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Fulgides as ligands
1. Synthesis and photochemistry of tricarbonyl-η^6-fulgide chromium(0) complexes

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Abstract

Three photochromic fulgides, *E*-1-(3′,4′,5′-trimethoxyphenyl)ethylidene(isopropylidene)succinic anhydride (**5**) and a mixture of *E*- and *Z*-1-(2′,4′,6′-trimethylphenyl)methylidene(isopropylidene)succinic anhydrides (**10**) and (**11**), were synthesised and reacted with chromium hexacarbonyl to give mixtures of the corresponding tricarbonyl-η^6-fulgide chromium(0) complexes. No evidence for formation of the corresponding diene or enone complexes was obtained. Irradiation of the purified chromium arene complexes gave *E*/*Z* isomerisation and decomposition of the complexes without photochromic ring closure.

Keywords: Chromium complexes; Carbonyl complexes; Fulgide complexes; Photochemistry

1. Introduction

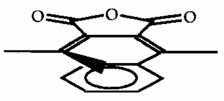
In our previous paper [1], we reported the synthesis of a family of ferrocene based organometallic fulgide complexes, examined their photochemistry and discussed their failure to act as photochromic systems. Here, we look at the synthesis and photochemistry of the related tricarbonyl-η^6-fulgide chromium(0) complexes. Chromium complexes were chosen because the carbonyl reacts more easily than that of tungsten [2–4] and the arene tricarbonyl complexes are much more stable than those of molybdenum [5].

The tricarbonyl-η^6-fulgide chromium complexes were synthesised by the usual method of heating the ligand under reflux with chromium hexacarbonyl in di-n-butyl ether with 10% by volume of THF [6].

$$[Cr(CO)_6] + \text{fulgide} \xrightarrow[\text{reflux}\ \ 12\text{–}14\ \text{h}]{(Bu^n)_2O/THF\ (10\%)} [Cr(CO)_3(\eta^6\text{-fulgide})] + 3CO$$

The authors of the method also claim that apart from washing the subliming chromium hexacarbonyl back into the reaction vessel, the more volatile THF also has a catalytic effect on the reaction by forming a quasi-stable complex of the form $(THF)_nCr(CO)_{6-n}$. Such complexes have been independently reported in the literature [7].

Examination of the *E*-fulgide structure **1** raises the possibility of three possible modes of coordination to a chromium carbonyl unit, i.e. as an arene complex (e.g. **2**), as a diene complex (e.g. **3**) or as an enone complex (e.g. **4**). (NB, each type of complex **2**–**4** has more than one possible isomer, some of which will be disfavoured due to steric interactions.) The work described below was carried out to determine which particular mode of complexation would occur and whether the chromium carbonyl moiety would affect the photochemistry of the fulgides.



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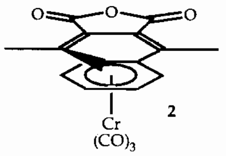

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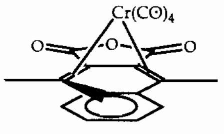

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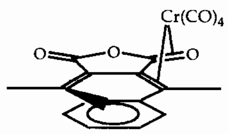

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2. Results and discussion

The highly electron rich fulgide, *E*-1-(3′,4′,5′-trimethoxyphenyl)ethylidene(isopropylidene)succinic an-

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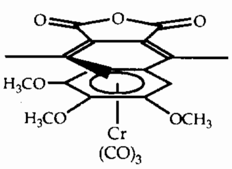
hydride (**5**), was selected to be complexed with chromium. It was prepared by a literature method [8]; only the *E* isomer was produced, probably due to steric considerations.

E-1-(3′,4′,5′-Trimethoxyphenyl)ethylidene(isopropylidene)succinic anhydride (**5**) was reacted with chromium hexacarbonyl [7]. The oily red product showed four spots by TLC, which were separated by rapid chromatography on a Chromatotron (Harrison Research, Palo Alto, CA, USA) (found to be necessary if decomposition were to be minimised). The bands were due to the *E*- and *Z*-isomers of both the complexed **7** (band 4) and **8** (band 2), and uncomplexed fulgides **5** (band 1) and **6** (band 3), respectively.



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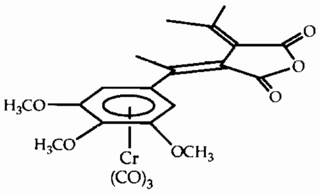

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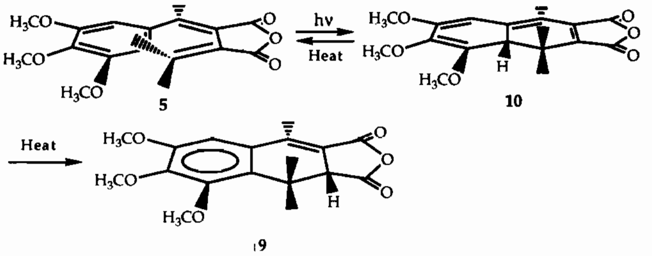
Tricarbonyl-η^6-[*E*-1-(3′,4′,5′-trimethoxyphenyl)ethylidene(isopropylidene)succinic anhydride]chromium(0) (**7**), yielded orange microcrystals (3.9%) from dichloromethane/ether/hexane at −20 °C and was identified from its ^{1}H NMR spectrum, which showed the characteristic upfield shift of the isopropylidene methyl group *trans* to the adjacent carbonyl combined with the expected upfield shift of the aromatic protons coordinated to the metal atom [7]. Tricarbonyl-η^6-[Z-1-(3′,4′,5′-trimethoxyphenyl)ethylidene(isopropylidene)succinic anhydride]chromium(0) (**8**) crystallised from dichloromethane/ether/hexane under argon at −20 °C as red needles in 5.1% yield. Its structure was also assigned from its ^{1}H NMR spectrum. Examination of the reaction mixtures by ^{1}H NMR spectroscopy showed that these complexes, and the ones mentioned below, had all been formed in >50% yield during the reaction. However, the complexes decomposed rapidly on silica to give a mixture of unidentified but highly polar byproducts. It is interesting to note that none of the possible diene or enone chromium tetracarbonyl complexes could be detected in the reaction mixture. It is of further interest that all attempts to synthesise such diene or enone complexes from a wide range of fulgides and metal complexes under a wide variety of thermal, photochemical or ultrasonication conditions, using the carbonyls of iron, molybdenum and tungsten or benzylideneacetoneiron tricarbonyl, were unsuccessful.

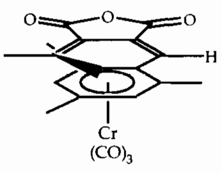
A few crystals of the *Z*-3′,4′,5′-trimethoxyphenyl fulgide chromium complex (**8**) were irradiated in dioxan-d^8 at 254 nm (which has such a small absorbance at this wavelength and sample thickness that it can be ignored). ^{1}H NMR spectroscopy and TLC showed that *E*/*Z* isomerisation had occurred. No trace of any ring closure product could be found and prolonged irradiation caused decomposition of the complex.

When the *Z*-isomer **8** was photolysed in benzene-d^6 at 350 nm, some isomerisation to the *E*-complex **7** was observed. However, competing with this process was decomplexation of the chromium complexes, almost total loss of chromium complexes occurring within 3 h. The decomposition products included a mixture of the *E*- and *Z*-isomers of the fulgides **5** and **6**, an intractable chromium-containing, flocculent precipitate (which had to be centrifuged to the bottom of the NMR tube to enable spectra of reasonable resolution to be recorded) and 1,2-dihydro-1,1,4-trimethyl-6,7,8-trimethoxy-naphthalene-2,3-dicarboxylic anhydride (**9**). This latter compound has been reported by Heller and co-workers [8] to be formed by a thermal [1,5]-H shift in the photochromic product **10**, which is derived by a photochemical ring closure of the *E*-fulgide. Very similar results were obtained with the *E*-isomer **7**.



One reason for the photoinstability of the tricarbonyl-η^6-fulgide chromium(0) complexes **7** and **8** may be the position and number of highly electron-donating methoxy groups on the arene rings. However, it is known that the position and electron-donating ability of the substituent groups on the aromatic ring has considerable influence on the photochemistry of fulgides [9]. Mesomeric electron-donating substituents in the 3′- and 5′-positions enhance ring closure by improving conjugation, whilst substituents in the 2′- or 6′-positions remove a potential route for decomposition of the photoproduct by preventing [1,5]-H migrations. Furthermore, a 4′-methoxy substituent depresses photochromic behaviour due to cross-conjugation in the photoproduct [9]. Thus, a 2′,4′,6′-trimethylphenyl fulgide becomes a suitable alternative to a 2′,4′,6′-trimethoxy fulgide as the combined +I effects of the three methyl groups are just sufficient to allow photochromic reaction, whilst still effectively blocking [1,5]-H migration. Unfortunately, 2′,4′,6′-trimethylacetophenone is too sterically hindered to undergo Stobbe condensation with a dialkyl isopropylidene-succinate, but fortunately 2′,4′,6′-trimethylbenzaldehyde (mesitaldehyde) will. The *E*- and *Z*-1-(2′,4′,6′-trimethylphenyl)methylidene fulgides **11** and **12** were synthesised [10] and complexed with the chromium tricarbonyl unit following the usual method. Tricarbonyl-η^6-[*E*-1-(2′,4′,6′-trimethylphenyl)-

methylidene(isopropylidene)succinic anhydride]chromium(0) (**13**) was isolated in 2.4% yield, while the corresponding *Z*-isomer, **14**, gave a 9.4% yield. The two isomers were, as usual, identified by means of their ^{1}H NMR spectra.



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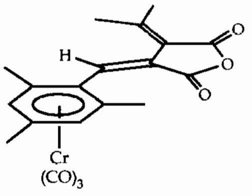

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Again, no traces of either 1,2- or 1,4-dihydronaphthalene chromium tricarbonyl complexes were found. However, this is not totally unexpected, since as mentioned earlier, this would require either a [1,5]- or a [1,7]-methyl shift, which are far less common than the corresponding hydrogen shifts. A photochemical ring closure was still not ruled out despite this and due to the higher yield, the *Z*-chromium tricarbonyl complex **14** was used for the photolysis. Irradiation of a benzene-d^6 solution of complex **14** in a quartz NMR tube at 350 nm resulted in the same pattern of *E*/*Z* isomerisation and decomposition as seen for the other fulgides in the series. Unlike the trimethoxyphenyl fulgide chromium complexes **7** and **8** though, it did not give a 1,2-dihydronaphthalene from the free fulgide generated by the photolysis; this would be because the potential migrating group is a methyl as opposed to a hydrogen atom.

3. Experimental

3.1. General

All reactions involving the synthesis or use of metal complexes were carried out under nitrogen or argon unless otherwise stated. All reagents were used as purchased without further refinement. Petroleum refers to the redistilled 60–80 °C boiling fraction, unless otherwise stated, and the hexane used was the hexane fraction of petroleum. All reaction solvents were dried over an appropriate desiccant, distilled and stored under nitrogen. Di-n-butyl ether (SureSeal) was purchased from Aldrich and used without further purification.

The ^{1}H NMR spectra were obtained on Perkin-Elmer R12 (60 MHz), Hitachi R1200 (60 MHz) and Bruker WM250 (250 MHz) spectrometers. The UV–Vis and FTIR spectra were recorded using Perkin-Elmer Lambda 3 and Mattson Polaris Icon spectrometers, respectively. GC mass spectra were obtained on a Perkin-Elmer 8500 gas chromatograph with an ITD ion trap detector. Melting points were found using a Gallenkamp melting point apparatus and were uncorrected. Hanovia 125W medium and low pressure mercury vapour lamps were used (as specified) for the photolyses, in conjunction with a Spectrophysics microphotolysis apparatus for some NMR tube scale work.

3.2. E-1-(3′,4′,5′-Trimethoxyphenyl)ethylidene(isopropylidene)succinicanhydride (5)

The title anhydride was synthesised using literature methods [8] and obtained by purification of the crude product in the usual way. Only the *E*-isomer was produced, probably for steric reasons due to the extra bulk given to the phenyl ring by the methoxy groups.

3.3. Tricarbonyl-η^6-[E- and Z-1-(3′,4′,5′-trimethoxyphenyl)ethylidene(isopropylidene)succinic anhydride]chromium(0) (7) and (8)

E-1-(3′,4′,5′-Trimethoxyphenyl)ethylidene(isopropylidene)succinic anhydride (2.80 g, 8.43 mmol) and chromium hexacarbonyl (4.64 g, 21 mmol) were heated under reflux in di-n-butyl ether (30 cm^3) and tetrahydrofuran (3 cm^3) under argon for 13 h. The reaction vessel was covered with aluminium foil to exclude light. The mixture was cooled, filtered through a short plug of Kieselguhr and evaporated down *in vacuo* to give a red oil. The product mixture was chromatographed rapidly on a Chromatotron (silica gel GF$_{254}$, ethyl acetate/hexane 1:3 until a good separation had been obtained then 3:2 ethyl acetate/hexane to completion). *E*- and *Z*-isomers of the 1-(3′,4′,5′-trimethoxyphenyl)ethylidene fulgides (**5**) and (**6**) were eluted as the first and third bands respectively.

The first of the two orange bands (band 2) gave tricarbonyl-η^6-[Z-1-(3,4,5-trimethoxyphenyl)ethylidene-(isopropylidene)succinic anhydride]chromium(0) (**8**) as dark red needles from dichloromethane/ether/hexane at −20 °C (0.20 g, 5.1%), m.p. > 160 °C (dec.). *Anal.* Found: C, 53.6; H, 4.3. Calc. for $C_{21}H_{20}CrO_9$: C, 53.84; H, 4.3%. ν_{max} (CH_2Cl_2, solution cell) (cm^{-1}): 1958, 1881, 1817 (w) (metal carbonyl C=O stretch); 1764 (α,β-unsaturated anhydride C=O stretch). λ_{max} (methanol): 311, 462 nm ($\log_{10} \epsilon$ 4.09, 3.46). δ_H ($CDCl_3$, 250 MHz): 2.10 (3H, s, isopropylidene CH_3 *trans* to C=O), 2.48 (3H, s, isopropylidene CH_3 *cis* to C=O), 3.87 (6H, s, OCH_3 3′ and 5′), 3.96 (3H, s, CH_3 4), 5.11 (2H, s, arene protons 2′ and 6′).

Tricarbonyl-η^6-[*E*-1-(3′,4′,5′-trimethoxyphenyl)ethylidene(isopropylidene)succinic anhydride]chromium(0) (**7**) was eluted as the second orange band (band 4) and recrystallised from dichloromethane/ether/hexane solution to give orange microcrystals (0.15 g, 3.9%), m.p. > 160 °C (dec.). *Anal.* Found: C, 52.8; H, 4.2. Calc. for $C_{21}H_{20}CrO_9$: C, 53.84; H, 4.3%. ν_{max} (CH_2Cl_2, solution cell) (cm^{-1}): 1964, 1888, 1815 (w) (metal carbonyl

C=O stretch); 1763 (α,β-unsaturated anhydride C=O stretch); 857 (m, isolated aromatic C–H out of plane bending). λ_{max} (dichloromethane): 316, 461 nm. δ_H ($CDCl_3$, 250 MHz) 1.55 (3H, s, isopropylidene CH_3 *trans* to C=O), 2.32 (3H, s, isopropylidene CH_3 *cis* to C=O), 2.66 (3H, s, phenylethylidene CH_3), 3.61 (6H, s, OCH_3 3′ and 5′), 3.94 (3H, s, OCH_3 4′), 4.85 (2H, s, arene 2′ and 6′).

3.4. E- and Z-1-(2′,4′,6′-Trimethylphenyl)methylidene-(isopropylidene)succinic anhydrides (11) and (12)

The *E*/*Z*-isomeric mixture of **11** and **12** was prepared by the literature method [10].

3.5. Tricarbonyl-η^6-[E- and Z-1-(2′,4′,6′-trimethylphenyl)-methylidene(isopropylidene)succinic anhydride]-chromium(0) (13) and (14)

The *E*/*Z*-isomeric mixture of fulgides **11** and **12** (6 g, 0.022 mol) and chromium hexacarbonyl (12.21 g, 0.056 mol) gave in the usual manner, a red oil which was chromatographed on a Chromatotron (Kieselgel 60 PF_{254}, 4 mm; hexane/diethyl ether 2:1). The unreacted *E*- and *Z*-isomers **11** and **12** were eluted as the first and third bands, respectively, whilst the fourth band gave tricarbonyl-η^6-[*E*-1-(2′,4′,6′-trimethylphenyl)methylidene(isopropylidene)succinic anhydride]chromium-(0) (**13**) as orange microcrystals (0.12 g, 2.35%) on recrystallisation, m.p. > 160 °C (dec.). *Anal.* Found: C, 58.8; H, 4.42. Calc. for $C_{20}H_{18}CrO_6$: C, 59.12; H, 4.46%. ν_{max} (CH_2Cl_2 solution cell) (cm^{-1}): 1959, 1882, 1810 (w) (metal carbonyl C=O stretch); 1769, 1712 (α,β-unsaturated anhydride C=O stretch); 1365 (m, CH_3 symmetrical deformation). δ_H ($CDCl_3$, 250 MHz) 1.54 (3H, s, isopropylidene CH_3 *trans* to C=O), 2.15 (6H, s, arene CH_3 2′ and 6′), 2.22 (3H, s, arene CH_3 4′), 2.45 (3H, s, isopropylidene CH_3 *cis* to C=O), 4.96 (2H, s, arene CH 3′ and 5′), 7.39 (1H, s, =CH).

The second band gave tricarbonyl-η^6-[*Z*-1-(2′,4′,6′-trimethylphenyl)methylidene(isopropylidene)succinic anhydride]chromium(0) (**14**) as red platelets (0.84 g, 9.4%) on recrystallisation from dichloromethane/diethyl ether/hexane, m.p. > 160 °C (dec.). *Anal.* Found: C, 59.14; H, 4.46. Calc. for $C_{20}H_{18}CrO_6$: C, 59.12; H, 4.46%. ν_{max} (CH_2Cl_2, solution cell) (cm^{-1}): 1960, 1883, 1820 (metal carbonyl C=O stretch); 1771, 1712 (w) (α,β-unsaturated anhydride C=O stretch); 1382 (m, CH_3 symmetrical deformation). λ_{max} (dichloromethane): 289, 455 nm ($\log_{10}\epsilon$ 4.15, 3.35). δ_H ($CDCl_3$, 250 MHz) 2.15 (6H, s, arene CH_3 2′ and 6′), 2.20 (3H, s, arene CH_3 4′), 2.36 (3H, s, isopropylidene CH_3 *trans* to C=O), 2.60 (3H, s, isopropylidene CH_3 *cis* to C=O), 5.07 (2H, s, arene CH 3′ and 5′), 7.07 (1H, s, =CH).

3.6. Photolysis of the tricarbonyl-η^6-fulgide chromium(0) complexes 7, 8, 13 and 14

Each of the fulgide complexes **7**, **8**, **13** and **14** (~25 mg) was dissolved in an appropriate solvent (dioxan-d_8 for <300 nm irradiation or benzene-d_6 for >300 nm) (0.3 cm^3) in a quartz NMR tube (4.5 mm) and the tube was de-gassed and sealed (Subaseal) under argon. The solutions were then photolysed with the appropriate mercury vapour lamp (low pressure for <300 nm and medium pressure for >300 nm) and the progress of the reactions monitored by ^1H NMR spectroscopy.

Each photolysis simply resulted in *E*/*Z* isomerisation of the complexes followed by decomposition to the corresponding uncomplexed fulgides **5**, **6**, **11** and **12** on prolonged irradiation.

Acknowledgements

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