(11) Bevington, J. C.; Toole, J.; Trossanelli, L. *Trans. Faraday Soc.* **1958**, *54*, 863–867.

First Direct Observation of the Simultaneous Presence and of the Interconversion of Chain-Propagating Metal–Carbene and Metallacyclobutane Complexes in a Catalytic Olefin Metathesis Reaction: The Ring-Opening Polymerization of Norbornene

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Received June 23, 1986

The central step of the catalytic olefin metathesis reaction is known to consist of the reversible [2 + 2] addition of an olefin to a metal–carbene complex to form a metallacyclobutane compound.[1] Examples of both structural types have been synthesized which effectively catalyze such reactions,[2-7] but, although the propagating metal–carbene[2-6] or metallacyclobutane[7] intermediates derived from these two types of initiators have been observed and even isolated and well characterized in a few cases, their *simultaneous* presence and thus their *interconversion* in the course of a metathesis reaction has never been directly established.

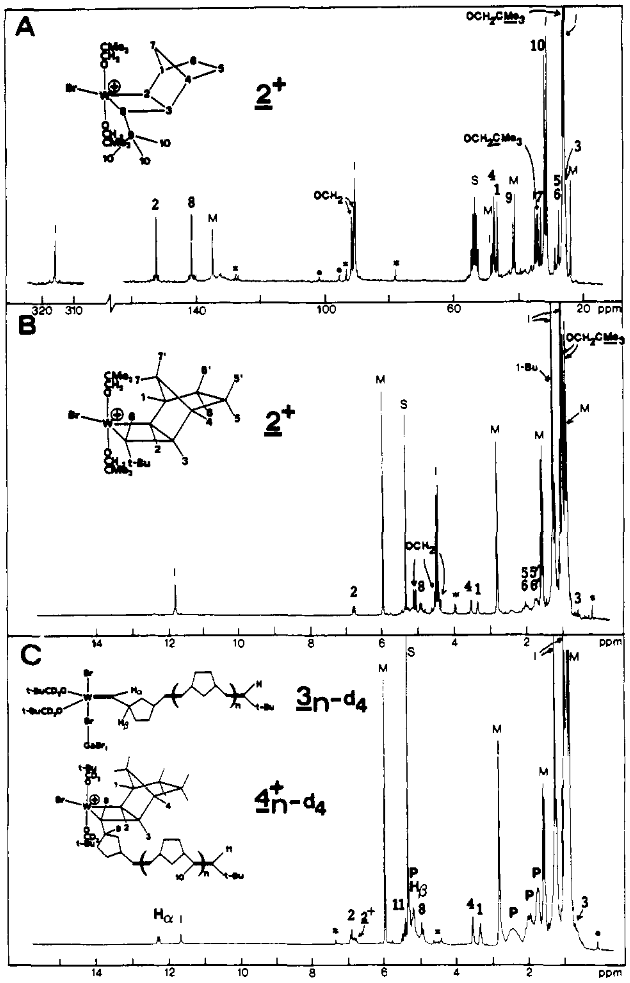

Figure 1. (A) $^{13}C[^1H]$ NMR spectrum, 50 MHz, at 205 K of the reaction mixture obtained after addition of ca. 1.5 equiv of NBE to a solution of 620 mg of $W(CH\text{-}t\text{-}Bu)(OCH_2\text{-}t\text{-}Bu)_2Br_2\cdot GaBr_3$ (**1**·$GaBr_3$) at 190 K in 2.0 mL of CD_2Cl_2 and 20 min of average reaction time at 205 K. (B) ^1H NMR spectrum, 200 MHz, at 220 K of the reaction mixture obtained after addition of ca. 2 equiv of NBE to a solution of 10 mg of **1** and 0.7 equiv of $GaBr_3$ at 190 K in 0.4 mL of CD_2Cl_2 and 1 h of reaction time at 220 K. (C) ^1H NMR spectrum, 200 MHz, at 235 K of the reaction mixture obtained after addition of ca. 4 equiv of NBE to a solution of 11 mg of $W(CH\text{-}t\text{-}Bu)(OCD_2\text{-}t\text{-}Bu)_2Br_2$ (**1**-d_4) and 0.9 equiv of $GaBr_3$ at 190 K in 0.4 mL of CD_2Cl_2, 1 h and 30 min of reaction time at 220 K and 30 min of reaction time at 235 K. Peaks arising from residual **1** and NBE monomer, from the solvent, the NBE polymer chain, and from impurities are marked respectively with I, M, S, P, and *.

In the course of our study of the tungsten–carbene compound $W(CH\text{-}t\text{-}Bu)(OCH_2\text{-}t\text{-}Bu)_2Br_2$ (**1**), an extremely active catalyst for the metathesis of olefins in the presence of $GaBr_3$, we reported the observation of the chain carrying tungsten–carbene species derived from **1** on addition of various olefins at room temperature.[2-5] Bicyclo[2.2.1]hept-2-ene (norbornene, NBE), in particular,

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[‡] The Queen's University of Belfast.

(1) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983.

(2) Kress, J.; Wesolek, M.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 514.

(3) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6346.

(4) Aguero, A.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 793.

(5) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1985**, 874; unpublished results including molecular weight determinations on resultant polymers after successive additions of monomer as well as the synthesis of block copolymers.

(6) Schrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249 and references therein.

(7) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733 and references therein.