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Photoinitiation of Acrylate Polymerization with (Arene)chromium Complexes

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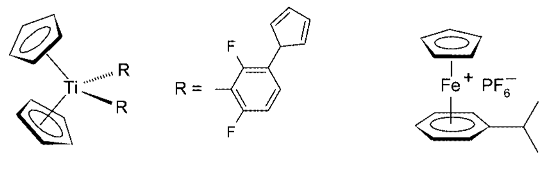
Photoinitiation of acrylate polymerization by [Cr(η^6-arene)(CO)$_3$] complexes in the presence of an organic chloro compound was investigated. For the bimolecular system, a good correlation between activity and metal–arene and metal–carbonyl bond strength was observed. The highest efficiency was found for an initiator in which the organic chloro compound was tethered to the complexed arene: [Cr(η^6-$C_6H_5CH_2OCOCCl_3$)(CO)$_3$]. The initial steps of the photoinitiation were probed and provided evidence for metal–arene bond cleavage in an Cr(η^2-acrylate)(η^6-arene)(CO)$_2$ complex. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

Photoinitiated polymerization, commonly termed radiation curing, is an important industrial process employed for the fabrication of a wide variety of products ranging from floor coatings to integrated circuit boards. Among the advantages of this technology are lower energy costs and the concomitant reduction in the use of organic solvents, issues of ever-increasing importance.[1]

One of the key elements in a radiation-curable system is the photoinitiator.[2] Most of the commercially available photoinitiators are organic compounds which absorb in the UV and near-UV regions of the electromagnetic spectrum. Prompted by a potential further reduction in energy costs through the use of standard light sources and the increased availability of visible-light lasers which are required for technically advanced applications, efforts to develop photoinitiators sensitive to visible light have multiplied. In this domain, transition-metal organometallic chemistry offers special opportunities, as most organometallic compounds absorb in the visible region because of the partial occupation of the metal d orbitals. In addition, the absorption characteristics of such complexes can be manipulated by modifying the nature of the metal-bound ligands.[2] The commercialization of two organometallic photoinitiators, Irgacure 784, a titanocene suitable for the polymerization of acrylate-based systems with the argon laser, and Irgacure 261, a ferrocenium salt which provides a Lewis acid upon irradiation and is used to cure epoxy resins, attest to the viability of this approach.[3,4]



Irgacure 784

Irgacure 261

The photochemistry of a large number of organometallic compounds under varying conditions has been investigated, and, in some cases, the generation of radicals or acidic species has been observed.[3,5] One well-documented example is the combination of carbonylmetal complexes with carbon tetrachloride, which serves to photoinitiate the polymerization of acrylates via the production of the trichloromethyl radical. Whereas the initial work of Bamford and coworkers concentrated on the homoleptic carbonylmetal complexes, decacarbonyldimanganese and decacarbonyldirhenium,[6] it was later extended to include organometallic derivatives of manganese[7] and (arene)tricarbonylchromium complexes.[8]

An abbreviated version of the mechanism of radical production proposed by Bamford for the bimolecular photoinitiator composed of (benzene)tricarbonylchromium (**1**) and carbon tetrachloride is shown in Scheme 1. Irradiation of **1** in the presence of methyl methacrylate (mma) is presumed to give rise to an exciplex of the acrylate and **1**, which undergoes further transformation to the (mma)chromium complexes **2** and **3**. The former, being at best a 16-electron complex when one assumes coordination of both the double bond and the ketone of mma to the metal, can interact directly with carbon tetrachloride and thereby provide an initiating trichloromethyl radical and, formally, a chromium(I) species. In the case of complex **3**, ligand dissociation, which also occurs in the dark but is greatly accelerated by irradiation, must precede radical generation, unless, of course, through-space electron transfer can occur. Accord-

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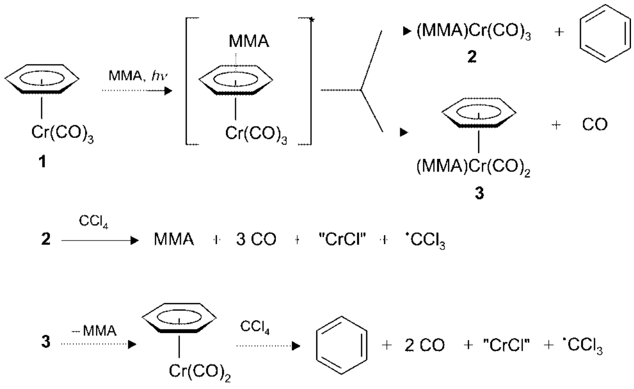
ing to this mechanism, the formation of one initiating radical is accompanied by the liberation of one molecule of arene. Indeed, this is observed experimentally in that the quantum yield for decomposition of the arene complex is indistinguishable from the quantum yield for initiation of polymerization. In addition, these quantities are dependent on the nature of the arene complex: the stronger the arene–chromium bond, the slower the rate of polymerization (and decomposition).



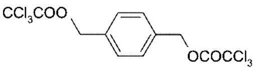
Scheme 1. Mechanism proposed by Bamford for the photoinitiation of methyl methacrylate (MMA) polymerization in the presence of [Cr(benzene)(CO)$_3$] (**1**)/CCl$_4$.[6]

A major drawback of the (arene)tricarbonylchromium/carbon tetrachloride photoinitiator system, from an industrial viewpoint, is the use of the highly volatile and carcinogenic carbon tetrachloride as coinitiator. Furthermore, the intermolecular nature of the radical production requires the use of a great excess of this component. One approach toward the resolution of both of these problems is to attach a functional group capable of producing radicals upon reduction directly to chromium. In addition to decreasing the volatility of the system, the presence of an intramolecularly bound coinitiator should lead to an increase in photoinitiator activity, since a high effective concentration of the coinitiator in the vicinity of the metal is assured. We have analyzed this approach and now report our results on the design, synthesis, and reactivity of a new class of unimolecular organometallic photoinitiators.

Results and Discussion

Bimolecular Photoinitiators

Initial work was aimed at the identification of an appropriate substitute for carbon tetrachloride which would exhibit similar reactivity in the presence of (benzene)tricarbonylchromium (**1**). On the basis of literature reports of the photoinitiator activity of decacarbonyldimanganese and ethyl trichloroacetate,[9] and the crosslinking of poly(vinyl trichloroacetate) with this carbonylmetal complex,[9a,10] phenalkyl trichloroacetates were targeted as potential coinitiators. The presence of a phenyl group was desired in order to allow introduction of the tricarbonylchromium moiety by using well-documented methodology.[11,12]



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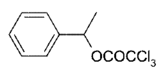

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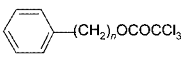


6, $n = 1$
7, $n = 2$

Synthesis of the trichloroacetates **4**–**7** was carried out by the reaction of the corresponding alcohols with trichloroacetyl chloride and pyridine in dichloromethane.[13] The coinitiator activity of these acetates in the presence of **1** was assessed under typical industrial conditions. The photoinitiator system to be tested was added to a clear lacquer consisting of a mixture of polyfunctional acrylates and vinylpyrrolidinone (for details, see Exp. Sect.). A 60–70-µm layer of the resulting formulation was applied to a sheet of aluminum, then covered first with a polyester foil and finally with a 21-step optical wedge. The sample was then placed at a distance of 30 cm from a 4-kW Xenon lamp and irradiated for 20 s. The reactivity of the various photoinitiator combinations, quantified as the number of completely hardened (cured) steps after development in ethanol, is shown in Figure 1. It should be noted at this point that a difference of two steps corresponds to a twofold increase in reactivity; i.e., the transmittance of light at step 1 is two times that at step 3. It is evident that even **1** alone is a photoinitiator, albeit of very low activity (step 0, which is 100% transparent, is cured). Given the fact that dissolved oxygen is present in the formulation and that one component of the formulation contains hydroxy groups (dipentaerythritol monohydroxypentacrylate), the unimolecular photoinitiator activity of the complexes may be due to oxidative ligand exchange rather than radical polymerization of the acrylate units. Wagner and Purbrick[14] previously reported that **1** promotes the photochemical crosslinking of polymers containing pendant hydroxy groups in the presence of oxygen. The formation of O–Cr^{III} bonds between polymer molecules was suggested to account for this observation (Scheme 2).

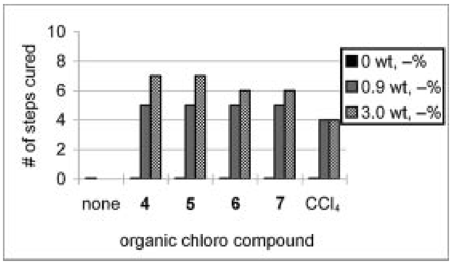
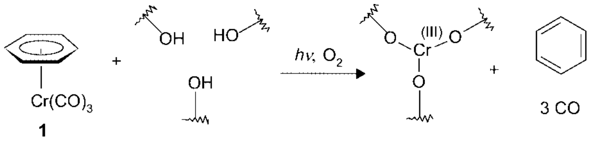


Figure 1. Reactivity of 0.3 wt.-% **1** in the presence of organic chlorides **4**–**7** and CCl$_4$ (0, 0.9, and 3.0 wt.-%) in a clear lacquer. 20-s irradiation with a 4-kW Xenon lamp through a 21-step optical wedge.

The addition of an organic chloro compound results in a substantial increase in activity. The most efficient coinitiators are the bis(trichloroacetate) **4** and 2-phenethyl trichloroacetate (**5**). They are 1.5 to 3 times more reactive than carbon tetrachloride over the concentration range studied (increase of 1–3 cured steps, Figure 1). The increased reactivity of the trichloroacetates can be ascribed to the forma-



Scheme 2. Formation of Cr^{III} species from the reaction of **1** with polymers containing pendant hydroxy groups in the presence of oxygen.

tion of a resonance-stabilized α-carbonyloxy radical. In the absence of **1**, all the trichloroacetates as well as carbon tetrachloride were inactive. As expected from the work of Bamford discussed previously, enhanced reactivity is observed for all the trichloroacetates when **1** is replaced with the chlorobenzene complex **8**, which has a weaker chromium–arene bond (Figure 2). In this case, however, trichloroacetates **4**, **6**, and **7** are twice as effective as **5** (increase of 2 cured steps). Surprisingly, carbon tetrachloride exhibits more or less the same coinitiator activity with both complexes. This may indicate that the rate-determining step in the case of carbon tetrachloride is its reaction with the active chromium species to provide the trichloromethyl radical rather than the generation of the latter from **1** or **8**.

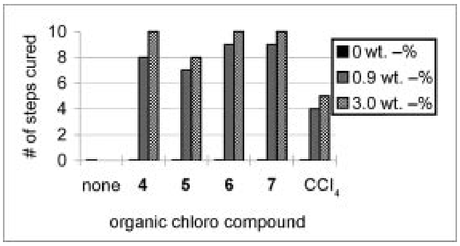
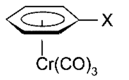
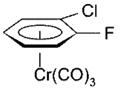


Figure 2. Reactivity of 0.3 wt.-% **8** in the presence of organic chlorides **4**–**7** and CCl$_4$ (0, 0.9, and 3.0 wt.-%) in a clear lacquer. 20-s irradiation with a 4-kW Xenon lamp through a 21-step optical wedge.

It is apparent from the order of reactivity that neither the nature of the tether between the phenyl and trichloroacetate groups nor the number of trichloroacetate groups per molecule has a significant effect on the rate of polymerization.



8, X = Cl **9**, X = F
10, X = CF$_3$ **11**, X = COCH$_3$
12, X = OCH$_3$



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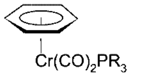


14, R = OPh
15, R = Ph

At this point, the influence of the arene substituent of the chromium complex upon its activity in the presence of **4** was investigated. Other than **13**, which was obtained via lithiation of **9** followed by treatment with hexachloroethane,[15] all complexes were prepared by direct ligand exchange in hexacarbonylchromium [11] or tricarbonyl(naphthalene)chromium.[16] With the exception of **14**, which can cure 2 steps, crosslinking of the formulation is negligible when the complexes are employed alone (at 100% transmittance, 0 steps). The superior photoinitiator activity of **14** may be connected to the lower oxidative stability of the 16-electron chromium fragment resulting from loss of carbon monoxide. In contrast, the phosphane complex **15**, which could formally yield a similar unsaturated fragment, does not undergo direct photodissociation of carbon monoxide.[17] When **4** is present, the highest reactivity is observed for the halogenated complexes **13** and **9** (9 steps). In general, complexes containing one electron-withdrawing group exhibit higher reactivity than that of the parent benzene complex **1**. The anisole complex **12** is about as active as **1**, whereas the phosphane- and phosphite-substituted complexes **14** and **15** are less reactive than **1** (Figure 3).

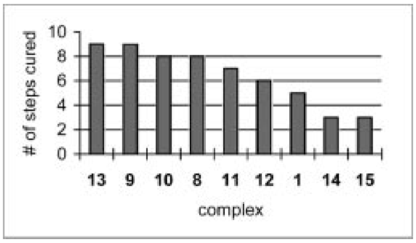


Figure 3. Reactivity of 0.9 wt.-% **4** and 0.3 wt.-% [Cr(arene)(CO)$_3$] complexes in a clear lacquer. 20-s irradiation with a 4-kW Xenon lamp through a 21-step optical wedge.

The results obtained with the (arene)tricarbonylchromium complexes are in accord with those of Bamford: reactivity increases with decreasing arene–chromium bond strength. Although the absolute bond strengths of all the complexes employed in this study are not reported in the literature, the bond strengths are directly related to the energy of the HOMOs of the complexes and, in turn, their oxidation potentials and their carbonyl stretching frequencies.[18] In fact, very good correlation is obtained between νCO and the number of steps cured. A higher carbonyl stretching frequency, indicative of a lower M–CO bond strength, results in higher reactivity. As proposed by Bamford, this can be explained by the more facile substitution of the arene or CO by acrylate, thus leading to higher concentrations of the active intermediates **2** and **3** (Scheme 1). It should be noted, however, that the photochemical generation of species related to **2** from (arene)tricarbonylchromium is not expected to be an important pathway as irradiation of (arene)tricarbonylchromium leads almost exclusively to loss of CO.[17a]

The effect of substituting a carbonyl ligand of **1** with phosphane or phosphite is a marked decrease in bimolecular photoinitiator activity. The combinations of complexes **14** and **15** with **4** exhibit the lowest reactivity of all the systems studied. Inspection of the carbonyl stretching frequencies indicates that these compounds have the strongest chromium–carbonyl bonds (νCO: 1915 and 1857 cm^{-1} for **14** and 1890 and 1831 cm^{-1} for **15** vs. 1974 and 1894 cm^{-1} for **1**), which is consistent with the mechanism based on initial carbonyl dissociation. Given that the drastic decrease in carbonyl stretching frequency is due to direct resonance of the phosphorus ligand with the carbonyl ligands through the metal atom and not to interactions with the benzene substituent, it is difficult to compare these complexes with the tricarbonyl series. There are indications, however, that the arene–chromium bond in such complexes is also stronger than that in **1**. For example, arene exchange reactions with dicarbonyl(naphthalene)(triphenylphosphane)chromium have not been successful,[19] whereas arene exchange in tricarbonyl(naphthalene)chromium is a well-proven, widely applied, mild method for the synthesis of (arene)tricarbonylchromium complexes.[12,16,20]

Unimolecular Photoinitiators

Having defined the factors affecting the bimolecular generation of radicals from (arene)chromium complexes and phenalkyl trichloroacetates, we then focused our attention on the synthesis and reactivity of the following unimolecular system: the tricarbonylchromium complexes of phenalkyl trichloroacetates. Of initial interest was the effect of the distance between the phenyl and trichloroacetate functionalities on the photoinitiating efficiency. The required complexes were prepared in two steps by starting from the phenalkyl alcohols. Ligand exchange of hexacarbonylchromium with the alcohols provided the complexes **16a**–**d** which were acetylated under standard conditions to afford complexes **17a**–**d** (Scheme 3).

These compounds were then evaluated in the acrylate formulation at a concentration of 0.3 wt.-% as described previously (Figure 4). The most active photoinitiator is the benzyl trichloroacetate complex **17a** (11 steps) which is 1.5 times more effective than the bimolecular combinations of 0.3 wt.-% **8** and 3.0 wt.-% organic chloride. Upon lengthening the chain by one carbon, as in **17b**, a fourfold decrease in activity results. Although the replacement of the ethylene bridge in **17b** by a propylene bridge (in **17c**) again causes a reduction in activity, further increases in chain length are without effect. It is interesting to note that the advantage of attaching the coinitiator directly to the chromium complex is lost when the methylene tether is longer than two carbons: the photoinitiator activity of **17c** and **17d** are exactly the same as that of the bimolecular combination of **1** and 0.9 wt.-% **4** or **6** (Figure 1). The fact that addition of 0.9 wt.-% of the bis(trichloroacetate) **4** to formulations containing the photoinitiators **17** leads to a slight increase in activity in almost all cases may indicate that decomplexation of the arene occurs prior to radical generation.

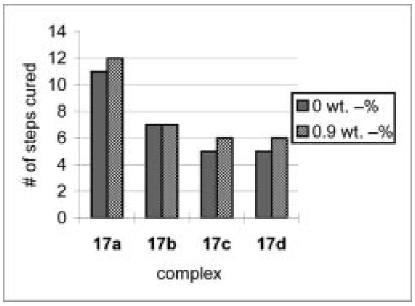


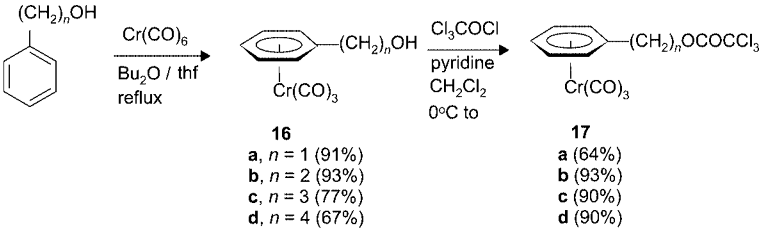
Figure 4. Reactivity of 0.3 wt.-% **17a**–**d** alone or with 0.9 wt.-% **4** in a clear lacquer. 20-s irradiation with a 4-kW Xenon lamp through a 21-step optical wedge.

Retaining the basic structure of complex **17a** as a template, two general strategies were employed in an attempt to enhance the photoinitiator activity of this class of compounds: (1) monitoring the orientation and number of trichloroacetate functionalities and (2) substitution of the arene moiety. With the first strategy, it is clear that the trichloroacetate group must be in proximity to the metal center to allow the generation of initiating radicals. Therefore, any interaction or structural constraint that forces these groups into a *syn* geometry should also result in higher reactivity.

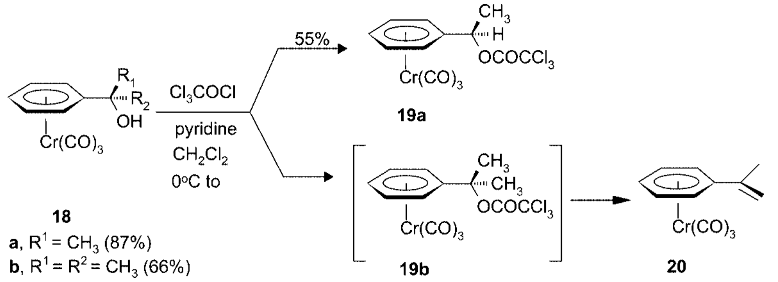
With this in mind, we undertook the synthesis of the derivatives of **17a** having methyl substitution at the benzyl carbon. The higher steric volume of the methyl group should lead compounds such as **19a** and **19b** to exhibit preferred conformations in which the acetate functionality resides on the same face of the arene as the tricarbonylchromium moiety.

Unfortunately, these two compounds were unstable and could not be evaluated in the acrylate-based lacquer. Although the arene complexes **18a** and **18b** could be obtained in good yields, their subsequent reactions with trichloroacetyl chloride led, in the first case, to an oil which decomposed at room temperature and, in the second case, to elimination to afford the methylstyrene complex **20** (Scheme 4).[21] A derivative with the desired structural constraint was found in the *syn*-1-tetrahydronaphthol complex *syn*-**21**.[22] Reaction with trichloroacetyl acetate furnished the desired trichloroacetate **22** in 93% yield. Attempted trichloroacetylation of the corresponding *anti* isomer (*anti*-**21**) led to decomposition via the metal-stabilized benzyl cation.[23] The assessment of **22** in the acrylate lacquer revealed that the structural constraint has little effect on the photoinitiator activity (Figure 5). It is feasible that the advantage gained by this modification is offset by the deactivating influence of the additional alkyl group.

Neither does the increase in the number of trichloroacetate groups of the photoinitiator have a measurable effect on its activity. Bis(trichloroacetate) **24**, prepared via the complexed diol **23**, exhibits the same activity as **17a** (11



Scheme 3. Synthesis of Cr(CO)$_3$ complexes of phenalkyl trichloroacetates.



Scheme 4. Attempted synthesis of α-methylated analogs of **17a**.

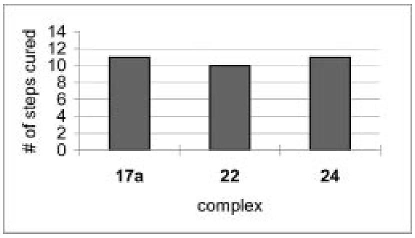
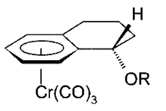
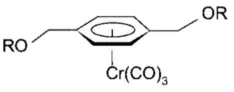


Figure 5. Reactivity of 0.3 wt.-% [Cr(arene)$(CO)_3$] complexes **17a**, **22**, and **24** in a clear lacquer. 20-s irradiation with a 4-kW Xenon lamp through a 21-step optical wedge.



21, R = H
22, R = COCCCl$_3$



23, R = H
24, R = COCCCl$_3$

steps, Figure 5). This is in accord with results obtained with the bimolecular photoinitiator systems which show that the coinitiator activity of **4** and **6** are approximately the same.

Since the bimolecular activity of the chromium complexes exhibited a strong dependence on the nature of the arene substituent, it was hoped that the activity of **17a** could be modified in the same fashion. The di- and trisubstituted tricarbonylchromium complexes **25** and **26** were prepared as usual. The direct reaction of *o*-chlorobenzyl alcohol with $Cr(CO)_6$ afforded complex **27a**[24] in low yield (19%). Protection of the alcohol functionality as its *tert*-butyldimethylsilyl ether prior to complexation gave a slightly improved yield of **27b** (27%) and, using [$Cr(CO)_3$-(naphthalene)] as the Cr(CO)3 source, this yield was raised to 40%.[16a] The complexes were then converted into their respective trichloroacetates **28**–**30** and compared to **17a** as photoinitiators in the acrylate lacquer. In contrast to the bimolecular photoinitiators, a slight decrease in activity was observed upon introduction of an *ortho*-methoxy or an *ortho*-chlorine substituent in **17a**: both **29** and **30** allow the curing of only 10 steps vs. 11 steps for **17a** (Figure 6). A further erosion of activity is found when a second alkoxy group is introduced: the catechol derivative **28** is four times less reactive than **17a**. Apparently, the upper limit of reactivity is already attained with complex **18a**. This could imply that the rate-determining step of radical production, at high levels of activity, is the interaction of the trichloroacetate with the metal fragment. With complexes of lower activity, the rate of radical production would be defined by the rate of ligand dissociation.

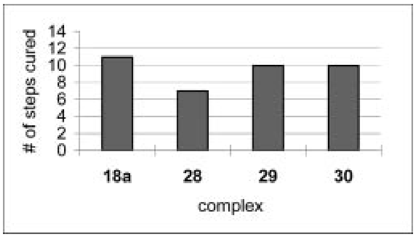
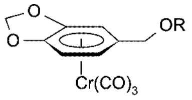
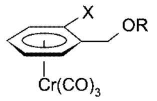


Figure 6. Reactivity of 0.3 wt.-% [Cr(arene)$(CO)_3$] complexes **18a**, **28**–**30** in a clear lacquer. 20-s irradiation with a 4-kW Xenon lamp through a 21-step optical wedge.



25, R = H (43%)
28, R = COCCl$_3$ (66%)

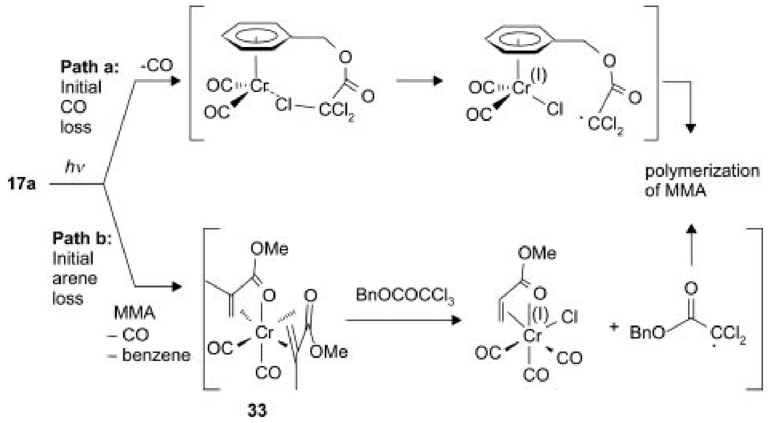


X = OCH$_3$ **26**, R = H (55%)
29, R = COCCl$_3$ (55%)

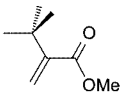
X = Cl **27a**, R = H (19%)
27b, R = OSi*t*BuMe$_2$(40%)
30, R = COCCl$_3$ (88%)

Having established that complex **17a** possessed optimum reactivity and synthetic accessibility, we then probed its photochemistry in the absence of polymerizable acrylates with the goal of identifying the initiating species. It is important to note that the test results obtained with the series of phenalkyl trichloroacetate complexes **17a**–**17d** can be rationalized in terms of initial carbonyl loss or arene loss. Dissociation of a carbonyl ligand would allow direct coordination of a chlorine atom of the trichloroacetate to chromium (Scheme 5, path a). Subsequent oxidation and fragmentation would engender an unstable 17-electron Cr^I arene complex containing a carboxydichloromethyl radical. As the energetics of the intramolecular interaction is clearly dependent upon the chain length, one would expect the highest reactivity with **17a**, as is observed. Likewise, postulating initial arene dissociation, the trichloroacetate moiety of **17a** would remain closer to the metal than in **17b**–**d** which have longer methylene chains.

First attempts to trap a radical intermediate were carried out in benzene solution in the presence of excess methyl 2-*tert*-butyl-2-propenoate (**31**).[25] Acrylate **31** has previously been employed to identify the initiating radicals for a



Scheme 5. Possible pathways of radical generation by irradiation of the Cr complex **17a** in methyl methacrylate.



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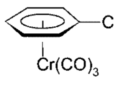


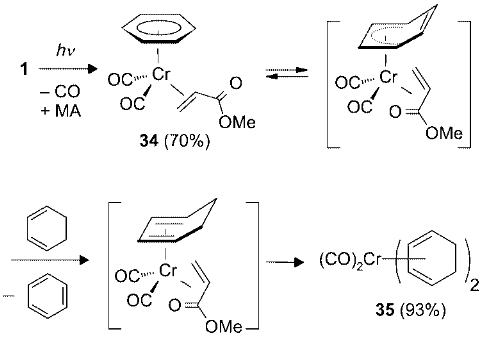
32

number of photoinitiators, as radical addition to **31** does not lead to polymerization.[26] Irradiation of a 0.25-M solution of **17a** containing 4 equiv. **31** at 350 nm (four lamps of 24 W each) in a Rayonet apparatus for 12 h led to the isolation of one new product, the benzyl chloride complex **32** in 17% yield along with 19% recovered starting material.

No trace of a radical addition product to **31** could be detected. An analogous result was obtained upon photolysis of **17a** in the absence of **31**. At a concentration of 0.25 M, **32** was obtained in 41% yield after irradiation for 2 d, whereas only a trace of **32** could be detected at a concentration of 0.08 M. These results show that **31** does not play a role in the formation of complex **32** and that it is unlikely that **32** is formed from **17a** by an intramolecular process. These results then appear to rule out path a (Scheme 5).

The failure to trap any radical species in the aforementioned photolysis of **17a** and **32** suggests that the polymerizable acrylate is an important component of this photoinitiator system. The role of the acrylate may be to displace the arene from the chromium complex, thereby generating an intermediate (a diacrylate complex of chromium, e.g. **33**) which is more reactive toward the organic halide (path b). This process is initiated by the loss of CO and olefin coordination of mma. Slippage of the arene from the η^6 to the η^4 coordination mode concomitant with η^4 coordination of mma leads to an intermediate that should readily undergo further association of mma with liberation of benzene. Photoinitiation of polymerization via initial loss of CO was dismissed by Bamford in order to explain the higher rates of decomposition of **1** (evolution of benzene) in mma as compared to isooctane *in the absence of an organic chloro compound* (CCl_4). It is unclear whether these observations are related to the generation of initiating radicals. In any event, it can been readily seen that the enhanced arene formation reported could also arise from the mode of substitution of arene by mma shown in Scheme 5, path b.

Neither the direct irradiation of **17a** in the presence of methyl methacrylate (mma) or methyl acrylate (ma) nor the two-step procedure based on cyclooctene[27] afforded the desired alkene complexes. Turning to the parent complex **1**, mma again yielded no isolable complex. However, as communicated earlier from this laboratory,[28] the two-step procedure, when combined with the use of ma, gave the acrylate complex **34** in good yield. The acrylate ligand strongly labilizes the metal–arene bond, presumably by a haptotropic rearrangement as shown in Scheme 6. The arene ligand in **34** is more labile than the acrylate, and **34** undergoes arene exchange at ambient temperature.[28] Mono- and dihapto ligands displace first the arene, and then the acrylate. An example pertinent to the subject of the present investigation is the reaction of **34** with 1,3-cyclohexadiene at ambient temperature to give [Cr(CO)$_2$(η^4-1,3-cyclohexadiene)$_2$] (**35**) in high yield.[28–30]



Scheme 6. Substitution of both benzene and methyl acrylate in **1** by cycohexadiene to give **35**.

The reactivity of **34** was then assayed under various conditions. In the absence of the organic chloro compound **4** in the dark, no polymerization of ma was observed. Nonetheless, after 3 h at room temp. complex **34** could no longer be detected, and this indicates an exchange of benzene for ma as previously noted by Bamford. Upon addition of **4** to the solution of **34** in ma in the absence of light, rapid polymerization of ma occurred. In contrast, the combination of **4** with complex **1** does not lead to polymerization in the absence of irradiation.

This provides substantial evidence for the intermediacy of an acrylate complex in the photopolymerization of acrylates with the arene chromium complex/organic chloro compound initiator system. Photoinitiation starts by CO substitution for an acrylate. The acrylate ligand, which can interconvert between an η^2 and an η^4 binding mode, renders the arene–metal bond labile. Arene displacement leads to a reactive intermediate, e.g. **33**, which can reduce suitable organic chlorides, thereby generating initiating radicals. Incorporation of the organic chloro compound in the chromium complex results in a more efficient photoinitiator, as the essential components remain in close proximity throughout the initiating process.

Experimental Section

All manipulations involving organometallic compounds were carried out under an atmosphere of purified nitrogen by using an inert gas/vacuum double manifold and standard Schlenk techniques. Solvents for the preparation of chromium complexes were dried and distilled under nitrogen immediately before use. Methyl acrylate was purified by washing twice with NaOH (5% aq.) to remove inhibitors, then twice with water, and then dried with $CaCl_2$, Na_2CO_3, $MgSO_4$, and finally distilled from CaH. Complexes **8**,[11] **9**,[11] **10**,[31] **12**,[11] **14**,[32] **15**[33] were prepared as described in the literature. A high pressure Hg-lamp (Philipps-125W) was used for the synthesis of phosphane- or phosphitechromium complexes. Photolysis of methyl acrylate in the presence of a chromium complex was carried out for mechanistic investigations by using a photochemical reactor (Rayonet-CAT NO RPR-100) equipped with RPR-3500 Å lamps (Southern New England Ultraviolet Company, USA). Analytical and preparative TLC: Merck silica gel 60 F_{254} plates. Flash column chromatography: silica gel 60, (Merck). M.p.: Büchi 510, not corrected. IR: Mattson Polaris or Perkin–Elmer 1650 FT-IR spectrometer, NaCl solution cells. ^1H and ^{13}C-NMR: Bruker 400 MHz or Varian-XL-200 spectrometer. MS: Varian CH 4 or SM 1, 70 eV; high-resolution MS (HRMS): VG analytical 7070E mass spectrometer.

4-(2,2,2-Trichloroacetoxymethyl)benzyl Trichloroacetate (4): To a mixture of 1,4-phenylenedimethanol (690 mg, 5 mmol) and pyridine (988 mg, 12.5 mmol) in dry CH_2Cl_2 (80 mL) was added dropwise trichloroacetyl chloride (2.0 g, 11 mmol) at 0 °C. The resulting mixture was stirred at room temp. for 1 h before removing the solvent. The residue was purified by chromatography on silica gel (pentane/diethyl ether 2/1) to give **4** as a white solid (1.56 g, 76%). M.p. 82–84 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 1766, 1227, 982, 831, 685 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.37 (s, 4 H, CH_2), 7.44 (s, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, CDC l_3): δ = 70.1, 89.7, 128.6, 134.6, 161.8 ppm. MS: *m/z* (%) = 428 (4) $[M]^+$, 393 (4), 335 (4), 281 (12), 265 (100), 231 (5), 119 (17), 104 (42), 91 (25), 77 (11), 36 (8), 28 (4). $C_{12}H_8Cl_6O_4$ (428.91): calcd. C 33.60, H 1.88; found C 33.61, H 1.88.

Tricarbonyl(4-hydroxymethylphenylmethanol)chromium (23):[34] Under N_2, a degassed mixture of (4-hydroxymethylphenyl)methanol (1.38 g, 10 mmol) and (naphthalene)tricarbonylchromium (2.64 g, 10 mmol) in thf (50 mL) was heated for 15 h at 60 °C. Solvent removal followed by chromatography on silica gel with diethyl ether and recrystallization in toluene afforded **23** (2.49 g, 90%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1969, 1892 cm^{-1}. ^1H NMR (400 MHz, CD_3COCD_3): δ = 4.43 (s, 4 H, CH_2), 4.66 (s, 2 H, OH), 5.73 (s, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $[D_6]$Acetone): δ = 62.1, 92.6, 112.5, 233.7 ppm. MS: *m/z* (%) = 274 (20) $[M]^+$, 218 (6), 190 (22), 172 (20), 104 (100), 78 (12), 52 (50), 28 (40). $C_{11}H_{10}CrO_5$ (274.19): calcd. C 48.19, H 3.68; found C 48.18, H 3.65.

General Procedure for the Synthesis of Chromium Complexes (Method A11) Tricarbonyl(η^6-1,2,3,4-tetrahydro-1-naphthol)chromium(0) (*syn*-21):[22] A degassed solution of 1,2,3,4-tetrahydro-1-naphthol (2.25 g, 15.20 mmol), $Cr(CO)_6$ (4.00 g, 18.17 mmol), and thf (4 mL) in Bu_2O (80 mL) was heated under reflux (oil bath *T* = 160 °C) for 40 h. After cooling to room temperature, the solution was filtered through Celite, then evaporated under reduced pressure. The yellow solid was recrystallized from CH_2Cl_2/hexane to give 2.85 g *syn*-**21**. The mother liquor was concentrated, and the residue chromatographed on silica gel (diethyl ether/hexane = 1:1) to give two fractions (0.61 g *syn*-**21** and 0.27 g *anti*-**21**). The total yield was 86%, and the ratio *syn*/*anti* was 93:7. Complex *syn*-**21**: IR (CH_2Cl_2): $\tilde{\nu}$ = 1963, 1885 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.55–2.20 (m, 5 H, OH and CH_2), 2.45–2.85 (m, 2 H, $PhCH_2$), 4.40–4.65 (m, 1 H, CHOH), 5.00–5.25 (m, 2 H, ArH), 5.50 (t, *J* = 6.2 Hz, 1 H, ArH), 5.82 (d, *J* = 6.4 Hz, 1 H, ArH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.2, 27.5, 32.1, 66.6, 89.0, 90.2, 93.5, 95.1, 112.8, 113.8, 233.3 ppm.

***anti*-21:** ^1H NMR (200 MHz, $CDCl_3$): δ = 1.45–2.20 (m, 4 H, CH_2), 2.45–2.85 (m, 3 H, OH and $PhCH_2$), 4.45–4.68 (br, 1 H, CHOH), 5.20 (d, *J* = 6.2 Hz, 1 H, ArH), 5.24 (t, *J* = 5.8 Hz, 1 H, ArH), 5.33 (t, *J* = 6.2 Hz, 1 H, ArH), 5.66 (d, *J* = 5.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.1, 28.0, 31.5, 67.0, 91.1, 92.2, 93.6, 94.4, 108.7, 110.0, 233.1 ppm.

Method B16b (Complex 27b): A degassed mixture of (2-chlorobenzyloxy)-*tert*-butyldimethylsilane (2.05 g, 8 mmol) and naphthalenetricarbonylchromium (1.06 g, 4 mmol) in thf/diethyl ether (5 mL, 4:1) was heated in a Carius tube with an o-ring tap for 22 h at 70 °C. Solvent removal followed by chromatography on silica gel (hexane/diethyl ether) afforded **27b** (628 mg, 40%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1910, 1978 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 0.04 (s, 3 H, SiMe), 0.09 (s, 3 H, SiMe), 0.97 (s, 9 H, *t*Bu), 4.14 (t, *J* = 6.3 Hz, 1 H, ArH), 4.29 (t, *J* = 6.3 Hz, 1 H, ArH), 4.46 (s, 2 H, CH2), 4.66 (d, *J* = 6.3 Hz, 1 H, ArH), 5.37 (d, *J* = 6.3 Hz, 1 H, ArH) ppm.

Method C: Tricarbonyl(η^6-1-chloro-2-fluorobenzene)chromium(0) (13):[15] *n*BuLi (1.57 N in hexane, 0.70 mL, 1.1 mmol) was added dropwise to a solution of complex **9** (0.232 g, 1.0 mmol) in thf (10 mL) at –78 °C. The solution was slowly warmed to –45 °C over 45 min. After recooling to –78 °C, hexachloroethane (1.19 g, 5.0 mmol) was added, and the reaction mixture was warmed to room temp. over a period of 3 h. After concentration of the solution, the residue was dissolved in diethyl ether, washed with water, then dried with $MgSO_4$. Removal of volatiles and chromatography on silica gel yielded complex **13** (180 mg, 68%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1986, 1914 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 3.57–3.66 (m, 1 H, ArH), 3.87–3.97 (m, 1 H, ArH), 4.30–4.38 (m, 1 H, ArH), 4.58–4.65 (m, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 78.9 (d, *J* = 21.0 Hz), 86.1, 89.7 (d, *J* = 6.6 Hz), 92.5, 100.4, 141.9 (d, *J* = 265 Hz), 230.7 ppm.

Complexes **16a**–**d**, **18a**,**b**, **25**, and **26** were obtained by method A.

(η^6-Benzyl alcohol)tricarbonylchromium(0) (16a):[35] IR (diethyl ether): $\tilde{\nu}$ = 1972, 1896 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 1.40–1.70 (br, 1 H, OH), 3.83 (s, 2 H, CH_2OH), 4.37 (t, *J* = 5.6 Hz, 1 H, ArH), 4.53 (t, *J* = 5.6 Hz, 2 H, ArH), 4.67 (d, *J* = 5.6 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 62.8, 90.8, 91.4, 92.9, 111.8, 233.5 ppm.

Tricarbonyl(η^6-2-phenylethanol)chromium(0) (16b):[36] IR (diethyl ether): $\tilde{\nu}$ = 1969, 1896 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 0.63–

0.75 (br, 1 H, OH), 1.98 (t, J = 6.0 Hz, 2 H, $PhCH_2$), 3.16 (t, J = 6.0 Hz, 2 H, CH_2OH), 4.25–4.60 (m, 5 H, ArH) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 37.9, 62.6, 90.6, 93.4, 110.4, 233.7 ppm.

Tricarbonyl(η^6-3-phenylpropan-1-ol)chromium(0) (16c): IR (diethyl ether): ṽ = 1970, 1896 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.75–1.05 (br, 1 H, OH), 1.34 (m, 2 H, CH_2), 2.05 (t, J = 8.0 Hz, 2 H, $PhCH_2$), 3.15–3.25 (br, 2 H, CH_2OH), 4.36 (t, J = 6.3 Hz, 1 H, ArH), 4.46 (d, J = 6.3 Hz, 2 H, ArH), 4.58 (t, J = 6.3 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 31.3, 33.8, 61.2, 90.2, 92.6, 93.7, 113.9, 233.5 ppm.

Tricarbonyl(η^6-4-phenylbutan-1-ol)chromium(0) (16d): Yellow oil. IR (diethyl ether): ṽ = 1971, 1896 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 0.85–1.40 (br, 5 H, OH and CH_2), 1.75–2.05 (m, 2 H, $PhCH_2$), 3.10–3.40 (m, 2 H, CH_2OH), 4.20–4.65 (m, 5 H, ArH) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 62.8, 90.8, 91.4, 93.0, 111.8, 233.5 ppm.

Tricarbonyl(η^6-1-phenylethanol)chromium(0) (18a):[37] Yellow oil. IR (C_6H_6): ṽ = 1968, 1892 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 1.18 (d, J = 6.5 Hz, 3 H, CH_3), 2.65–2.75 (br, 1 H, OH), 4.18–4.50 (br, 1 H, CHOH), 4.53–4.77 (m, 4 H, ArH), 5.25 (d, J = 6.5 Hz, 1 H, ArH) ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 25.2, 67.6, 90.8, 91.3, 92.5, 92.7, 92.9, 116.5, 118.0, 233.9 ppm.

Tricarbonyl(η^6-2-phenyl-2-propanol)chromium(0) (18b): Yellow oil. IR (CH_2Cl_2): ṽ = 1967, 1888 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 1.16 (s, 6 H, CH_3), 1.59 (s, 1 H, OH), 4.43 (t, J = 6.2 Hz, 2 H, ArH), 4.55 (t, J = 6.2 Hz, 1 H, ArH), 5.05 (d, J = 6.2 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 31.3, 70.3, 91.0, 91.7, 93.4, 121.4, 233.8 ppm.

(η^6-1,3-Benzo[1,3]dioxol-5-methanol)tricarbonylchromium(0) (25):[38] Yellow oil. ^{1}H NMR (200 MHz, C_6D_6): δ = 1.40–1.65 (br, 1 H, OH), 3.60–3.80 (br, 2 H, CH_2OH), 4.20 (d, J = 5.9 Hz, 1 H, ArH), 4.72 (d, J = 5.9 Hz, 1 H, ArH), 4.91 (s, 2 H, OCH_2O), 5.09 (s, 1 H, ArH) ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 62.7, 75.9, 76.5, 84.4, 100.3, 106.3, 129.6, 233.7 ppm.

Tricarbonyl(η^6-2-methoxybenzyl alcohol)chromium(0) (26):[39] IR (diethyl ether): ṽ = 1966, 1890 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 1.45–1.85 (br, 1 H, OH), 2.91 (s, 3 H, OCH_3), 3.80–4.25 (m, 3 H, CH_2OH and ArH), 4.34 (d, J = 6.2 Hz, 1 H, ArH), 4.64 (t, J = 6.2 Hz, 1 H, ArH), 5.30 (d, J = 5.7 Hz, 1 H, ArH) ppm.

General Procedure for the Synthesis of Trichloroacetate Derivatives: Tricarbonyl(η^6-1,2,3,4-tetrahydro-1-naphthyl trichloroacetate)chromium(0) (22): To a mixture of complex **21** (1.34 g, 4.70 mmol) and Et_3N (0.86 mL, 6.12 mmol) in CH_2Cl_2 was added dropwise trichloroacetyl chloride (0.58 mL, 5.10 mmol) at 0 °C. The resulting mixture was stirred at room temp. for 1 h, then poured into water, and extracted with CH_2Cl_2. The organic solution was dried with $MgSO_4$ and then concentrated. The residue was purified by chromatography on silica gel (diethyl ether/hexane = 1–2:2) to give 1.89 g (94%) of **22** as a light yellow crystalline solid. M.p. 81.0–81.5 °C. IR (hexane): ṽ = 1982, 1920, 1908, 1766 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.75 (m, 4 H, CH_2), 2.60–2.90 (m, 2 H, $PhCH_2$), 5.05 (d, J = 6.6 Hz, 1 H, ArH), 5.09 (t, J = 6.6 Hz, 1 H, ArH), 5.50 (t, J = 6.6 Hz, 1 H, ArH), 5.56 (d, J = 6.6 Hz, 1 H, ArH), 5.80 (dd, J = 6.6, 6.8 Hz, 1 H, PhCHOH) ppm. ^{13}C NMR (50 MHz, C_6DCl_3): δ = 18.3, 27.5, 27.9, 73.6, 87.6, 88.8, 92.9, 94.7, 104.1, 111.9, 161.8, 232.1 ppm.

1-Phenethyl Trichloroacetate (5): IR (CH_2Cl_2): ṽ = 1763, 1496, 1453, 1248, 1059, 883, 828 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60 (d, J = 6.8 Hz, 3 H, CH_3), 5.90 (q, J = 6.8 Hz, 1 H, OCH), 7.20–7.35 (m, 5 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8 78.2, 99.3, 126.0, 128.6, 128.7, 139.5 161.1 ppm.

Benzyl Trichloroacetate (6): IR (CH_2Cl_2): ṽ = 1766, 1498, 1456, 1228, 965, 829.0 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.37 (s, 2 H, $PhCH_2O$), 7.30–7.45 (m, 5 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.7, 99.3, 128.3, 128.8, 129.0, 133.7, 161.8 ppm.

(η^6-Benzyl trichloroacetate)tricarbonylchromium(0) (17a): Yellow solid. M.p. 98.50–100 °C. IR (hexane): ṽ = 1987, 1923, 1774 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 4.10–4.37 (br, 5 H, ArH and CH_2O), 4.37–4.56 (br, 2 H, ArH) ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 68.9, 91.6, 92.0, 93.1, 100.9, 161.5, 232.2 ppm. $C_{12}H_7Cl_3CrO_5$ (389.54): calcd. C 37.00, H 1.81; found C 37.15, H 1.81.

Tricarbonyl(η^6-phenethyl trichloroacetate)chromium(0) (17b): Yellow solid. M.p. 85.5–86.0 °C. IR (diethyl ether): ṽ = 1973, 1900, 1772 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.90 (t, J = 6.0 Hz, 2 H, $PhCH_2$), 3.96 (t, J = 6.0 Hz, 2 H, CH_2O), 4.16–4.55 (m, 5 H, ArH) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 33.7, 68.5, 90.1, 91.5, 92.6, 93.2, 107.1, 161.5, 233.1 ppm. $C_{13}H_9Cl_3CrO_5$ (403.57): calcd. C 38.69, H 2.25; found C 38.66, H 2.21.

Tricarbonyl(η^6-3-phenylpropyl trichloroacetate)chromium(0) (17c): Yellow solid. M.p. 57.50–58.0 °C. IR (diethyl ether): ṽ = 1973, 1900, 1791 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.17–1.40 (br, 2 H, CH_2), 1.70–1.98 (br, 2 H, $PhCH_2$), 3.58–3.87 (br, 2 H, CH_2O), 4.15–4.42 (br, 3 H, ArH), 4.42–4.68 (br, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 29.1, 30.8, 67.8, 90.2, 92.1, 93.4, 111.3, 161.8, 233.4 ppm. $C_{14}H_{11}Cl_3CrO_5$ (417.59): calcd. C 40.27, H 2.65; found C 40.30, H 2.65.

Tricarbonyl(η^6-4-phenylbutyl trichloroacetate)chromium(0) (17d): Yellow oil. IR (diethyl ether): ṽ = 1971, 1896, 1770 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 0.70–1.40 (br, 4 H, CH_2), 1.50–2.00 (br, 2 H, $PhCH_2$), 3.45–4.00 (br, 2 H, CH_2O), 4.15–4.43 (br, 3 H, ArH), 4.43–4.85 (br, 2 H, ArH) ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 27.0, 27.5, 34.2, 68.6, 90.2, 92.2, 93.6, 112.6, 161.9, 233.5 ppm. MS: m/z (%) = 430 (85) $[C_{13}H_9Cl_3CrO_6]^{+\cdot}$, 346 (18), 311 (14), 236 (100), 117 (16), 91 (100), 52 (53). HRMS: m/z calcd. for $C_{15}H_{13}Cl_3CrO_5$ 429.9233; found 429.9268.

Tricarbonyl(η^6-1-phenethyl trichloroacetate)chromium(0) (19a): Yellow oil. IR (CH_2Cl_2): ṽ = 1974, 1898, 1767 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 1.14 (d, J = 3.98 Hz, 3 H, CH_3), 4.20–5.50 (m, 6 H, ArH and CHO) ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 20.3, 75.6, 90.6, 91.1, 91.2, 91.5, 92.6, 107.8, 160.7, 232.4 ppm.

Tricarbonyl(η^6-α-methylstyrene)chromium(0) (20): IR (CH_2Cl_2): ṽ = 1968, 1891 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.65 (dd, J = 0.8, 1.4 Hz, 3 H, CH_3), 4.40–4.50 (m, 3 H, ArH), 4.70–4.78 (m, 2 H, ArH), 4.78 (d, J = 1.4 Hz, 1 H, $C{=}CH_2$), 5.02 (d, J = 0.8 Hz, 1 H, $C{=}CH_2$) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 20.4, 90.3, 91.7, 91.8, 109.2 114.3, 139.6, 233.4 ppm.

Tricarbonyl[4-(2,2,2-trichloroacetoxymethyl)benzyl trichloroacetate]chromium(0) (24): Yellow solid. M.p. 98.5–100 °C. IR (C_6H_6): ṽ = 1979, 1912, 1770 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.14 (s, 4 H), 5.53 (s, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 68.4, 89.3, 91.8, 100.8, 161.6, 230.5 ppm. MS: m/z (%) = 564 (1) [M]$^+$, 438 (2), 265 (8), 139 (40), 104 (100), 52 (15), 28 (36). $CrC_{15}H_8Cl_6O_7$ (564.94): calcd. C 31.89, H 1.43; found 31.86, H 1.42.

(η^6-Benzo[1,3]dioxol-5-ylmethyl trichloroacetate)tricarbonylchromium(0) (28): Yellow crystals. M.p. 75 °C (decomp.). IR (CH_2Cl_2): ṽ = 1971, 1894, 1768 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.92 (d, J = 12.2 Hz, 1 H, CH_2O), 5.01 (d, J = 12.2 Hz, 1 H, CH_2O), 5.11 (d, J = 6.3 Hz, 1 H, ArH), 5.50 (d, J = 6.3 Hz, 1 H, ArH), 5.65 (s, 1 H, ArH), 5.77 (s, 1 H, OCH_2O), 6.00 (s, 1 H, OCH_2O) ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 69.4, 71.4, 75.8, 78.0, 88.0, 95.3, 95.3, 101.5, 129.2, 129.8, 162.1, 232.4 ppm.

Tricarbonyl(η^6-2-methoxybenzyl trichloroacetate)chromium(0) (29): Yellow solid. M.p. 95 °C (decomp.). IR (diethyl ether): $\tilde{\nu}$ = 1975, 1902, 1770 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 2.4–3.15 (br, 3 H, OCH_3), 3.52–4.20 (br, 2 H, $PhCH_2O$), 4.20–5.40 (br, 4 H, ArH) ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 55.4, 65.0, 73.0, 84.2, 89.9, 90.1, 94.2, 97.0, 142.5, 161.5, 232.4 ppm. MS: *m*/*z* (%) = 418 (1.62) $[C_{13}H_9Cl_3CrO_6]^{+\cdot}$, 257 (2.39), 173 (3.89), 157 (3.13), 121 (100), 91 (50.95), 52 (45.6). HRMS: *m*/*z* calcd. for $C_{13}H_9Cl_3CrO_6$ 417.8955; found 417.8893.

Tricarbonyl(η^6-2-chlorobenzyl trichloroacetate)chromium(0) (30): IR (diethyl ether): $\tilde{\nu}$ = 1985, 1920, 1773 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 3.90–4.16 (m, 1 H, ArH), 4.40–4.44 (m, 1 H, ArH), 4.47 (d, *J* = 12.5 Hz, 1 H, $PhCH_2O$), 4.79 (d, *J* = 12.5 Hz, 1 H, $PhCH_2O$), 4.69–4.86 (m, 1 H, ArH) ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 66.7, 87.3, 89.9, 90.7, 93.0, 94.4, 97.5, 113.8, 161.2, 230.9 ppm.

Evaluation of Photoinitiator Reactivity in an Acrylate Formulation: A base formulation of the following composition was prepared: 50 g Actylan 200 (urethane acrylate, Akcros), 10 g Sartomer SR 399 (dipentaerythritol monohydroxypentaacrylate), 15 g TPGDA (Tripropyleneglycol diacrylate), 10 g TMPTA (Trimethylolpropane triacrylate), 15 g *N*-vinylpyrrolidone, 0.3 g BYK 300 (silicon resin for scratch resistance, 50% polymer in a mixture of xylene/butanol).

The photoinitiator component(s) were incorporated into a portion of the base formulation by stirring at 60 °C. The formulation was coated on an 300 µm aluminum foil with an electrical applicator equipped with a 100-µm wire-wound rod. The resulting film was successively laminated with a 76-µm Mylar foil, which serves as an oxygen barrier, a Stouffer 21-step optical wedge, which allows the determination of the relative reactivity of the photoinitiator systems, and a UV-transparent polyester foil, and then fixed on a vacuum table. Broad-band exposure was performed with a 4-kW Xenon lamp at a distance of 30 cm with a fixed dose of 291 $mJ\,cm^{-2}$. After exposure, the laminated foils were removed, and the film was developed in an ultrasonic bath of ethanol for 10 s. The number of fully cured steps, which serves as a measure of reactivity, was determined after drying for 5 min at 40 °C. Step 0 of the Stouffer optical wedge is 100% transparent. From step 1 to step 21, the transparency decreases from 89.13 to 0.09%, whereby every 2 steps corresponds to a halving of the transparency. Thus, a photoinitiator system which can cure 10 steps is twice as reactive as one which effects the curing of 8 steps.

Irradiation of Complex 17a to Give (η^6-Benzyl chloride)tricarbonylchromium (32):[40] A solution of **17a** (0.385 g, 0.99 mmol) in benzene (5 mL) was irradiated in a Rayonet photoreactor (Four 3500 Å lamps) until complete disappearance of starting material (2 d, followed by TLC). The reaction mixture was filtered (Celite) and concentrated. Chromatography on silica gel (eluent hexane/EtOAc = 5:1) afforded complex **32** as a yellow solid (0.107 g, 41%). 1H NMR (200 MHz, C_6D_6): δ = 3.47 (s, 2 H, CH_2Cl), 4.15–4.40 (m, 5 H, ArH) ppm. MS: *m*/*z* (%) = 262 (11) $[M^+]$, 178 (26), 143 (8), 91 (100), 52 (60). HRMS: *m*/*z* calcd. for $C_{10}H_7ClCrO_3$ 261.9489; found 261.9477.

(η^6-Benzene)dicarbonyl(η^2-methyl acrylate)chromium(33b): Following a literature method,[27] a solution of (η^6-benzene)(η^2-*cis*-cyclooctene)$Cr(CO)_2$ was prepared by photolysis (Philips, HPK 125) of complex **1** (0.642 g, 3 mmol) in benzene (200 mL)/cyclooctene (16 mL). Methyl acrylate (270 µL, 3 mmol) was added to the reaction mixture after completion of the irradiation. After 16 h, the mixture was filtered through Celite. Volatiles were removed in vacuo. The residue was taken up in hexane/benzene (20:1) and recrystallized at –40 °C to give red-orange crystals of **33b** (0.586 g, 72%). M.p. 82–83 °C. IR (hexane): $\tilde{\nu}$ = 1948 (s), 1896 (s), 1704 (m) cm^{-1}. 1H NMR (C_6D_6, 200 MHz): δ = 4.35 (s, 6 H, C_6H_6), 3.56 (s, 3 H, OCH_3), 2.93 (dd, *J* = 11.3, 7.7 Hz, 1 H, $C{=}CH\text{-}CO_2Me$), 2.76 (dd, *J* = 11.3, 0.8 Hz, 1 H, $CH_2{=}C$), 2.37 (dd, *J* = 7.7, 0.8 Hz, 1 H, $CH_2{=}C$) ppm. 13C NMR (C_6D_6, 50 MHz): δ = 246.6, 245.9, 177.2, 95.9, 50.1, 41.4, 38.6 ppm. MS: *m*/*z* (%) = 272 (0.4) $[M^+]$, 186(4), 158(7), 130(18), 78(100), 52(65). $C_{12}H_{12}CrO_4$ (272.22): calcd. C 52.95, H 4.44; found C 52.72, H 4.36.

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