

Preparation of η^5 -pyranyltricarbonylmanganese complexes and pyrylium triiodide salts from cyclomanganated chalcones and alkynes

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Abstract

Derivatives of [[1-phenyl-2-phenylcarbonyl- κO]ethenyl- κC^1]tetracarbonylmanganese, i.e. chalcone (1, 3-diphenylprop-2-en-1-one) cyclomanganated at the β -position, undergo insertion reactions with alkynes under reflux in carbon tetrachloride to give [2,4-diphenylpyranyl- η^5]Mn(CO)₃ derivatives, the reaction being highly regioselective in the case of unsymmetrical alkynes. Reaction of the pyranyl-Mn(CO)₃ complexes with iodine in carbon tetrachloride gives pyrylium triiodide salts in excellent yield. The reaction of one pyranyl complex, [2-(4-chlorophenyl)-6-phenyl-4-(4-trifluoromethylphenyl)pyranyl- η^5]tricarbonylmanganese (**2d**), with Na[Fe(CO)₂Cp], gave the demetallated ring-opened isomers *E,E*-1-phenyl-3-(4-trifluoromethylphenyl)-5-(4-chlorophenyl)penta-2, 4-dien-1-one (**10a**) and *E, E*-1-(4-chlorophenyl)-3-(4-trifluoromethylphenyl)-5-phenylpenta-2,4-dien-1-one (**10b**). X-ray crystal structure determinations of [2-methyl-4,6-diphenylpyranyl- η^5]tricarbonylmanganese (**5**) and 2,6-diphenyl-4-(4-trifluoromethylphenyl)pyrylium triiodide (**3b**) are described, the former being the first reported for a pyranyl- η^5 metal complex.

Keywords: Manganese; Alkyne; Pyranyl complexes; Pyrylium salt; Crystal structure; Metallacycle

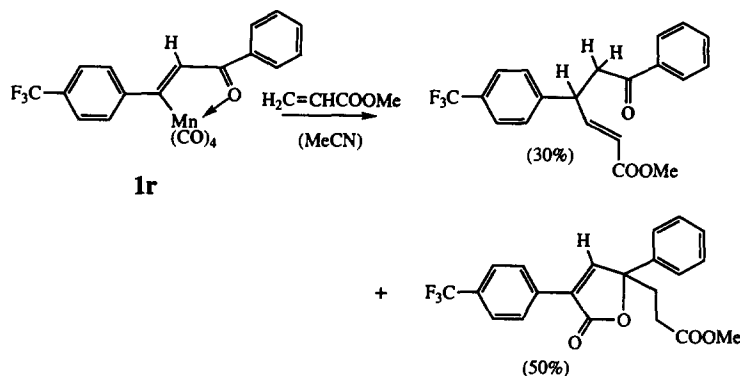
1. Introduction

Much study of cyclomanganated compounds has been centred on arylmanganese compounds with ortho-carbonyl donor substituents. Their preparation and the application of their coupling reactions with alkenes and alkynes in organic synthesis is well established [1]. Their alkenyl analogues, β -manganated enones (e.g. **1r**; Scheme 1), are less well known, but we recently reported [2] the synthesis of several, including those listed in Table 1, by reacting chalcones (1,3-diarylpropenones) with benzylpentacarbonylmanganese. Coupling reactions of these β -manganated chalcones with alkenes were shown [2] to provide useful synthetic routes to β -alkenyldihydrochalcones and 5-alkanyl-substituted 3,5-diarylfuran-2(5H)-ones (e.g. Scheme 1), products without analogy in the coupling of alkenes with orthomanganated aryl ketones.

In this report we discuss coupling reactions of alkynes

with β -manganated chalcones which, as for alkenes, give different products from those obtained with orthomanganated aryl ketones. The latter couple with alkynes to form indenols, presumably (Scheme 2) via insertion of alkyne into the C–Mn bond, followed by cyclization. This reaction illustrates the significant potential that exists more generally for the application of cyclometallated compounds to the synthesis of cyclic organic products in which the original donor function is incorporated in the new ring. Although the cyclic alkenylmanganese insertion intermediate (Scheme 2) has not been detected, its existence receives support from the formation of the corresponding species (**4**; various R₁, R₂) when orthomanganated triphenylphosphite reacts with acetylenes under UV irradiation [3], and in the many analogous cases [4–7] of alkyne insertion into metal–carbon bonds of orthopalladiated *N,N*-dimethylbenzylamines. The difference in these cases from that of the ketone (Scheme 2) is that there is no unsaturation in the phosphite or amine donor group to allow the metallated carbon to add so that cyclization does not occur. Sometimes a second [3,4a,5,7] or third [4b] alkyne insertion occurs. A recent example was reported [7] by

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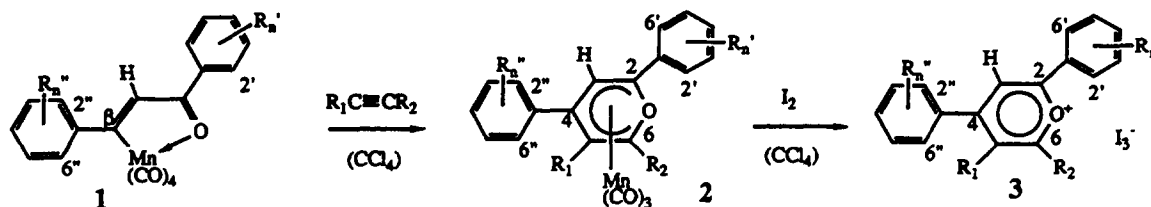
Scheme 1. Alkene-coupling products from a β -manganated chalcone.

Rheingold, Heck and coworkers who found that reaction of diphenylacetylene with the orthopalladiated *N,N*-dimethylbenzylamine 5 (Scheme 3) led, via the double insertion product 6 to the benzofulvene 7, as identified by X-ray crystal structure analysis. This corrected an earlier [4a] NMR-based assignment which had suggested incorporation of the donor amine into a cyclic product (8). Literature examples of insertion reactions of alkynes with cyclometalated compounds of metals other than Pd and Mn are more sporadic. Little systematic work has been carried out to test the undoubted synthetic potential which exists, as evident for instance

in the recently reported reaction of a cyclorutheniated *N,N*-dimethylbenzylamine with alkyne followed by CuBr_2 oxidation which leads to dihydroisoquinoline derivatives [8].

In this report, the synthetic potential of reactions of alkynes with β -manganated chalcones is explored. Cyclic products incorporating the donor carbonyl oxygen are obtained. These are the relatively little-known η^5 -pyranyltricarbonylmanganese derivatives (2; Table 1) of the type (9) first reported by Booth and Hargreaves [9] as the minor byproduct from the reaction (Scheme 4) of $\text{Mn}(\text{CO})_5$ with phenylacetylene to

Table 1
Structures and yields of pyranyltricarbonylmanganese complexes and pyrylium triiodide salts

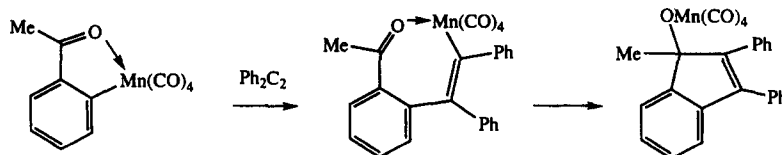


β -Manganated chalcone (1)			Alkyne	Pyranyl complex (2)		Pyrylium salt (3)	
Code ^a	R'' _n	R' _n	R ₁ , R ₂	Code	(Yield) ^b	Code	(Yield) ^b
1i	3'', 4'', 5''-(OMe) ₃	4''-Cl	H, Ph	2a	(62%)	3a	(92%)
1r	4''-CF ₃	H	H, Ph	2b	(72%)	3b	(84%)
1b	H	H	H, Ph	2c	(72%)	3c	(72%)
1q	4''-CF ₃	4''-Cl	H, Ph	2d	(52%)	3d	(79%)
1i	3'', 4'', 5''-(OMe) ₃	4''-Cl	H, Si(Me) ₃	2e	(48%)	3e	(85%)
1e	4''-OMe	3', 4', 5''-(OMe) ₃	H, Ph	2f	(91%)	3f	(88%)
1r	4''-CF ₃	H	Me, Pr	2g	(39%) ^c	3g	(87%)
			(Pr, Me)	(2g')	(5%) ^c	3g'	(87%)
1q	4''-CF ₃	4''-Cl	Ph, Ph	2h	(46%)	3h	(64%)
1r	4''-CF ₃	H	Ph, Ph	2j	(61%)	3j	(84%)

^a Letter codes correlate with those of the same compounds (3b, e, i, q, r) in the earlier paper [2] describing their preparation.

^b Yields are for chromatographically purified samples before final crystallization.

^c Yields estimated from NMR spectra of the inseparable mixture of **2g** (R₁ = Me; R₂ = Pr) and **2g'** (R₁ = Pr; R₂ = Me).



Scheme 2. Indenol formation via alkyne insertion of orthomanganated acetophenone.

form the manganated enone **8**. These pyranil complexes (**2**) provide a ready source of pyrylium salts (**3**; Table 1) by reaction with iodine.

2. Experimental details

2.1. General

The preparation of the cyclomanganated chalcones (**1b**, **e**, **i**, **q**, **r**) by reaction with benzylpentacarbonylmanganese has been described [2].

Coupling reactions of cyclomanganated chalcones with alkynes were carried out under nitrogen, but subsequent workup was without exclusion of air. There were no special precautions for the reactions with iodine.

Preparative scale layer chromatography (referred to as PLC in the text) was performed on Merck Kieselgel 60 silica gel, and alumina (Brockmann activity II) was used for column chromatography. The composition of mixed solvents is expressed on a volume:volume basis. Petroleum spirit (b.p. 60–80 °C) was redistilled and carbon tetrachloride was of AnalaR grade.

Infrared spectra (in dichloromethane) were obtained on a Digilab FTS-45 FTIR spectrometer. FAB mass spectra were from a VG ZAB 2HF instrument using a 2-nitrophenol matrix.

NMR spectra were recorded on a Bruker AC300 instrument using CDCl_3 as solvent except for pyrylium

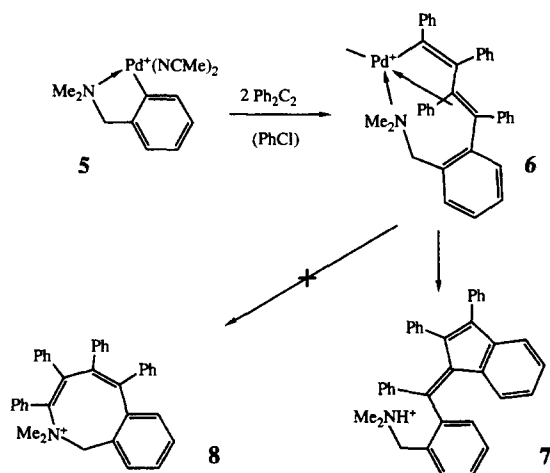
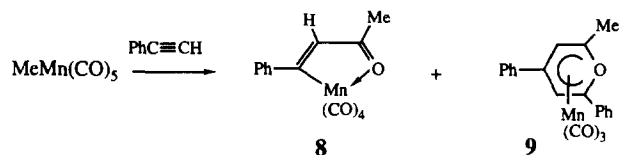
triiodide salts for which $(\text{CD}_3)_2\text{CO}$ or $(\text{CD}_3)_2\text{SO}$ was used. For indicating NMR signal assignments, unprimed numbers relate to the pyranil or pyrylium ring. Prime, double-prime and triple-prime symbols are used to distinguish phenyl substituents. Prime and double-prime are used respectively for the phenyl rings at C2 and C4, i.e. those with R_n and $\text{R}_{n'}$ generalized substituents in structures **2** and **3** in Table 1. The triple-prime symbol applies to the phenyl ring at C6 ($\text{R}_2 = \text{Ph}$) in structures **2** and **3** when phenylacetylene is used, except in the special case when $\text{R}_n = \text{H}$ in which case the two phenyl groups at positions 2 and 6 of the pyranil or pyrylium ring are identical, and the single-prime symbol is used to indicate assignments for both. For diphenylacetylene-derived products ($\text{R}_1 = \text{R}_2 = \text{Ph}$) spectral complexity prevented detailed NMR assignment.

2.2. Preparation of pyraniltricarbonylmanganese complexes

[2-Methyl-4,6-diphenylpyranil- η^5]tricarbonylmanganese (**9**) was obtained as the minor byproduct from the reaction of $\text{MeMn}(\text{CO})_5$ and phenylacetylene (Scheme 2) according to the method of Booth and Hargreaves [9]. Crystallized from petroleum spirit, it had m.p. 97 °C (ref. [9] 97–8 °C). The X-ray crystal structure of **9** is described below.

2.2.1. General method for reaction of cyclomanganated chalcones and alkynes

The following preparation of [2-(4-chlorophenyl)-6-phenyl-4-(3,4,5-trimethoxyphenyl)pyranil- η^5]tricarbonylmanganese (**2a**) illustrates the standard method; variations in reaction time, workup or recrystallization method for the other complexes (**2b–2j**) are indicated individually with their spectral and analytical data. The letter codes for the starting compounds **1** are, for convenience,

Scheme 3. Benzofulvene formation via double alkyne insertion of orthopalladiated *N,N*-dimethylbenzylamine.Scheme 4. Booth and Hargreaves' synthesis [9] of a $[\eta^5\text{-pyranil}]$ tricarbonylmanganese complex.

nience in cross-referencing, those used in the previous paper on their preparation [2].

[2-(4-Chlorophenyl)-6-phenyl-4-(3,4,5-trimethoxyphenyl)pyranyl- η^5]tricarbonylmanganese (**2a**). (i) A mixture of [[1-(3,4,5-trimethoxyphenyl)-2-(4-chlorophenylcarbonyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**1i**) (0.50 g, 1.0 mmol) and phenylacetylene (0.12 ml, 1.1 mmol) in CCl_4 (20 ml) was refluxed under nitrogen for 6 h. The solvent was removed under vacuum and dichloromethane (10 ml) and deactivated neutral alumina (4 g) were added to the dark red oil. The solvent was removed under vacuum on a rotary evaporator. The alumina carrying the product was transferred to the top of a column (2 \times 12 cm) of alumina. Elution with CH_2Cl_2 /hexane gave [2-(4-chlorophenyl)-6-phenyl-(3,4,5-trimethoxyphenyl)pyranyl- η^5]tricarbonylmanganese (**2a**) as a red oil (0.36 g; 62%), which was crystallized from dichloromethane/pentane by vapour diffusion as ruby-red crystals, m.p. 208 °C. Anal. Found: C, 60.64; H, 3.85; $C_{26}H_{22}ClO_7Mn$ Calc.: C, 60.80; H, 3.87%. IR: $\nu(CO)$ 2013 (vs), 1950 (s), 1932 (m) cm^{-1} . 1H NMR: δ 7.40 (m, 9H), 7.13 (s, 2H, $H2''$, $6''$), 5.56 (s, 1H, $H3$), 5.52 (s, 1H, $H5$), 3.99 (s, 6H, $3''$, $5''$ - OCH_3), 3.96 (s, 3H, $4''$ - OCH_3). ^{13}C NMR: δ 153.8 (s, $C3''$, $5''$), 138.8 (s, $C4''$), 135.2 (s, $C1''$), 134.7 (s, $C4'$), 134.0 (s, $C1'$), 132.4 (s, $C1''$), 129.2 (d, $C3'$, $5'$), 129.0 (d, $C3'''$, $5'''$), 128.5 (d, $C4'''$), 124.4 (d, $C2'$, $6'$), 123.4 (d, $C2''$, $6''$), 104.9 (d, $C2''$, $6''$), 98.7 (s, $C6$), 96.0 (s, $C2$), 92.5 (s, $C4$), 81.6 (d, $C3$), 81.3 (d, $C5$), 61.1 (q, $4''$ - OCH_3), 56.4 (q, $3''$, $5''$ - OCH_3).

(ii) The following one-pot synthesis of **2a** starting from the chalcone and benzylpentacarbonylmanganese and involving treatment of the unisolated manganated chalcone directly with the alkyne in hexane gives a 45% yield overall. This gives no improvement in yield over that obtained by two separate steps (78% for the preparation of the manganated chalcone [2], and 62% for the alkyne coupling in carbon tetrachloride (above)) but it is more convenient if the intermediate manganated chalcone is not required. (See however the yield advantage of the one-pot sequence in preparation of pyrylium salts **3a** and **3e** described in Section 2.3.)

A mixture of 1-(4-chlorophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (**1i**; 0.508 g, 1.53 mmol) and benzyltetracarbonylmanganese (0.437 g, 1.53 mmol) in nitrogen-saturated hexane were refluxed for 4 h. Phenylacetylene (0.34 g, 3.1 mmol) was then added and refluxing was continued overnight. Hexane was removed under vacuum and workup as above gave [2-(4-chlorophenyl)-6-phenyl-4-(3,4,5-trimethoxyphenyl)pyranyl- η^5]tricarbonylmanganese (**2a**; 0.39 g, 45%).

[2,6-Diphenyl-4-(4-trifluoromethylphenyl)pyranyl- η^5]tricarbonylmanganese (**2b**). Prepared by the general method described for **2a** from [[1-(4-trifluoromethylphenyl)-2-phenylcarbonyl- κO]]ethenyl- κC^1]tetracarbonylmanganese (**1r**) and phenylacetylene under reflux in

CCl_4 for 6 h, **2b** was obtained as a red oil (71%) which crystallized from petroleum spirit as dark red crystals, m.p. 178 °C. Anal. Found: C, 62.76; H, 3.06; $C_{27}H_{16}F_3O_4Mn$ Calc.: C, 62.81; H, 3.12%. IR: $\nu(CO)$ 2015 (vs), 1950 (s), 1935 (s) cm^{-1} . 1H NMR: δ 8.06 (d, 2H, $J = 8.1$ Hz, $H2''$, $6''$), 7.78 (d, 2H, $J = 8.1$ Hz, $H3''$, $5''$), 7.52 (m, 4H, $H2'$, $6'$) 7.44 (m, 4H, $H3'$, $5'$), 7.35 (m, 2H, $H4'$), 5.63 (s, 2H, $H3$, 5). ^{13}C NMR: δ 141.1 (s, $C1''$), 135.2 (s, $C1'$), 129.0 (d, $C3'$, $5'$), 128.6 (d, $C4'$), 126.9 (d, $C2''$, $6''$), 126.3 (d, $J = 3.4$ Hz, $H3''$, $5''$), 123.4 (d, $C2'$, $6'$), 96.4 (s, $C2$, 6), 94.6 (s, $C4$), 80.6 (d, $C3$, 5).

[2,4,6-Triphenylpyranyl- η^5]tricarbonylmanganese (**2c**). Prepared by the general method described for **2a** from [[1-phenyl-2-phenylcarbonyl- κO]]ethenyl- κC^1]tetracarbonylmanganese (**1b**) and phenylacetylene under reflux in CCl_4 for 4 h, **2c** was obtained as a red oil (72%) that crystallized from petroleum spirit as small red crystals, m.p. 183 °C. Anal. Found: C, 69.12; H, 3.58; $C_{26}H_{17}O_4Mn$ Calc.: C, 69.65; H, 3.82%. IR: $\nu(CO)$ 2012 (vs), 1947 (s), 1934 (s, sh) cm^{-1} . 1H NMR: δ 7.94 (d, 2H, $J = 7.0$ Hz, $H2''$, $6''$), 7.51 (m, 4H, $H2'$, $6'$), 7.44 (m, 7H, $H3'$, $5'$, $3''$, $4''$, $5''$), 7.35 (d, 2H, $J = 7.1$ Hz, $H4'$), 5.63 (s, 2H, $H3$, 5). ^{13}C NMR: δ 136.9 (s, $C1''$), 135.7 (s, $C1'$), 129.2 (d, $C3''$, $5''$), 128.9 (d, $C3'$, $5'$), 128.7 (d, $C4''$), 128.3 (d, $C2'$), 126.9 (d, $C2''$, $6''$), 123.3 (d, $C2'$, $6'$), 97.5 (s, $C4$), 95.3 (s, $C2$, 6), 81.0 (d, $C3$, 5).

[2-(4-Chlorophenyl)-6-phenyl-4-(4-trifluoromethylphenyl)pyranyl- η^5]tricarbonylmanganese (**2d**). Prepared by the general method described for **2a** from [[1-(4-trifluoromethylphenyl)-2-(4-chlorophenyl)carbonyl- κO]]ethenyl- κC^1]tetracarbonylmanganese (**1q**) and phenylacetylene under reflux in CCl_4 for 6 h, **2d** was obtained as a red oil (52%) which crystallized from petroleum spirit as bright red crystals, m.p. 164 °C. Anal. Found: C, 59.53; H, 2.57; $C_{27}H_{15}F_3ClO_4Mn$ Calc.: C, 58.88; H, 2.74%. IR: $\nu(CO)$ 2016 (vs), 1953 (s), 1937 (s, sh) cm^{-1} . 1H NMR: δ 8.03 (d, 2H, $J = 8.2$ Hz, $H2''$, $6''$), 7.79 (d, 2H, $J = 8.2$ Hz, $H3''$, $5''$), 7.47 (m, 4H, $H2'''$, $3'''$, $5'''$, $6'''$), 7.41 (m, 5H, $H2'$, $3'$, $5'$, $6'$, $4''$), 5.61 (s, 1H, $H3$), 5.57 (s, 1H, $H5$). ^{13}C NMR: δ 140.9 (s, $C1''$), 134.8 (s, $C1'''$), 134.3 (s, $C1'$), 134.2 (s, $C4'$), 129.3 (d, $C3'$, $5 \times$), 129.0 (d, $C3'''$, $5'''$), 128.8 (d, $C4'''$), 126.9 (d, $C2''$, $6''$), 126.3 (d, $J = 3.7$ Hz, $C3''$, $5''$), 124.4 (d, $C2'$, $6'$), 123.4 (d, $C2'''$, $6'''$), 97.5 (s, $C6$), 94.9 (s, $C4$), 93.9 (s, $C2$), 80.8 (d, $C3$), 80.4 (d, $C5$).

[2-(4-Chlorophenyl)-4-(3,4,5-trimethoxyphenyl)-6-trimethylsilylpyranyl- η^5]tricarbonylmanganese (**2e**). Prepared by the general method described for **2a** from [[1-(3,4,5-trimethoxyphenyl)-2-(4-chlorophenylcarbonyl- κO)]ethenyl- κC^1]tetracarbonylmanganese (**1i**) and trimethylsilylacetylene under reflux in CCl_4 overnight, **2e** was obtained as a red oil (48%) which crystallized from petroleum spirit as small red crystals, m.p. 149 °C. Anal. Found: C, 55.00; H, 4.67; $C_{26}H_{26}ClSiO_7Mn$

Calc.: C, 54.89; H, 4.61%. IR: $\nu(\text{CO})$ 2011 (vs), 1944 (s), 1929 (s) cm^{-1} . ^1H NMR: δ 7.34 (d, 2H, $J = 8.8$ Hz, H3', 5'), 7.25 (d, 2H, $J = 8.8$ Hz, H2', 6'), 7.08 (s, 2H, H2'', 6''), 5.32 (d, 1H, $J = 1.2$ Hz, H3), 5.03 (d, 1H, $J = 1.2$ Hz, H5), 3.97 (s, 6H, 3'', 5''-OCH₃), 3.94 (s, 3H, 4''-OCH₃), 0.30 (9H, s, Si(CH₃)₃). ^{13}C NMR: δ 153.7 (s, C3'', 5''), 138.7 (s, C4''), 134.1 (s, C1', 4'), 132.6 (s, C1''), 129.0 (d, C3', 5'), 124.8 (d, C2', 6'), 104.8 (d, C2'', 6''), 101.2 (s, C2), 95.4 (s, C4), 92.2 (d, C5), 88.8 (s, C6), 81.5 (d, C3), 61.0 (q, 4''-OCH₃), 56.4 (q, 3'', 5''-OCH₃), -2.1 (q, Si(CH₃)₃). FAB-MS (m/e): 568 (M⁺, 10), 484 (M⁺-3CO, 16), 429 (M⁺-Mn(CO)₃, 100).

[4-(4-Methoxyphenyl)-6-phenyl-2-(3,4,5-trimethoxyphenyl)pyranyl- η^5]tricarbonylmanganese (**2f**). Prepared by the general method described for **2a** from [[1-(4-methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)carbonyl- κO]ethenyl- κC^1]tetracarbonylmanganese (**1e**) and phenylacetylene under reflux in CCl₄ overnight, **2f** was obtained as a red oil (91%) which crystallized by diffusion (CH₂Cl₂, pentane) as ruby-red crystals, m.p. 165 °C. Anal. Found: C, 63.11; H, 4.42; C_{30.25}O₃Mn. Calc.: C, 63.39; H, 4.43%. IR: $\nu(\text{CO})$ 2010 (vs), 1946 (s), 1928 (s) cm^{-1} . ^1H NMR: δ 7.85 (d, 2H, $J = 8.8$ Hz, H2'', 6''), 7.45 (m, 4H, H2''', 3''', 5''' 6'''), 7.34 (d, 1H, $J = 7.9$ Hz, H4'''), 7.06 (d, 2H, $J = 8.8$ Hz, H3'', 5''), 6.70 (s, 2H, H2', 6'), 5.57 (s, 1H, H5), 5.47 (s, 1H, H3), 3.91 (9H, s, 4''-OCH₃, 3', 5'-OCH₃), 3.90 (s, 3H, 4'-OCH₃). ^{13}C NMR: δ 160.2 (s, C4''), 153.5 (s, C3', 5'), 138.3 (s, C4'), 135.9 (s, C1'''), 131.4 (s, C1'), 128.9 (d, C3''', 5'''), 128.8 (s, C1''), 128.2 (d, C4''', 2'', 6''), 123.2 (d, C2''', 6'''), 114.6 (d, C3'', 5''), 100.8 (d, C2', 6'), 98.0 (s, C4), 95.1 (s, C2), 94.9 (s, C6), 80.8 (d, C3, 5), 61.0 (q, 4'-OCH₃), 56.2 (q, 3', 5'-OCH₃), 55.5 (q, 4''-OCH₃). FAB-MS (m/e): 568 (M⁺, 8), 540 (M⁺-CO, 15), 484 (M⁺-3CO, 12), 429 (M⁺-Mn(CO)₃, 100).

[5-Methyl-2-phenyl-6-propyl-4-(4-trifluoromethylphenyl)pyranyl- η^5]tricarbonylmanganese (**2g**). Prepared from [[1-(4-trifluoromethylphenyl)-2-phenylcarbonyl- κO]ethenyl- κC^1]tetracarbonylmanganese (**1r**) and 2-hexyne under reflux in CCl₄ for 9 h, the product was isolated by the following modification of the workup procedure described for **2a**. The solvent was removed under vacuum. PLC (dichloromethane/petroleum spirit (1:2)) of the residual oil gave one major band. This yielded a non-crystallizing red oil which from NMR was a mixture (net 44% yield; ca. 8:1) of [5-methyl-2-phenyl-6-propyl-4-(4-trifluoromethylphenyl)pyranyl- η^5]tricarbonylmanganese (**2g**) and its regioisomer [6-methyl-2-phenyl-5-propyl-4-(4-trifluoromethylphenyl)pyranyl- η^5]tricarbonylmanganese (**2g'**). For the mixture the following spectral data were recorded. IR: $\nu(\text{CO})$ 2000 (vs), 1940 (s), 1928 (s) cm^{-1} . FAB-MS (m/e): 496 (M⁺, 5), 468 (M⁺-CO, 21), 440 (M⁺-2CO, 10), 412 (M⁺-3CO, 13), 367 (M⁺-Mn(CO)₃, 100), 337 (80). From relative signal intensity in NMR spectra the

following assignments were possible for the major and minor isomers. For **2g**: ^1H NMR: δ 8.00 (d, 2H, $J = 9.3$ Hz, H2'', 6''), 7.80 (d, 2H, $J = 9.3$ Hz, H3'', 5''), 7.33 (m, 5H, H2', 3', 4', 5', 6'), 5.01 (s, 1H, H3), 2.52 (m, 1H, H8a), 2.16 (m, 1H, H8b), 1.84 (s, 3H, 7-CH₃), 1.76 (m, 1H, H9a), 1.56 (m, 1H, H9b), 1.05 (t, 3H, $J = 7.0$ Hz, 10-CH₃). ^{13}C NMR: δ 140.9 (s, C1''), 135.0 (d, C4'), 134.7 (s, C1'), 132.1 (d, C2'', 6''), 128.7 (d, C3', 5'), 125.7 (d, $J = 3.6$ Hz, C3'', 5''), 123.4 (d, C2', 6'), 101.0 (s, C5), 97.7 (s, C6), 96.4 (s, C2), 95.8 (s, C4), 81.0 (d, C3), 35.0 (t, C8), 18.6 (t, C9), 16.7 (q, C7), 14.2 (q, C10). For the regioisomer [6-methyl-2-phenyl-5-propyl-4-(4-trifluoromethylphenyl)pyranyl- η^5]tricarbonylmanganese (**2g'**): ^1H NMR: δ 4.89 (s, 1H, H3), 2.04 (s, 3H, 10-CH₃), 0.88 (t, 3H, $J = 7.0$ Hz, 9-CH₃). ^{13}C NMR: δ 140.4 (s, C1'), 133.6 (d, C2'', 6''), 128.3 (d, C3', 5'), 125.6 (d, $J = 3.6$ Hz, C3'', 5''), 92.2 (s, C5), 80.5 (d, C3), 32.5 (t, C7), 18.6 (t, C8), 16.7 (q, C10), 14.2 (q, C9).

[2-(4-Chlorophenyl)-5,6-diphenyl-4-(4-trifluoromethylphenyl)pyranyl- η^5]tricarbonylmanganese (**2h**). Prepared from [[1-(4-trifluoromethylphenyl)-2-(4-chlorophenyl)carbonyl- κO]ethenyl- κC^1]tetracarbonylmanganese (**1q**) and diphenylacetylene under reflux in CCl₄ for 10 h, the product was isolated by the following modification of the workup procedure described for **2a**. Carbon tetrachloride was removed under vacuum. PLC (dichloromethane/petroleum spirit (1:3)) of the residual oil gave one major band which yielded **2h** as a red oil (46%) which failed to crystallize. IR: $\nu(\text{CO})$ 2015 (vs), 1953 (s), 1934 (s) cm^{-1} . FAB-MS (m/e): 626 (M⁺, 4), 543 (M⁺-3CO, 62), 488 (M⁺-Mn(CO)₃, 100), 469 (30). ^1H and ^{13}C NMR suggest the presence of 2 isomers, which unlike those (**2g**, **2g'**) in the case above, cannot be regioisomers given the symmetrical nature of the alkyne. There may possibly be some form of rotational isomerism associated with the extensively crowded aryl substituents but we have been unable to rationalise these observations in any satisfactory fashion. NMR assignment is very limited. In the following the symbol * indicates the minor isomer. ^1H NMR: δ 7.68 (d, 2H, H3''*, 5''*), 7.50 (m, Ar-H), 5.15 (s, 1H, H3*), 5.13 (s, 1H, H3). ^{13}C NMR: δ 136.0 (s), 135.6 (s), 132.5 (d), 132.2 (s), 131.9 (s), 131.8 (d), 131.4 (d), 129.4 (d), 129.3 (d), 129.0 (d), 128.6 (d), 127.9 (d), 126.0 (d), 125.5 (d), 125.4 (d), 125.3 (d), 124.6 (d, $J = 4.2$ Hz, C3''*, 5''*), 105.0 (s), 103.4 (s), 103.3 (s), 79.5 (d, C3*), 79.4 (d, C3).

[2,5,6-Triphenyl-4-(4-trifluoromethylphenyl)pyranyl- η^5]tricarbonylmanganese (**2j**). Prepared by the general method described for **2a** from [[1-(4-trifluoromethylphenyl)-2-phenylcarbonyl- κO]ethenyl- κC^1]tetracarbonylmanganese (**1r**) and diphenylacetylene under reflux in CCl₄ for 5.5 h, **2j** was obtained as a red oil (61%) which was crystallized by solvent diffusion (dichloromethane, pentane) as small red crystals, m.p. 152 °C.

Anal. Found: C, 66.95; H, 3.47. $C_{33}H_{20}F_3O_4Mn$ calc.: C, 66.90; H, 3.40 %. IR: $\nu(\text{CO})$ 2013 (vs), 1951 (s), 1932 (s) cm^{-1} . NMR indicated as for **2h** the presence of isomers (ca 3:1 by signal integration), but again the nature of the isomerism is not apparent. Major isomer: ^1H NMR: δ 7.59 (m, 4H), 7.42 (m, 4H), 7.32 (m, 3H), 7.18 (d, 4H, $J = 8.2$ Hz), 7.09 (m, 4H), 5.09 (s, 1H, H3). ^{13}C NMR: δ (DEPT only: all doublets) 132.5, 131.5, 129.8, 129.1, 128.9, 128.5, 128.0, 127.9, 125.9, 124.5 (C2', 6'), 78.7 (C3). Minor isomer: ^1H NMR: δ 7.71 (d, 2H, $J = 8.0$ Hz, H3'', 5''), 7.59 (m, 4H), 7.42 (m, 4H), 7.18 (m, 9H), 5.13 (s, 1H, H3). ^{13}C NMR: δ (DEPT only: all doublets) 132.6, 131.8, 129.5, 129.0, 128.9, 127.8, 127.7, 127.0, 126.3, 125.5 (C3'', 5''), 124.3 (C2', 6'), 78.9 (C3).

2.3. Preparation of pyrylium triiodide salts (**3**) from pyranyltricarbonylmanganese complexes and iodine

The following preparation of 2-(4-chlorophenyl)-6-phenyl-4-(3,4,5-trimethoxyphenyl)pyrylium triiodide (**3a**) illustrates the standard method; any variations for other pyrylium salts (**3b-3j**) are indicated individually with their spectral and analytical data.

2-(4-Chlorophenyl)-6-phenyl-4-(3,4,5-trimethoxyphenyl)pyrylium triiodide (**3a**). (i) To [2-(4-chlorophenyl)-6-phenyl-3-(3,4,5-trimethoxyphenyl)pyranyl- η^5]tricarbonylmanganese (**2a**; 1 mmol) in CCl_4 (20 ml) was added an excess of I_2 (ca. 4 mmol). After stirring for 1 h, solvent was removed under vacuum to leave an oil, and addition of diethyl ether led to separation of the pyrylium triiodide salt (**3a**) (92%) which was recrystallized by solvent diffusion (MeCN/Et₂O) as dark red crystals, m.p. 182 °C. Anal. Found: C, 38.60; H, 2.69; $C_{26}H_{22}ClI_3O_4$ Calc.: C, 38.34; H, 2.72%. λ_{max} (relative absorbance) in MeCN: 288 (100), 403 (76) nm. ^1H NMR ($(\text{CD}_3)_2\text{CO}$): δ 9.28 (d, 1H, $J = 1.7$ Hz, H3), 9.26 (d, 1H, $J = 1.7$ Hz, H5), 8.75 (d, 2H, $J = 7.0$ Hz, H2', 6'), 8.71 (d, 2H, $J = 7.6$ Hz, H2'', 6''), 8.02 (s, 2H, H2'', 6''), 7.97 (m, 5H, H3', 5', 3'', 4'', 5''), 4.19 (s, 6H, 3'', 5''-OCH₃), 4.13 (s, 3H, 4''-OCH₃). ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$): δ 171.2 (s, C2), 169.9 (s, C6), 166.4 (s, C4), 155.1 (s, C3'', 5''), 146.5 (s, C4''), 141.6 (s, C4'), 135.9 (d, H4''), 131.2 (d, C2', 6'), 131.0 (d, C3', 5'), 130.8 (d, C3'', 5''), 130.2 (s, C1''), 129.7 (d, C2'', 6''), 129.1 (s, C1''), 128.5 (s, C1'), 116.1 (d, C3, 5), 109.1 (d, C2'', 6''), 61.2 (q, 4''-OCH₃), 57.4 (q, 3'', 5''-OCH₃). FAB-MS (m/e): 433 (M⁺, 36), 307 (11), 289 (9), 154 (100), 136 (79).

(ii) The following one-pot method, starting from the chalcone, incorporates the initial manganese to form **2a**: 1-(4-chlorophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (1 mmol) and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (1 mmol) were heated under reflux in hexane (25 ml) for 5h. Phenylacetylene (1.4 mmol) was added and the solution refluxed overnight. On cooling, I_2 (4 mmol) was added.

After stirring for 1 h, hexane was removed under vacuum, ether added, and the collected product (**3a**) recrystallized as described. The yield of 79% based on chalcone was nearly twice the net yield obtained (45%) by the sequence of individual reactions with isolation of manganese, insertion and oxidation products (yields of 78% [2], 62% and 92% respectively). See also the similar improvement in yield for the one-pot sequence for **3e**.

2,6-Diphenyl-4-(4-trifluoromethylphenyl)pyrylium triiodide (**3b**). Prepared by the general method described for **3a** from [2,6-diphenyl-4-(4-trifluoromethylphenyl)pyranyl- η^5]tricarbonylmanganese (**2b**) and iodine in CCl_4 , **3b** was obtained as a solid (84%) which was recrystallized as dark red crystals, m.p. 230 °C. Anal. Found: C, 38.02; H, 2.13; $C_{24}H_{16}F_3I_3O$ Calc.: C, 38.02; H, 1.91%. λ_{max} (relative absorbance) in MeCN: 290 (100), 343 (76), 407 (53) nm. ^1H NMR ($(\text{CD}_3)_2\text{CO}$): δ 9.45 (s, 2H, H3, 5), 8.88 (d, 2H, $J = 8.2$ Hz, H2'', 6''), 8.83 (d, 4H, $J = 7.4$ Hz, H2', 6'), 8.28 (d, 2H, $J = 8.2$ Hz, H3'', 5''), 8.09 (t, 2H, $J = 7.4$ Hz, H4'), 7.99 (t, 4H, $J = 7.4$ Hz, H3', 5'). ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$): δ 172.8 (s, C2, 6), 166.1 (s, C4), 138.0 (s, C1''), 136.5 (d, C4'), 131.4 (d, C2'', 6''), 131.1 (d, C3', 5'), 130.1 (s, C1'), 130.0 (d, C2', 6'), 127.6 (d, $J = 3.4$ Hz, C3'', 5''), 117.7 (d, C3, 5). This compound was further characterised by a single crystal X-ray structure determination (see below).

2,4,6-Triphenylpyrylium triiodide (**3c**). Prepared by the general method described for **3a** from [2,4,6-triphenylpyranyl- η^5]tricarbonylmanganese (**2c**) and iodine in CCl_4 , **3c** was obtained as a solid (72%) which was recrystallized as dark red crystals, m.p. 210 °C. λ_{max} (relative absorbance) in MeCN: 285 (89), 355 (100), 398 (66) nm. ^1H NMR ($(\text{CD}_3)_2\text{CO}$): δ 9.33 (s, 2H, H3, 5), 8.80 (d, 4H, $J = 7.6$ Hz, H2', 6'), 8.70 (d, 2H, $J = 7.6$ Hz, H2'', 6''), 8.05 (m, 3H, H4', 4''), 7.97 (t, 6H, $J = 7.6$ Hz, H3', 5', 3'', 5''). ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$): δ 172.0 (s, C2, 6), 167.3 (s, C4), 136.1 (d, C4'), 136.0 (d, C4''), 133.9 (s, C1''), 130.9 (d, C3', 5', 3'', 5''), 130.7 (d, C2'', 6''), 130.1 (s, C1'), 129.7 (d, C2', 6'), 116.5 (d, C3, 5).

2-(4-Chlorophenyl)-6-phenyl-4-(4-trifluoromethylphenyl)pyrylium triiodide (**3d**). Prepared by the general method described for **3a** from [2-(4-chlorophenyl)-6-phenyl-4-(4-trifluoromethylphenyl)pyranyl- η^5]tricarbonylmanganese (**2d**) and iodine in CCl_4 , **3d** was obtained as a solid (79%) which was recrystallized as dark red crystals, m.p. 232 °C. Anal. Found: C, 36.57; H, 1.64; $C_{24}H_{15}F_3ClI_3O$ Calc.: C, 36.37; H, 1.91%. λ_{max} (relative absorbance) in MeCN: 290 (100), 347 (71), 415 (47) nm. ^1H NMR ($(\text{CD}_3)_2\text{CO}$): δ 9.49 (d, 1H, $J = 1.5$ Hz, H3), 9.48 (d, 1H, $J = 1.5$ Hz, H5), 8.88 (d, 2H, $J = 8.3$ Hz, H2'', 6''), 8.86 (m, 4H, H2', 6', 2'', 6''), 8.29 (d, 2H, $J = 8.3$ Hz, H3'', 5''), 8.03 (m, 5H, H3', 5', 3'', 4'', 5''). ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$): δ 172.9 (s, C2),

171.5 (s, C6), 166.1 (s, C4), 142.3 (s, C4'), 137.8 (s, C1''), 136.6 (d, C4'''), 131.6 (d, C2', 6'), 131.4 (d, C2'', 6''), 131.2 (d, C3', 5'), 131.0 (d, C3''', 5'''), 130.0 (d, C2''', 6'''), 129.9 (s, C1'''), 128.8 (s, C1'), 127.5 (d, $J = 4.2$ Hz, C3'', 5''), 117.9 (d, C3), 117.8 (d, C5).

2-(4-Chlorophenyl)-4-(3,4,5-trimethoxyphenyl)-6-trimethylsilylpyrylium triiodide (**3e**). (i) Prepared by the general method described for **3a** from [2-(4-chlorophenyl)-4-(3,4,5-trimethoxyphenyl)-6-trimethylsilylpyryl- η^5]tricarbonylmanganese (**2e**) and iodine in CCl_4 , **3e** was obtained as a solid (85%) which was recrystallized as red crystals, m.p. 157 °C. Anal. Found: C, 33.90; H, 3.11; $\text{C}_{28}\text{H}_{26}\text{SiClI}_3\text{O}_4$ Calc.: C, 34.08; H, 3.23%. λ_{max} (relative absorbance) in MeCN: 290 (100), 362 (96), 419 (61) nm. ^1H NMR ($(\text{CD}_3)_2\text{CO}$): δ 9.31 (s, 1H, H3), 8.96 (s, 1H, H5), 8.65 (d, 2H, $J = 6.8$ Hz, H2', 6'), 7.98 (d, 2H, $J = 6.8$ Hz, H3', 5'), 7.90 (s, 2H, H2'', 6''), 4.16 (s, 6H, 3'', 5''-OCH₃), 4.11 (s, 3H, 4''-OCH₃), 0.82 (9H, s, Si(CH₃)₃). ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$): δ 190.3 (s, C6), 173.8 (s, C2), 163.1 (s, C4), 155.1 (s, C3'', 5''), 146.5 (s, C4'), 141.9 (s, C4''), 131.2 (d, C2', 6'), 131.0 (d, C3', 5'), 129.4 (s, C1'), 128.1 (s, C1''), 126.5 (d, C5), 117.7 (d, C3), 109.2 (d, C2'', 6''), 61.2 (q, 4''-OCH₃), 57.4 (q, 3'', 5''-OCH₃), -2.5 (q, Si(CH₃)₃).

(ii) The one-pot sequence as described under (ii) for **3a** above but with trimethylsilylacetylene in place of phenylacetylene gave the pyrylium salt **3e** in 46% yield from chalcone, as compared with a net yield of 31% by the stepwise sequence, based on the 78% yield reported [2] for the chalcone manganation.

4-(4-Methoxyphenyl)-6-phenyl-2-(3, 4, 5-trimethoxyphenyl)pyrylium triiodide (**3f**). Prepared by the general method described for **3a** from [4-(4-methoxyphenyl)-6-phenyl-2-(3,4,5-trimethoxyphenyl)pyryl- η^5]tricarbonylmanganese (**2f**) and iodine in CCl_4 , **3f** was obtained as a solid (88%) which was recrystallized as dark red crystals, m.p. 179 °C. Anal. Found: C, 40.32; H, 3.08; $\text{C}_{27}\text{H}_{25}\text{I}_3\text{O}_5$ Calc.: C, 40.03; H, 3.11 %. λ_{max} (relative absorbance) in MeCN: 292 (88), 407 (100) nm. ^1H NMR ($(\text{CD}_3)_2\text{SO}$): δ 9.02 (s, 1H, H5), 8.97 (s, 1H, H3), 8.71 (d, 2H, $J = 8.3$ Hz, H2'', 6''), 8.54 (d, 2H, $J = 7.1$ Hz, H2''', 6'''), 7.89 (m, 3H, H3''', 4''', 5'''), 7.75 (s, 2H, H2', 6'), 7.37 (d, 2H, $J = 8.3$ Hz, H3'', 5''), 4.07 (s, 6H, 3', 5'-OCH₃), 4.06 (s, 3H, 4''-OCH₃), 3.94 (s, 3H, 4'-OCH₃). ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$): δ 172.4 (s, C2), 172.3 (s, C6), 169.7 (s, C4'), 167.1 (s, C4), 157.5 (s, C3', 5'), 147.4 (s, C4''), 138.4 (d, C4'''), 136.9 (d, C2'', 6''), 133.8 (d, C3''', 5'''), 133.2 (s, C1'''), 132.3 (d, C2''', 6'''), 128.4 (s, C1''), 128.1 (s, C1'), 119.5 (d, C3'', 5''), 117.2 (d, C3, 5), 116.9 (d, C2', 6'), 64.6 (q, 4''-OCH₃), 60.7 (q, 3', 5'-OCH₃), 60.2 (q, 4'-OCH₃).

5-Methyl-2-phenyl-6-propyl-4-(4-trifluoromethylphenyl)pyrylium triiodide (**3g**). Prepared by the general method described for **3a** from [5-methyl-2-phenyl-6-

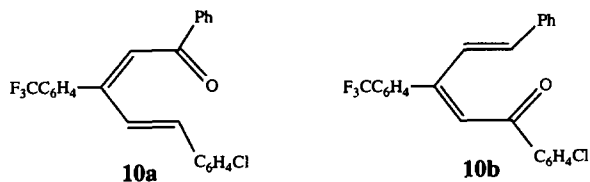
propyl-4-(4-trifluoromethylphenyl)pyryl- η^5]tricarbonylmanganese (**2g**; ca. 89% pure, containing 11% **2g'**: see Section 2.2) and iodine in CCl_4 , **3g** was obtained as a solid (87%) which was recrystallized as small red crystals, m.p. 128 °C. Anal. Found: C, 35.82; H, 2.54; $\text{C}_{22}\text{H}_{20}\text{F}_3\text{I}_3\text{O}$ Calc.: C, 35.80; H, 2.73%. λ_{max} (relative absorbance) in MeCN: 292 (100), 365 (71) nm. ^1H NMR ($(\text{CD}_3)_2\text{CO}$): δ 9.01 (s, 1H, H3), 8.64 (d, 2H, $J = 7.5$ Hz, H2', 6'), 8.19 (m, 4H, H2'', 3'', 5'', 6''), 8.01 (t, 1H, $J = 7.5$ Hz, H4'), 7.92 (t, 2H, $J = 7.5$ Hz, H3', 5'), 3.74 (t, 2H, $J = 7.5$ Hz, 8-CH₂), 2.78 (s, 3H, 7-CH₃), 2.37 (m, 2H, 9-CH₂), 1.38 (t, 3H, $J = 7.3$ Hz, 10-CH₃). ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$): δ 181.1 (s, C6), 170.7 (s, C2), 168.3 (s, C4), 139.8 (s, C1''), 136.1 (d, C4'), 133.1 (d, $J = 30$ Hz, C4'' (seen in BIRDTRAP only)), 131.8 (s, C5), 130.9 (d, C3', 5'), 130.7 (d, C2'', 6''), 129.5 (s, C1'), 129.3 (d, C2', 6'), 126.9 (d, $J = 3.6$ Hz, C3'', 5''), 120.7 (d, C3), 36.7 (t, C8), 20.7 (t, C9), 15.7 (q, C7), 14.1 (q, C10). The regioisomer 6-methyl-2-phenyl-5-propyl-4-(4-trifluoromethylphenyl)pyrylium triiodide (**3g'**) was detected in trace amount in the NMR spectrum; assignment of the following signals was possible. ^1H NMR ($(\text{CD}_3)_2\text{CO}$): δ 8.97 (s, 1H, H3), 3.48 (s, 3H, 10-CH₃), 3.13 (t, 2H, $J = 7.3$ Hz, 7-CH₂), 1.78 (m, 2H, 8-CH₂), 1.04 (t, 3H, $J = 7.3$ Hz, 9-CH₃).

2-(4-Chlorophenyl)-5,6-diphenyl-4-(4-trifluoromethylphenyl)pyrylium triiodide (**3h**). Prepared according to the general method described for **3a** from [2-(4-chlorophenyl)-5,6-diphenyl-4-(4-trifluoromethylphenyl)pyryl- η^5]tricarbonylmanganese (**2h**) and iodine in CCl_4 , **3h** was obtained as a solid (64%) which was recrystallized as small dark red crystals, m.p. 178 °C. Anal. Found: C, 41.33; H, 2.11; $\text{C}_{30}\text{H}_{19}\text{F}_3\text{ClI}_3\text{O}$ Calc.: C, 41.48; H, 2.20%. λ_{max} (relative absorbance) 290 (100), 375 (73) nm. ^1H NMR ($(\text{CD}_3)_2\text{CO}$): δ 9.34 (s, 1H, H3), 8.82 (d, 2H, $J = 8.8$ Hz, H2', 6') 8.12 (d, 2H, $J = 8.6$ Hz), 8.03 (d, 2H, $J = 9.0$ Hz), 8.02 (d, 2H, $J = 8.8$ Hz, H3', 5'), 7.59 (m, 10H).

2,5,6-Triphenyl-4-(4-trifluoromethylphenyl)pyrylium triiodide (**3j**). Prepared by the general method described for **3a** from [2,5,6-triphenyl-4-(4-trifluoromethylphenyl)pyryl- η^5]tricarbonylmanganese (**2j**) and iodine in CCl_4 , **3j** was obtained as a black oil (84%) which could not successfully be crystallized. λ_{max} (relative absorbance) in MeCN: 291 (100), 365 (60) nm. ^1H NMR ($(\text{CD}_3)_2\text{CO}$): δ 9.21 (s, 1H, H3), 8.68 (d, 2H, $J = 7.5$ Hz, H2', 6'), 7.90 (m, 17H). ^{13}C NMR assignments were difficult owing to the large number of aryl carbons as well as the apparent isomerism: only the DEPT (doublets) spectrum was recorded (* indicates minor isomer). ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$): δ 136.9 (C4'), 136.8 (C4'*), 134.1, 132.7, 132.3, 131.6, 131.0, 130.6, 130.5, 130.1, 129.9, 129.8, 129.6, 126.5 ($J = 2.3$ Hz, C3'', 5''), 126.3 ($J = 3.8$ Hz, C3''*, 5''*), 122.2 (C3), 121.7 (C3*). FAB-MS (m/e): 453 (M^+ , 100), 307 (3), 289 (3), 173 (11), 154 (28), 136 (22).

2.4. Attempted transmetalation of the pyranil ligand by FeCp: reaction of [2-(4-chlorophenyl)-6-phenyl-4-(2-trifluoromethylphenyl)pyranil- η^5]tricarbonylmanganese (2d) with Na[Fe(CO)₂Cp]

[2-(4-Chlorophenyl)-6-phenyl-4-(2-trifluoromethylphenyl)pyranil- η^5]tricarbonylmanganese (2d; 0.17 g, 0.34) and Na[Fe(CO)₂Cp] (0.165 g pre-dissolved in 5 ml tetrahydrofuran [10]) were mixed in nitrogen-saturated tetrahydrofuran and refluxed overnight. Tetrahydrofuran was removed under vacuum. PLC (dichloromethane/petroleum spirit 1:1) gave two bands. The top band was removed and identified by IR and ¹H NMR as the dimer [Fe(CO)₂Cp]₂. Removal of the lower band followed by extraction with dichloromethane and solvent removal under vacuum gave 0.064 g (50%) of a mixture of the isomers 1-phenyl-3-(4-trifluorophenyl)-5-(4-chlorophenyl)penta-2, 4-dien-1-one (10a) and 1-(4-chlorophenyl)-3-(4-trifluoromethylphenyl)-5-phenylpenta-2, 4-dien-1-one (10b) in a 1:1 ratio (based on ¹H and ¹³C-NMR). Crystallization by diffusion (dichloromethane/pentane) gave small yellow crystals that were mainly 1-phenyl-3-(4-trifluoromethylphenyl)-5-(4-chlorophenyl)penta-2, 4-dien-1-one (10a) which was fully purified by further recrystallization, m.p. 140 °C. Anal. Found: C, 69.90; H, 3.83; C₂₄H₁₆F₃ClO Calc.: C, 69.83; H, 3.91%. ¹H-NMR: δ 8.46 (d, 1H, *J* = 16.3 Hz, H4), 7.99 (d, 2H, *J* = 7.2 Hz, H2', 6'), 7.73 (d, 2H, *J* = 8.2 Hz, H3'', 5''), 7.57 (m, 3H, H4', 2'', 6''), 7.47 (t, 2H, *J* = 7.2 Hz, H3', 5'), 7.43 (d, 2H, *J* = 8.5 Hz, H3''', 5'''), 7.32 (d, 2H, *J* = 8.5 Hz, H2''', 6'''), 6.87 (s, 1H, H2), 6.57 (d, 1H, *J* = 16.3 Hz, H5). ¹³C NMR: δ 190.8 (s, C1), 153.8 (s, C3), 144.0 (s), 139.7 (d, C5), 139.1 (s), 135.0 (s), 134.8 (s), 132.9 (d, C4'), 129.5 (d, C2'', 6''), 129.0 (d, C2''', 6'''), 128.8 (d, C3''', 5'''), 128.7 (d, C3', 5'), 128.4 (d, C2', 6'), 127.0 (d, C4), 125.5 (d, *J* = 3.8 Hz, C3'', 5''), 123.5 (d, C2). MS (*m/e*): 412 (M⁺, 100), 377 (M⁺-Cl, 20), 301 (M⁺-PhCl), 202 (36), 105 (PhCO⁺, 60), 77 (C₆H₅⁺, 28).



When the solvent remaining from the crystallization supernatant was evaporated, the residual yellow oil was mainly 1-(4-chlorophenyl)-3-(4-trifluorophenyl)-5-phenylpenta-2,4-dien-1-one (10b) enabling NMR assignments as follows. ¹H NMR: δ 8.48 (d, 1H, *J* = 16.2 Hz, H4), 7.93 (d, 2H, *J* = 8.5 Hz, H2', 6'), 7.74 (d, 2H, *J* = 8.2 Hz, H3'', 5''), 7.47 (m, H3', 5', 2''', 4''', 6'''), 6.79 (s, 1H, H2), 6.65 (d, 1H, *J* = 16.2 Hz, H5). ¹³C NMR δ

189.4 (s, C1), 154.9 (s, C3), 144.0 (s), 141.8 (d, C5), 139.2 (s), 137.6 (s), 136.2 (s), 129.8 (d, C2', 6'), 129.6 (d, C2'', 6''), 129.4 (d, C4'''), 129.0 (d, C3', 5'), 128.8 (d, C2''', 6'''), 127.8 (d, C3''', 5'''), 126.3 (d, C4), 125.5 (d, *J* = 3.8 Hz, C3'', 5''), 122.4 (d, C2).

In both of the above isomers, the 4,5-double bond has *E*-stereochemistry from the coupling constants for H4 and H5; the stereochemistry of the 2,3-double bond is not established but is most likely also *E* as this would retain the relative stereochemistry of the parent pyranil (cf. Scheme 4).

2.5. X-ray crystal structure determinations

[(2-Methyl-4,6-diphenylpyranil- η^5)tricarbonylmanganese (9). Red crystals (m.p. 97°C) were obtained from petroleum spirit. Preliminary precession photography showed an orthorhombic lattice with absences suggesting space group *Pbca*. Intensity data were collected on a Nicolet R3 four-circle diffractometer at -100 °C using monochromated Mo-K α radiation (λ = 0.7107 Å).

Crystal data: C₂₁H₁₅MnO₄, *M_r* 654.5, orthorhombic, space group *Pbca*, *a* = 18.746(1), *b* = 15.368(1), *c* = 12.107(1)Å, *V* = 3487.9(4) Å³, *D_c* = 1.47 g cm⁻³ for *Z* = 8. *F*(000) 1584, μ (Mo-K α) 8.00 cm⁻¹. Crystal size 0.56 × 0.20 × 0.40 mm.

A total of 3059 unique reflections in the range 2° < 2 θ < 45° were collected. After correction for Lorentz and polarisation effects and for linear absorption (Ψ -scan method, *T_{max, min}* 0.94, 0.51) 1403 with *I* > 2 σ (*I*) were used in calculations.

The coordinates of the manganese atom were located from a Patterson map (SHELXS-86) [11a] and all other non-hydrogen atoms were located in a subsequent difference map. The manganese atom was assigned anisotropic temperature factors while all other atoms were treated isotropically because of the shortage of observed data. The phenyl rings were included as rigid hexagons, and hydrogen atoms were included in calculated positions with tied *U_{iso}* values for each type. Full-matrix least-squares refinement (SHELX-76) [11b] converged with *R* = 0.0814, *R_w* = 0.0630, where *R* = [$\sigma(F^2) + 0.000122F^2$]⁻¹. In the last cycle the largest parameter shift Δ/σ was 0.008 and a final difference map showed no feature > 0.65 e Å⁻³.

Refined coordinates are listed in Table 2 and selected bond parameters are included in the caption to Fig. 1 which illustrates the structure.

2,6-Diphenyl-4-(4-trifluoromethylphenyl)pyrylium triiodide (3b). Dark red rhombs were formed by vapour diffusion of pentane into a saturated dichloromethane solution of 3b at 4°C. Preliminary precession photography suggested a triclinic lattice. Intensity data and accurate cell dimensions were obtained on an Enraf-Nonius CAD4 automatic four-circle diffractometer at

Table 2
Final atom coordinates and equivalent isotropic temperature factors for (2-methyl-4,6-diphenylpyranyl- η^5)tricarbonylmanganese (9)

Atom	x	y	z	U
Mn (1)	0.3353 (1)	0.1212 (1)	0.2213 (1)	0.021 *
C (1)	0.3999 (5)	0.0329 (6)	0.1225 (8)	0.020 (3)
C (2)	0.4446 (5)	0.0876 (6)	0.1855 (7)	0.018 (3)
C (3)	0.4338 (5)	0.0868 (6)	0.3026 (7)	0.016 (2)
C (4)	0.3772 (5)	0.0318 (6)	0.3451 (8)	0.021 (3)
C (5)	0.3423 (5)	-0.0220 (5)	0.2688 (8)	0.024 (2)
C (6)	0.2812 (5)	-0.0810 (6)	0.3003 (8)	0.025 (3)
C (7)	0.2603 (5)	0.0883 (6)	0.1361 (8)	0.030 (3)
C (8)	0.3455 (5)	0.2248 (6)	0.1532 (8)	0.024 (3)
C (9)	0.2867 (5)	0.1749 (6)	0.3282 (9)	0.025 (3)
C (11)	0.3996 (3)	0.0277 (4)	0.0000 (4)	0.018 (3)
C (12)	0.4248 (3)	0.0981 (4)	-0.0613 (4)	0.028 (3)
C (13)	0.4258 (3)	0.0939 (4)	-0.1764 (4)	0.037 (3)
C (14)	0.4015 (3)	0.0193 (4)	-0.2302 (4)	0.029 (3)
C (15)	0.3762 (3)	-0.0511 (4)	-0.1689 (4)	0.027 (3)
C (16)	0.3753 (3)	-0.0469 (4)	-0.0538 (4)	0.022 (3)
C (21)	0.4818 (3)	0.1372 (4)	0.3781 (5)	0.015 (2)
C (22)	0.5257 (3)	0.2032 (4)	0.3374 (5)	0.026 (3)
C (23)	0.5742 (3)	0.2445 (4)	0.4074 (5)	0.030 (3)
C (24)	0.5787 (3)	0.2199 (4)	0.5181 (5)	0.028 (3)
C (25)	0.5349 (3)	0.1540 (4)	0.5588 (5)	0.027 (3)
C (26)	0.4864 (3)	0.1126 (4)	0.4888 (5)	0.024 (3)
O (1)	0.3772 (3)	-0.0483 (4)	0.1716 (5)	0.024 (2)
O (7)	0.2146 (4)	0.0637 (5)	0.0822 (6)	0.039 (2)
O (8)	0.3502 (4)	0.2913 (5)	0.1098 (6)	0.039 (2)
O (9)	0.2541 (4)	0.2109 (4)	0.3965 (6)	0.037 (2)

* U_{eq} value from anisotropic parameters

20°C using monochromated Mo-K α radiation ($\lambda = 0.7107 \text{ \AA}$).

Crystal data: $C_{24}H_{16}OF_3I_3$, M_r 758.0, triclinic space group $P\bar{1}$, $a = 9.705(2)$, $b = 11.455(5)$, $c = 11.575(5) \text{ \AA}$, $\alpha = 101.68(3)$, $\beta = 106.83(3)$, $\gamma = 89.55(2)^\circ$, $V = 1204.3(8) \text{ \AA}^3$. $D_c = 2.090 \text{ g cm}^{-3}$ for $Z = 2$. $F(000) 708$, $\mu(\text{Mo-K}\alpha) 36.60 \text{ cm}^{-1}$.

A total of 2907 unique reflections in the range $2 < 2\theta < 44^\circ$ was collected. After correction for Lorentz and polarisation effects and for linear absorption (Ψ -scan

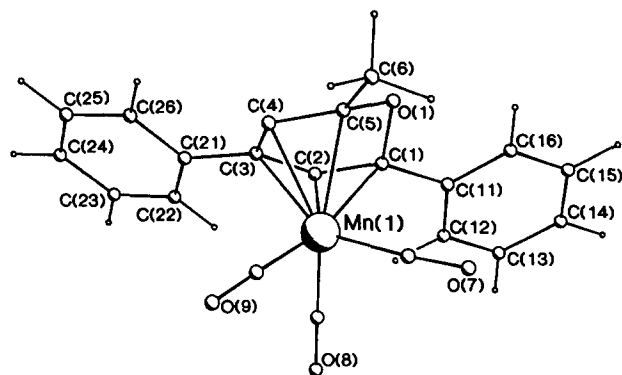


Fig. 1. The structure of (2-methyl-4,6-diphenylpyranyl- η^5)tricarbonylmanganese (9). Bond distances include: Mn-C(1) 2.178(9), Mn-C(2) 2.157(9), Mn-C(3) 2.159(9), Mn-C(4) 2.180(9), Mn-C(5) 2.280(9) \AA . The C-C and C-O distances within the pyran ring are between 1.40(1) and 1.45(1) \AA .

Table 3
Final atom parameters for 2,6-diphenyl-4-(4-trifluoromethylphenyl)pyrylium triiodide (3b)

Atom	x	y	z	U_{eq}
I (1)	0.1319 (1)	0.3490 (1)	0.4727 (1)	0.075
I (2)	0.0473 (1)	0.1206 (1)	0.2933 (1)	0.059
I (3)	-0.0463 (1)	-0.1049 (1)	0.1271 (1)	0.113
O (1)	0.7916 (6)	0.5331 (5)	0.7756 (5)	0.043
C (1)	0.892 (1)	0.4570 (9)	0.7573 (9)	0.043
C (2)	0.855 (1)	0.3518 (9)	0.6757 (9)	0.047
C (3)	0.710 (1)	0.3221 (8)	0.6067 (8)	0.040
C (4)	0.610 (1)	0.4065 (8)	0.6263 (9)	0.042
C (5)	0.6511 (9)	0.5116 (8)	0.7123 (9)	0.040
C (11)	1.037 (1)	0.4976 (8)	0.8420 (9)	0.040
C (12)	1.062 (1)	0.6105 (9)	0.9151 (9)	0.053
C (13)	1.195 (1)	0.649 (1)	0.998 (1)	0.070
C (14)	1.307 (1)	0.572 (1)	1.010 (1)	0.059
C (15)	1.286 (1)	0.460 (1)	0.936 (1)	0.061
C (16)	1.151 (1)	0.421 (1)	0.8516 (9)	0.054
C (31)	0.6655 (9)	0.2066 (8)	0.5163 (8)	0.039
C (32)	0.766 (1)	0.1275 (9)	0.490 (1)	0.058
C (33)	0.725 (1)	0.0203 (9)	0.406 (1)	0.058
C (34)	0.581 (1)	-0.0094 (9)	0.3447 (9)	0.046
C (35)	0.480 (1)	0.0671 (9)	0.3714 (9)	0.048
C (36)	0.519 (1)	0.1739 (9)	0.4566 (8)	0.048
C (37)	0.537 (1)	-0.118 (1)	0.249 (1)	0.062
C (51)	0.563 (1)	0.6059 (8)	0.7476 (8)	0.043
C (52)	0.410 (1)	0.5892 (9)	0.704 (1)	0.053
C (53)	0.327 (1)	0.679 (1)	0.741 (1)	0.057
C (54)	0.386 (1)	0.783 (1)	0.8217 (9)	0.057
C (55)	0.536 (1)	0.799 (1)	0.865 (1)	0.062
C (56)	0.622 (1)	0.7147 (9)	0.8293 (9)	0.052
F (1)	0.619 (1)	-0.2057 (8)	0.267 (1)	0.173
F (2)	0.527 (1)	-0.1055 (8)	0.1426 (8)	0.162
F (3)	0.412 (1)	-0.1650 (8)	0.2414 (8)	0.133

method, $T_{max, min}$ 0.993, 0.763), 2218 with $I > 2\sigma(I)$ were used in calculations.

The structure was solved by direct methods (SHELXS-86) [11a] and routinely developed. All non-hydrogen atoms were assigned anisotropic temperature factors and hydrogen atoms were included in calculated positions with tied U_{iso} values. Full-matrix least-squares refinement (SHELX-76) [11b] converged with $R = 0.0450$, $R_w = 0.0488$, where $R = [\sigma(F^2) + 0.000663F^2]^{-1}$. In the last cycle the largest parameter shift Δ/σ was 0.003 and the largest feature in a final difference map was 1.2 e \AA^{-3} adjacent to an iodine atom.

Refined coordinates are listed in Table 3, and selected bond parameters are listed in the caption to Fig. 2 which shows the structure.

3. Results and discussion

3.1. Pyranyltricarbonylmanganese complexes (2)

Cyclohexadienyltricarbonylmanganese compounds are well known [12] and can be formed directly, for

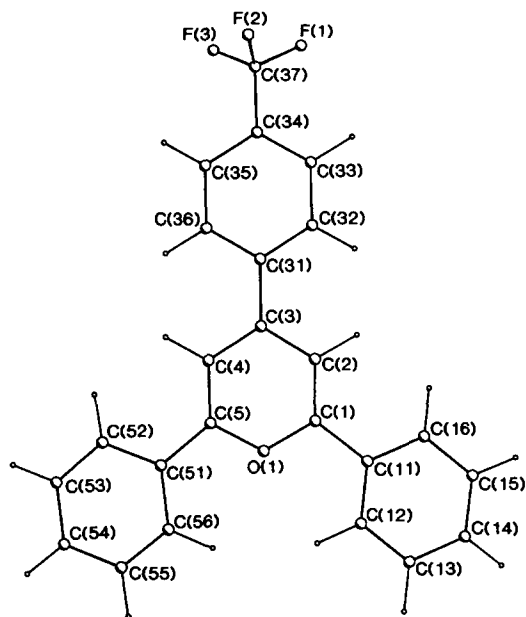


Fig. 2. The structure of the cation of 2,6-diphenyl-4-(4-trifluoromethylphenyl)pyrylium triiodide (**3b**). Bond parameters include: C(1)–O(1) 1.34(1), C(5)–O(1) 1.35(1), C(1)–C(2) 1.35(1), C(2)–C(3) 1.41(1), C(3)–C(4) 1.39(1), C(4)–C(5) 1.38(1), C(37)–F (av.) 1.28(1) Å. The anion has I(1)–I(2) 2.946(1), I(2)–I(3) 2.865(1) Å, I(1)–I(2)–I(3) 176.5(1)°.

instance, by the nucleophilic addition to the coordinated benzene ring in $[(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3]^+$ by hydride [13] or cyclopentadienyl anion [10]. Less directly, the triple insertion of acetylene into the Mn–C bond of orthomanganated *N,N*-dimethylbenzamide ($[(2\text{-}N,N\text{-dimethylamido-}\kappa\text{O-phenyl-}\kappa\text{C}^1)\text{tetracarbonylmanganese}]$ forms $[2\text{-}(\text{Me}_2\text{NCO})\text{C}_6\text{H}_4\text{-cyclohexadienyl-}\eta^5]\text{Mn}(\text{CO})_3$ [1a, 14].

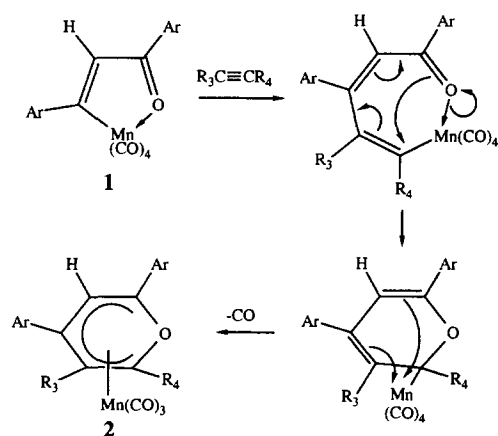
The structurally analogous pyryltricarbonylmanganese compounds are more rare. When Booth and Hargreaves [9] reacted $\text{MeMn}(\text{CO})_5$ with phenylacetylene in a 1:1 mole ratio, the major product was the manganated enone $[2\text{-phenylcarbonyl-}\kappa\text{O-1-phenylethenyl-}\kappa\text{C}^1]\text{tetracarbonylmanganese}$ (**8**), but the pyryl complex **9** was also formed in a minor amount, presumably as suggested by the authors by further reaction of **8** with another molecule of phenylacetylene. In the present study, preformed β -manganated enones (chalcones) were reacted with alkynes in carbon tetrachloride and analogues of **9** were obtained in high yield (Table 1). In one case, a one-pot sequence was tested starting with chalcone manganation in hexane followed by direct addition of phenylacetylene and refluxing without isolation of the manganated chalcone. This gave $[2\text{-}(4\text{-chlorophenyl})\text{-6-phenyl-3-(3,4,5-trimethoxyphenyl)pyryl-}\eta^5]\text{tricarbonylmanganese}$ (**2a**; see experimental section 2.2) but there was no advantage in yield, only in convenience if the intermediate manganated chalcone is not required. In some cases, the alternative

manganation byproduct in which the benzoyl chalcone ring is orthomanganated instead of the β -carbon of the enone [2] may lead to indenol-type byproducts [1b,c] in this one-pot sequence.

The mechanism for the formation of the pyryl complex from the β -manganated chalcone (Scheme 5), essentially as suggested by Booth and Hargreaves [9], involves insertion of alkyne, rearrangement of the π -system as the enone oxygen bonds across the 7-membered ring to the terminal (manganated) carbon, followed by coordination of the remaining two π -bonds to the metal with expulsion of CO. The insertion reaction is regioselective for PhCCH and Me_3SiCCH with the bulkier group (R_4 in Scheme 3) finishing up preferentially on the carbon bonded to the pyryl O atom. This is consistent with the usual steric explanation for such regioselectivity of insertion of nonsymmetrical alkynes into metal–carbon bonds [4a]. For 2-hexyne with manganated chalcone **1r**, both regioisomers are formed but the isomer derived from insertion with the bulkier propyl group terminal ($R_4 = \text{Pr}$; $R_3 = \text{Me}$ in Scheme 3) dominates by a factor of 8 to 1.

An unexplained observation for the products **2h** and **2j** derived from diphenylacetylene was the doubling of some signals in the NMR spectra. As mass spectra and microanalytical data gave no indication of impurity, this suggested some form of isomerism. With the alkyne symmetrical in this case, regioisomerism of the type observed for 2-hexyne is not possible. Perhaps with the extensive steric crowding associated with the 2,3,4-triaryl substitution pattern, some form of rotational isomerism exists but we have no satisfactory explanation. Whatever its origin, it appears from NMR to be retained in the planar pyrylium salt **3j** prepared by iodine oxidation of the pyryl complex **2j**.

Spectral data allow easy distinction between the pyryl- $\text{Mn}(\text{CO})_3$ complexes and the β - $\text{Mn}(\text{CO})_4$ chalcone (**1**) starting materials. In the metal carbonyl



Scheme 5.

stretching region of the infrared spectrum, the pyranil complexes show three bands at frequencies ($\pm 10 \text{ cm}^{-1}$) of 2010 (vs), 1947 (s, br) and 1932 (s, br), typically lower than those for the $\text{Mn}(\text{CO})_4$ group of the reactant compounds. NMR spectra for **2** are characterized by ^1H signals between 5 and 5.7 ppm for H3 and H5 when present, and ^{13}C signals between 80 and 90 ppm for C3 and C5, and around 95 ppm for C2, C4 and C6.

3.2. Pyrylium triiodide salts (**3**)

Reaction of the pyranil tricarbonylmanganese complexes with excess I_2 in carbon tetrachloride routinely gave good-to-high yields of pyrylium triiodide salts (**3**; Table 1), to our knowledge the first time that oxidation of metal pyranil compounds has been used to synthesize pyryliums, an important class of reagents in a wide variety of organic syntheses [15]. The ease of preparation of chalcones from acetophenones and benzaldehydes and the availability of a variety of alkynes commercially means that regioisomerically controlled syntheses of specifically substituted pyrylium ions are readily accessible.

In two cases studied, a one-pot method starting with chalcone in hexane and carrying out the sequence manganation/alkyne insertion/ I_2 oxidation without change of solvent led to pyrylium salts in yields approaching twice those obtained stepwise with isolation of intermediates. The two examples chosen for this test were chalcones which did not undergo significant orthomanganation of the benzoyl ring in competition with manganation of the β -carbon of the enone. Such competitive orthomanganation for other examples [2] would no doubt lead to indenol-type coupling byproducts in the reaction with alkynes [1b,c,d] but these are unlikely to interfere with the ready oxidation by iodine of the pyranil- $\text{Mn}(\text{CO})_3$ complexes and they should be soluble in the ether used in the workup and therefore easily separable from the pyrylium salts. Although more work remains to be done on the one-pot method, indications are that it provides a simple method of pyrylium salt synthesis.

In some cases it is possible to synthesize a pyrylium salt from a chalcone and alkyne without a manganation step: in 1963 Bos and Arens reported [16] that BF_3 in $\text{CCl}_4/\text{Et}_2\text{O}$ promoted the reaction of 1,3-diphenylpro-

penone (chalcone) and phenylacetylene to form 2,4,6-triphenylpyrylium tetrafluoroborate (ca. 40%). There has apparently been no significant follow-up to test the generality of this synthetic method. It is clearly a cheaper general route if yields are reasonable, but whether the degree of regio-control for unsymmetrical alkenes would match that provided by the alkyne insertion step in the manganated chalcone method remains to be seen.

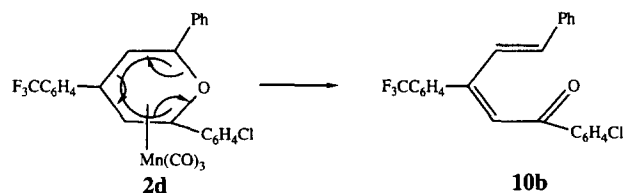
3.3. Attempted transmetallation of [2-(4-chlorophenyl)-6-phenyl-4-(2-trifluoromethylphenyl)pyranil- η^5]tricarbonylmanganese (**2d**) with $\text{Na}[\text{Fe}(\text{CO})_2\text{Cp}]$

The attempted preparation of an $(\eta^5\text{-pyranil})(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$ analogue of ferrocene by reaction of **2d** with $[\text{Fe}(\text{CO})_2\text{Cp}]^-$ was not successful, but the formation of the demetalated isomers 1-phenyl-3-(4-trifluorophenyl)-5-(4-chlorophenyl)penta-2, 4-dien-1-one (**10a**) and 1-(4-chlorophenyl)-3-(4-trifluoromethylphenyl)-5-phenylpenta-2, 4-dien-1-one (**10b**) in equal amounts was an interesting finding. Although the nature of the interaction with the FeCp anionic species is not known, there is clearly a subsequent ring-opening of the type indicated in Scheme 6 leading to **10b**, with the analogous opening in the reverse ring direction leading to **10a**.

3.4. Crystal structures

3.4.1. [2-Methyl-4,6-diphenylpyranil- η^5]tricarbonylmanganese (**9**)

The structure is shown in Figure 1. It is the first example of a structurally characterised η^5 -pyranil complex. Molecules consist of an $\text{Mn}(\text{CO})_3$ fragment bonded in η^5 fashion to the five carbon atoms of the pyranil ring, so are directly comparable to $(\eta^5\text{-cyclohexadienyl})\text{Mn}(\text{CO})_3$ complexes and substituted analogues [12]. The $\text{Mn}(\text{CO})_3$ group is tilted so that the plane defined by the three carbonyl-carbon atoms is at an angle of 10° to the plane defined by the C(1)..C(5) atoms, and individual Mn-C bond lengths vary between 2.15 (to C(2)) and 2.28 Å (to C(5)) so the coordination is unsymmetrical. This is presumably due to crystal packing effects, since there are no severe intramolecular interactions and the displacement does not maximise bonding interactions with a particular part of the ring. The average Mn-C(ring) distance to the pyranil ring is 2.188 Å, slightly longer than the equivalent distance in $(\eta^5\text{-cyclohexadienyl})\text{Mn}(\text{CO})_3$ (2.177 Å) [12] or (1-methylcyclohexadienyl- η^5) $\text{Mn}(\text{CO})_3$ (2.176 Å) [18]. These distances are all longer than the Mn-C distances in the smaller ring compound $(\eta^5\text{-cyclopentadienyl})\text{Mn}(\text{CO})_3$ (2.138 Å) [19] but are shorter than the Mn-C bonds in η^6 -bonded cations of the type $[(\eta^6\text{-arene})\text{Mn}(\text{CO})_3]^+$ (2.22 Å) [20].



Scheme 6.

The Mn–C–O vectors project onto the unsubstituted carbon atoms (C(2) and C(4)) and the O(1) atom of the ring. This orientation will direct the bonding orbitals of the octahedral Mn atom towards the mid-point of the C(1)–C(2) and C(4)–C(5) bonds and the C(3) atom which will be the regions of highest π -electron density. Again this is the same as in (η^5 -cyclohexadienyl)-Mn(CO)₃ compounds. The ring oxygen atom is displaced 0.65 Å from the pyranil ring, away from the Mn atom, so that the plane defined by the C(1)–O(1)–C(5) atoms makes an angle of 47° to that of the rest of the ring. For (η^5 -cyclohexadienyl)Mn(CO)₃ the CH₂ carbon atom is 0.64 Å from the plane, and the corresponding angle between the five-carbon and three-carbon planes is 43°, so the two species are directly comparable.

The phenyl substituents are twisted out of the plane of the pyranil ring by 24.6° (ring 1) and 19.3° (ring 2). This does not appear to arise from intramolecular interactions since both project between two CO ligands, and are well distant from them, so the deviations from planarity must result from intermolecular forces in the lattice.

3.4.2. 2,6-Diphenyl-4-(4-trifluoromethylphenyl)pyrylium triiodide (3b)

The structure of the pyrylium cation is shown in Figure 2. The crystal structure confirms the 2,4,6-substituent pattern on the pyrylium ring in accord with the assignment based on NMR. The greatest deviation from the plane of the pyrylium ring is for C(1) (0.016 Å). The planes of the phenyl rings at C(1) and C(5) are rotated by 9.7° and 8.3° respectively, and the CF₃-substituted ring at C(3) by 5.1°; all substituent rings are therefore essentially conjugated to the pyrylium ring. Bond lengths and angles within the pyrylium ring are in accord with those previously reported for 2,4,6-triphenylpyrylium (as the 1,1,3,3-tetracyanopropenide charge transfer complex) [21] and for (3-acetyl-2,4,6-trimethylpyrylium) (WO₂Cl₂acac) [22]. All C–C–C and C–C–O bond angles in the ring are close to 120° with the exception of C(2)–C(3)–C(4) which is 116.7°. The relatively high e.s.d.'s for the C–C and C–O bonds (because of the dominance of the heavy I₃⁻ ion in the refinement) preclude detailed analysis but there are suggestions of the same bond length trends of C–O < C(1)–C(2) < C(2)–C(3) found for the structure of the triphenylpyrylium ion [21].

The triiodide ion (not shown) is nearly linear with an I–I–I angle of 176.5° but with unequal I–I bond lengths of 2.946 and 2.865 Å. The unit cell packing indicates the likelihood of secondary interactions between proximate I₃⁻ ions which may account for the non-symmetrical nature of the bonding. Similar cases of unequal bond lengths in I₃⁻ have been reported previously [23].

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