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Preparation of cyclomanganated chalcones and their reactions with methyl acrylate and other α,β-unsaturated carbonyl compounds

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Abstract

Chalcones [(*E*)-1,3-diarylprop-2-en-1-ones] react with benzyltetracarbonylmanganese under reflux in petroleum spirit to give two types of cyclomanganation products. The first, involving metallation at the alkenyl β-carbon of the enone, are derivatives of [[1-phenyl-2-phenylcarbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese, while the second type, manganated at the aryl ring *ortho*-carbon, are derivatives of [2-[3-phenylprop-2-en-1-onyl-κO]phenyl-κC^1]tetracarbonylmanganese. In general, more "alkene-manganated" than "ring-manganated" product is formed, with the ratio influenced significantly by certain substituents, e.g. a 4-CF_3 substituent on the phenyl ring at C3 of the enone strongly promotes "alkene-manganation". In some cases there are minor by-products derived from coupling of two chalcone molecules after initial cyclomanganation. The crystal structures are reported for two such products, [2-((1S*,2R*,3S*)-1-hydroxy-1-((*E*)-2-(2-trifluoromethylphenyl)ethenyl)-3-(2-trifluoromethylphenyl)-6-methoxy-2-indanylcarbonyl-κO)-6-methoxyphenyl-κC^1]tetracarbonylmanganese and (1S*,4S*,5R*)-5-(4-bromobenzoyl)-1-(4-bromophenyl)-3,4-di-(4-trifluoromethylphenyl)cyclopent-2-en-1-ol.

In acetonitrile under reflux, alkene-manganated chalcones react with methyl acrylate (methyl propenoate) to form derivatives of methyl (*E*)-4,6-diphenyl-6-oxohex-2-enoate and of 5-(2-methoxycarbonylethyl)-3,5-diphenylfuran-2(5H)-one. The latter butenolides are not formed when the reactions are carried out in carbon tetrachloride, only the former α,β-unsaturated esters. By contrast, in a few reactions studied, acrolein (propenal) and methyl vinyl ketone (but-3-en-2-one) give only the butenolide products when treated with alkene-manganated chalcones in refluxing acetonitrile. An exception is the reaction of methyl vinyl ketone with [[1-(3,4,5-trimethoxyphenyl)-2-(4-chlorophenylcarbonyl-κO)]ethenyl-κC^1]tetracarbonylmanganese to form the cyclized product 5-acetyl-1-(4-chlorophenyl)-3-(3,4,5-trimethoxyphenyl)cyclopent-2-en-1-ol.

Keywords: Manganese; Alkene; Chalcones; Crystal structure; Cyclometallation; Metallacycle

1. Introduction

The reaction of aromatic ketones with $PhCH_2Mn(CO)_5$ is a very general one, giving derivatives of type **1** for a wide range of benzenoid and heteroaromatic substrates. This cyclomanganation of an *O*-donor substrate parallels well-established preparations of cyclopalladiated *N*-donor aromatic molecules. The aryl-manganese compounds have proven generally to be more useful than the aryl-palladium *N*-donor series for subsequent functionalization at the metallated carbon atom, giving novel species with alkynes and alkenes and elusive ortho-substitution products with $HgCl_2$ and halogens. A review covers the developments to 1992 [1].

Cyclomanganation reactions involving non-aromatic substrates are much rarer. One early example of a direct manganation of an enone was Cabral's preparation of **2** by reaction of $PhCH_2Mn(CO)_5$ with 1-acetylcyclohexene [2], and more recently Robinson prepared **3a** in a procedure directly analogous to those used for aromatic substrates [3]. Tully [4] extended this work to chalcones (1,3-diphenylpropenones) and Cambie et al. subsequently reported [5] cyclomanganation of chalcone itself to give **3b**. Other compounds of type **3** are reported in the literature, but they were prepared via alkyne-insertion reactions rather than by direct metallation. Thus, following Harbourne and Stone's reported [6] insertion of 3,3,3-trifluoroethyne into $HMn(CO)_5$, Booth and Hargreaves treated $RMn(CO)_5$ (R = Ph, Me) with alkynes to give **3a** and related examples [7], and subsequent work, including the use of high-pressure condi-

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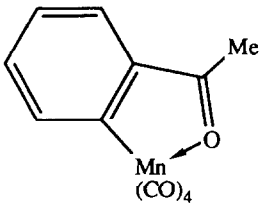

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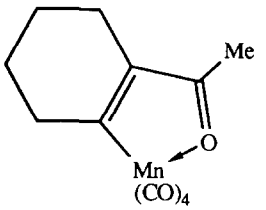

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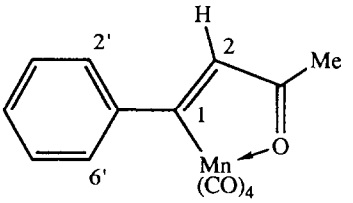


3a

tions, by DeShong and co-workers extended the range [8].

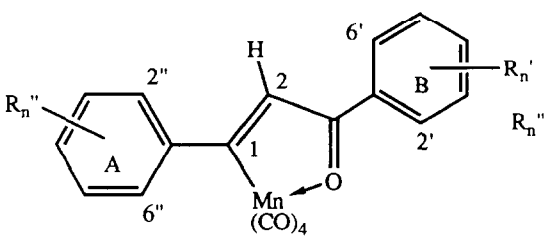
The present paper describes some new compounds of type **3**, prepared by direct cyclometallation reactions, and coupling reactions of these complexes with methyl acrylate (methyl propenoate), methyl vinyl ketone (but-3-en-2-one) and acrolein (propenal) related to previously reported coupling reactions of such alkenes with orthomanganated aryl ketones [1].

2. Experimental details

2.1. General

The carbonyl $PhCH_2Mn(CO)_5$ was prepared by the standard literature method [9a] (see also Ref. [9b]) and the chalcones by standard base-catalyzed condensation of aryl ketones and aldehydes. Other commercial reagents were used without purification. Petroleum spirit had a boiling point of 60–80°C. Reactions were con-

Table 1
Structures and yields of cyclomanganation products obtained from the reaction of chalcones with benzylpentacarbonylmanganese



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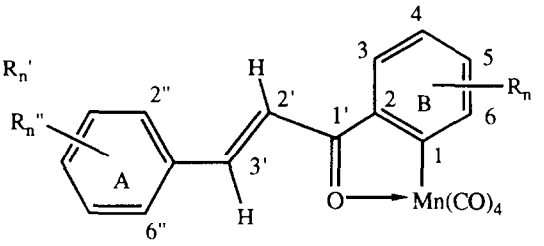

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Compound (% yield) [a]	R''_n	R'_n	Compound (% yield) [a]	R''_n	R_n
3b (69)	H	H			
3c (66)	H	2′,6′-$(OMe)_2$			
3d (73)	H	3′,4′,5′-$(OMe)_3$	**4d** (8)	H	4,5,6-$(OMe)_3$
3e (58)	4″-OMe	3′,4′,5′-$(OMe)_3$	**4e** (14)	4″-OMe	4,5,6-$(OMe)_3$
3f (61)	4″-NMe_2	3′,4′,5′-$(OMe)_3$	**4f** (10)	4″-NMe_2	4,5,6-$(OMe)_3$
3g (21)	3″,4″,5″-$(OMe)_3$	3′,4′-(OCH_2O)	**4g** (21)	3″,4″,5″-$(OMe)_3$	5,6-(OCH_2O)
3h (78)	3″,4″,5″-$(OMe)_3$	4′-CF_3			
3i (78)	3″,4″,5″-$(OMe)_3$	4′-Cl			
			4j (45)	2″-CF_3	6-OMe
			4j′ (17)	2″-CF_3	4-OMe
			4k (44)	2″-CF_3	6-Cl
			4k′ (20)	2″-CF_3	4-Cl
3l (35)	2″-CF_3	3′,4′,5′-$(OMe)_3$	**4l** (52)	2″-CF_3	4,5,6-$(OMe)_3$
3m (23)	2″-CF_3	H	**4m** (35)	2″-CF_3	H
3n (28)	2″-CF_3	4′-Br	**4n** (38)	2″-CF_3	5-Br
3o (72)	4″-CF_3	4′-Br			
3p (65)	4″-CF_3	3′,4′,5′-$(OMe)_3$	**4p** (10)	4″-CF_3	4,5,6-$(OMe)_3$
3q (94)	4″-CF_3	4′-Cl			
3r (88)	4″-CF_3	H			

[a] Yields determined by ^{1}H-NMR signal integration on mixtures of isomers when inseparable by chromatography (see Section 2 for individual cases).

ducted under nitrogen, but subsequent work-up was without any precautions to exclude air. Preparative-scale layer chromatography (PLC) 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.

NMR spectra were recorded on a Bruker AC300 instrument in $CDCl_3$, and infrared spectra (in dichloromethane unless specified) were obtained on a Digilab FTS-45 FTIR. FAB mass spectra were from a VG ZAB 2HF instrument using a 2-nitrophenol matrix.

2.2. Cyclomanganation reactions

2.2.1. Note on nomenclature, terminology and numbering in cyclomanganated chalcones

The structures of the chalcone cyclomanganation products are shown at the head of Table 1. For convenience in the text, products **3** are referred to as "alkene-manganated" and products **4** as "ring-manganated". Rings A and B as labeled are referred to as the "β-phenyl" and the "benzoyl" ring respectively.

Using systematic 'kappa' notation, the alkenylmanganese compound **3b** is named [[1-phenyl-2-phenylcarbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese, while the phenylmanganese compounds **4** are derivatives of the parent [2-[3-phenylprop-2-en-1-onyl-κO]phenyl-κC^1]tetracarbonylmanganese.

Unprimed numbers on the structures are based on the nomenclature priorities. Prime and double prime symbols are not part of systematic numbering or nomenclature, but are used on substituents in order to allow distinction when making NMR assignments.

2.2.2. General procedure for the preparation of cyclomanganated chalcones

A solution of the chalcone (about 1–3 mmol) and $PhCH_2Mn(CO)_5$ (1.1 mmol equivalent) in petroleum spirit (25–60 ml) was heated under reflux under nitrogen for 5 h (unless otherwise stated). The solvent was evaporated under vacuum and the residue was purified by either PLC or column chromatography, generally with petroleum spirit/dichloromethane (4:1) as eluent. Standard work-up procedure after PLC involved band removal and extraction with dichloromethane followed by solvent evaporation under vacuum. Recrystallizations were carried out from dichloromethane/pentane unless otherwise specified. Yields are given in Table 1, which does not include the by-products formed in some cases.

(a) Manganation of (E)-1-methyl-3-phenylprop-2-en-1-one. Column chromatography with petroleum spirit/dichloromethane (3:1) as eluent gave one major band identified as [3-oxo-κO-1-phenylbutyl-κC^1]tetracarbonylmanganese (**3a**), which was recrystallized from petroleum spirit as yellow crystals (65%), m.p. 62°C (literature [10]: 64–65°C). IR: ν(CO) 2083 (m), 1996 (vs), 1953 (s) cm^{-1}. ^1H NMR: δ 7.36 (m, 5H, H2′–H6′), 6.97 (s, 1H, H2), 2.31 (s, 3H, CH_3).

The following work-up details for individual reactions are letter-coded (b)–(r) to the compound codes in Table 1.

(b) Manganation of (E)-1,3-diphenylprop-2-en-1-one. PLC (with petroleum spirit as solvent) gave one major band identified as [[1-phenyl-2-phenylcarbonyl-κO]-ethenyl-κC^1]tetracarbonylmanganese (**3b**), which recrystallized from chloroform/petroleum spirit as red crystals (69%), m.p. 63°C. IR: ν(CO) 2083 (m), 1998 (vs), 1944 (s) cm^{-1}. ^1H NMR: δ 8.02 (m, 2H, H2′, H6′), 7.72 (s, 1H, H2), 7.44 (m, 8H, H3′–H5′, H2″–H6″). Anal. Found: C, 61.24; H, 2.83. $C_{19}H_{11}O_5Mn$. Calc.: C, 60.98; H, 2.96%.

(c) Manganation of (E)-1-(2,6-dimethoxyphenyl)-3-phenylprop-2-en-1-one. PLC (with dichloromethane/petroleum spirit 1:1) gave one major band at R_f 0.7. Standard work-up gave [[1-phenyl-2-(2,6-dimethoxyphenyl)carbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese **3c** (66%) as a red oil, which was crystallized from petroleum spirit as small orange crystals, m.p. 122°C. IR: ν(CO) 2083 (m), 1999 (vs, br), 1940 (s) cm^{-1}. ^1H NMR: δ 7.50 (t, 2H, $J = 7.5$ Hz, H3″, 5″), 7.44 (d, 2H, $J = 7.5$ Hz, H2″, 6″), 7.37 (d, 1H, $J = 7.5$ Hz, H4″), 7.32 (d, 1H, $J = 8.4$ Hz, H4′), 7.24 (s, 1H, H2), 6.57 (d, 2H, $J = 8.4$ Hz, H3′, 5′), 3.80 (s, 6H, 2′, 6′-$(OMe)_2$). FAB–MS (m/e): 434 (M^+, 30), 378 (M^+-2CO, 15), 350 (M^+-3CO, 70), 322 (M^+-4CO, 100). Anal. Found: C, 58.20; H, 3.72. $C_{21}H_{15}O_7Mn$. Calc.: C, 58.08; H, 3.48.

(d) Manganation of (E)-3-phenyl-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one. PLC (with dichloromethane/petroleum spirit 3:2) gave one major band at R_f 0.2. This gave a red oil which crystallized as large orange crystals, m.p. 113 °C, of [[1-phenyl-2-(3,4,5-trimethoxyphenyl)carbonyl-κO]ethenyl-κC^1] tetracarbonylmanganese **3d** (73%). IR: ν(CO) 2083 (m), 1996 (vs), 1943 (s) cm^{-1}. ^1H NMR: δ 7.66 (s, 1H, H2), 7.46 (m, 5H, H2″–6″), 7.26 (s, 2H, H2′, 6′), 3.94 (s, 9H, 3′, 4′, 5′-$(OMe)_3$). FAB–MS (m/e): 464 (M^+, 2), 436 (M^+-CO, 2), 408 (M^+-2CO, 1), 378 (M^+-3CO, 14), 352 (M^+-4CO, 100). Anal. Found: C, 56.88; H, 3.87. $C_{22}H_{17}O_8Mn$. Calc.: C, 56.91; H, 3.69.

A small amount (about 8%) of the ring-manganated product [4,5,6-trimethoxy-2-[3-phenylprop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese (**4d**) was evident in the NMR spectrum of crude **3d**, and it formed small red crystals, m.p. 146°C, which were

hand-separated. IR: ν(CO) 2079 (m), 1991 (vs, br), 1940 (s) cm^{-1}. ^1H NMR: δ 7.84 (d, 1H, $J = 15.6$ Hz, H3′), 7.67 (m, 2H, H2″, 6″), 7.45 (m, 4H, H2′, H3″, 5″, H4″), 7.41 (s, 1H, H3), 4.08 (s, 3H, 6-OMe), 3.95 (s, 3H, 5-OMe), 3.91 (s, 3H, 4-OMe).

(e) Manganation of (E)-3-(4-methoxyphenyl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one. PLC (with dichloromethane/petroleum spirit 5:1) gave one major band at R_f 0.6, which yielded a red oil from which was crystallized [[1-(4-methoxyphenyl)-2-(3,4,5-trimethoxyphenylcarbonyl-κO)]ethenyl-κC^1]tetracarbonylmanganese (**3e**) (58%) as large orange crystals, m.p. 129°C. IR: ν(CO) 2081 (m), 1993 (vs, br), 1939 (s) cm^{-1}. ^1H NMR: δ 7.65 (s, 1H, H2), 7.53 (d, 2H, $J = 8.8$ Hz, H2″, 6″), 7.25 (s, 2H, H2′, 6′), 7.01 (d, 2H, $J = 8.8$ Hz, H3″, 5″), 3.95 (s, 6H, 3′, 5′-$(OMe)_2$), 3.94 (s, 3H, 4′-OMe), 3.86 (s, 3H, 4″-OMe). FAB–MS (*m/e*): 494 (M^+, 40), 466 (M^+-CO, 30), 410 (M^+-3CO, 45), 382 (M^+-4CO, 100). Anal. Found: C, 56.18; H, 3.85. $C_{23}H_{19}O_9Mn$. Calc.: C, 55.88; H, 3.87.

A small amount (about 14%) of the ring-manganated product [4,5,6-trimethoxy-2-[3-(4-methoxyphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese (**4e**), small red crystals, m.p. 144°C, was hand-separated. IR: ν(CO) 2078 (m), 1989 (vs, br), 1938 (s) cm^{-1}. ^1H NMR: δ 7.82 (d, 1H, $J = 15.4$ Hz, H3′), 7.64 (d, 2H, $J = 8.8$ Hz, H2″, 6″), 7.39 (s, 1H, H3), 7.31 (d, 1H, $J = 15.4$ Hz, H2′), 6.96 (d, 2H, $J = 8.8$ Hz, H3″, 5″), 4.07 (s, 3H, 6-OMe), 3.93 (s, 3H, 5-OMe), 3.91 (s, 3H, 4-OMe), 3.86 (s, 3H, 4″-OMe). FAB–MS (*m/e*): 494 (M^+, 2), 466 (M^+-CO, 2), 410 (M^+-3CO, 8), 382 (M^+-4CO, 100).

(f) Manganation of (E)-3-(4-N,N-dimethylaminophenyl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one. PLC (with dichloromethane/petroleum spirit 1:1) gave one major band at R_f 0.25. Standard work-up gave a red oil from which was crystallized [[1-(4-*N*,*N*-dimethylaminophenyl)-2-(3,4,5-trimethoxyphenyl)carbonyl-κO]-ethenyl-κC^1]tetracarbonylmanganese **3f** (61%) as large red crystals, m.p. 156°C. IR: ν(CO) 2079 (m), 1992 (vs), 1936 (s)cm^{-1}. ^1H–NMR: δ 7.67 (s, 1H, H2), 7.65 (d, 2H, $J = 8.8$ Hz, H2″, 6″), 7.24 (s, 2H, H2′, 6′), 6.78 (d, 2H, $J = 8.8$ Hz, H3″, 5″), 3.94 (s, 6H, 3′, 5′-$(OMe)_2$), 3.92 (s, 3H, 4′-OMe), 3.07 (s, 6H, NMe_2). FAB–MS(*m/e*): 507 (M^+, 6), 479 (M^+-CO, 3), 423 (M^+-3CO, 12), 410 (M^+-3CO-Mc, 6), 395 (M^+-4CO, 100). Anal. Found: C, 56.79; H, 4.58; N, 2.78. $C_{24}H_{22}NO_8Mn$. Calc.: C, 56.81; H, 4.37; N, 2.76.

Also evident from the NMR spectrum of crude **3f**, before crystallization a small amount (about 10% by NMR) of the ring-manganated product [4,5,6-trimethoxy-2-[3-(4-*N*,*N*-dimethylaminophenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese (**4f**) was present. This was not isolated, but the following assignments are analogous to those for **4c** and **4d**. ^1H NMR: δ 7.81 (d, 1H, $J = 15.0$ Hz, H3′), 7.59 (d, 2H, $J = 8.8$ Hz, H2″, 6″), 7.38 (s, 1H, H3), 7.24 (d, 1H, $J = 15.0$ Hz, H2′), 6.70 (d, 2H, $J = 8.8$ Hz, H3″, 5″), 4.06 (s, 3H, 6-OMe), 3.93 (s, 6H, 5-OMe), 3.90 (s, 3H, 4-OMe), 3.07 (s, 6H, NMe_2).

(g) Manganation of (E)-1-(3′,4′-methylenedioxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one. PLC (with ethyl acetate/petroleum spirit 1:1) gave one major band at R_f 0.25. Standard work-up gave a mixture (about 1:1 by NMR spectroscopy) of [5,6-methylenedioxy-2-[3-(3,4,5-trimethoxyphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese (**4g**) and [[1-(3,4,5-trimethoxyphenyl)-2-(3,4-methylenedioxyphenylcarbonyl-κO)]ethenyl-κC^1]tetracarbonylmanganese (**3g**) as a red oil (43%). This mixture was crystallized by the diffusion of pentane into a dichloromethane solution with the ring-manganated product (**4g**) crystallizing first as small dark orange crystals, m.p. 138°C. IR: ν(CO) 2083 (m), 1994 (vs, br), 1943 (s) cm^{-1}. ^1H NMR: δ 7.77 (d, 1H, $J = 8.2$ Hz, H3), 7.73 (d, 1H, $J = 15.4$ Hz, H3′), 7.33 (d, 1H, $J = 15.4$ Hz, H2′), 6.87 (s, 2H, H2″, 6″), 6.72 (d, 1H, $J = 8.2$ Hz, H4), 6.12 (s, 2H, OCH_2O), 3.93 (s, 6H, 3″, 5″-$(OMe)_2$), 3.92 (s, 3H, 4″-OMe). FAB–MS (*m/e*): 508 (M^+, 2), 452 (M^+-2CO, 1), 424 (M^+-3CO, 9), 396 (M^+-4CO, 100). Anal. Found: C, 54.72; H, 3.55. $C_{23}H_{17}O_{10}Mn$. Calc.: C, 54.35; H, 3.37.

[[1-(3,4,5-Trimethoxyphenyl)-2-(3,4-methylenedioxyphenylcarbonyl-κO)]ethenyl-κC^1]tetracarbonylmanganese (**3g**) crystallized subsequently as small orange crystals, m.p. 125°C. IR: ν(CO) 2082 (m), 1994 (vs, br), 1938 (s) cm^{-1}. ^1H NMR: δ 7.64 (dd, 1H, $J =$ 8.1/1.7 Hz, H6′), 7.62 (s, 1H, H2), 7.49 (d, 1H, $J = 1.7$ Hz, H2′), 6.89 (s, 2H, H2″, 6″), 6.89 (d, 1H, $J = 8.1$ Hz, H5′), 6.07 (s, 2H, OCH_{2O}), 3.94 (s, 6H, 3″, 5″-$(OMe)_2$), 3.92 (s, 3H, 4″-OMe).

(h) Manganation of (E)-1-(4-trifluoromethylphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one. PLC (with dichloromethane/petroleum spirit 3:1) gave one major band at R_f 0.4. Standard work-up gave [[1-(3,4,5-trimethoxyphenyl)-2-(4-trifluoromethylphenylcarbonyl-κO)]ethenyl-κC^1]tetracarbonylmanganese (**3h**) as a red oil (78%), which was crystallized from petroleum spirit as small red crystals, m.p. 120°C. IR: ν(CO) 2084 (m), 1998 (vs), 1944 (s). ^1H NMR: δ 8.14 (d, 2H, $J = 8.1$ Hz, H2′, 6′), 7.76 (s, 1H, H2), 7.75 (d, 2H, $J = 8.1$ Hz, H3′, 5′), 6.78 (s, 2H, H2″, 6″), 3.95 (s, 6H, 3″, 5″-$(OMe)_2$), 3.94 (s, 3H, 4″-OMe). FAB–MS (*m/e*): 532 (M^+, 5), 504 (M^+-CO, 2), 448 (M^+-3CO, 13), 420 (M^+-4CO, 100). Anal. Found: C, 52.16; H, 3.31. $C_{23}H_{16}F_3O_8Mn$. Calc.: C, 51.90; H, 3.03.

(i) Manganation of (E)-1-(4-chlorophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one. Column chromatogra-

phy gave [[1-(3,4,5-trimethoxyphenyl)-2-(4-chlorophenylcarbonyl-κO)]ethenyl-κC^1]tetracarbonylmanganese (**3i**) (78%) as a red oil, which crystallized from warm petroleum spirit/dichloromethane (10:1) as chunky dark orange crystals, m.p. 103°C. IR: ν(CO) 2083 (m), 1998 (vs, br), 1942 (s). ^{1}H NMR: δ 7.96 (d, 2H, J = 8.6 Hz, H2′, 6′), 7.69 (s, 1H, H2), 7.47 (d, 2H, J = 8.6 Hz, H3′, 5′), 6.76 (s, 2H, H2″, 6″), 3.94 (s, 9H, 3″, 4″, 5″-(OMe)$_3$). Anal. Found: C, 53.25; H, 3.17. $C_{22}H_{16}ClO_8$Mn. Calc.: C, 52.98; H, 3.23.

(j) Manganation of (E)-1-(3-methoxyphenyl)-3-(2-trifluoromethylphenyl)prop-2-en-1-one. This reaction required refluxing overnight. PLC (with dichloromethane/petroleum spirit 3:2) gave four bands at R_f 0.95, 0.90, 0.3 and 0.2, from which were obtained, in sequence, [6-methoxy-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese (**4j**), [4-methoxy-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese (**4j′**), [2-((1S*,2R*,3S*)-1-hydroxy-1-((*E*)-2-(2-trifluoromethylphenyl)-ethenyl)-3-(2-trifluoromethylphenyl)-6-methoxy-2-indanylcarbonyl-κO)-6-methoxyphenyl-κC^1]tetracarbonylmanganese (**7a**) and an unassigned isomer of **7a**.

[6-Methoxy-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese **4j** (45%) was crystallized from petroleum spirit as small dark red crystals, m.p. 127°C. IR: ν(CO) 2080 (m), 1992 (vs, br), 1946 (s) cm^{-1}. ^{1}H NMR: δ 8.17 (dq, 1H, J = 15.4/2.0 Hz, H3′), 7.84 (d, 1H, J = 7.6 Hz, H6″), 7.76 (d, 1H, J = 7.6 Hz, H3″), 7.68 (d, 1H, J = 7.5 Hz, H3), 7.63 (t, 1H, J = 7.6 Hz, H4″), 7.54 (t, 1H, J = 7.6 Hz, H5″), 7.47 (d, 1H, J = 15.4 Hz, H2′), 7.23 (t, 1H, J = 7.8 Hz, H4), 6.94 (d, 1H, J = 7.8 Hz, H5), 3.90 (s, 3H, 3′-OMe). FAB–MS (m/e): 472 (M$^+$, 18), 444 (M$^+$-CO, 9), 388 (M$^+$-3CO, 88), 360 (M$^+$-4CO, 100). Anal. Found: C, 53.50; H, 2.58. $C_{21}H_{12}F_3O_6$Mn. Calc.: C, 53.41; H, 2.56%.

[4-Methoxy-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese **4j′** (17%) was crystallized from petroleum spirit as small dark red crystals, m.p. 136°C. IR: ν(CO) 2080 (m), 1993 (vs, br), 1937 (s) cm^{-1}. ^{1}H NMR: δ 8.19 (dq, 1H, J = 15.4/2.0 Hz, H3′), 8.02 (d, 1H, J = 8.2 Hz, H6), 7.84 (d, 1H, J = 7.7 Hz, H6″), 7.77 (d, 1H, J = 7.7 Hz, H3″), 7.64 (t, 1H, J = 7.7 Hz, H4″), 7.55 (t, 1H, J = 7.7 Hz, H5″), 7.54 (d, 1H, J = 2.6 Hz, H3), 7.42 (d, 1H, J = 15.4 Hz, H2′), 7.16 (dd, 1H, J = 8.2/2.6 Hz, H5), 3.87 (s, 3H, 5′-OMe). FAB–MS (m/e): 472 (M$^+$, 6), 444 (M$^+$-CO, 3), 388 (M$^+$-3CO, 24), 360 (M$^+$-4CO, 100). Anal. Found: C, 53.62; H, 2.83. $C_{21}H_{12}F_3O_6$Mn. Calc.: C, 53.41; H, 2.56.

[2-((1S*,2R*,3S*)-1-Hydroxy-1-((*E*)-2-(2-trifluoromethylphenyl)ethenyl)-3-(2-trifluoromethylphenyl)-6-methoxy-2-indanylcarbonyl-κO)-6-methoxyphenyl-κC^1]tetracarbonylmanganese **7a** (26%) was crystallized by diffusion of pentane into a dichloromethane solution, as small yellow crystals, m.p. 123°C, which were characterized by X-ray crystallography (see below). IR: ν(CO) 2082 (m), 1994 (vs, br), 1946 (s) cm^{-1}. ^{1}H NMR: δ 7.73 (d, 1H, J = 7.7 Hz, Ar–H), 7.68 (d, 1H, J = 7.7 Hz, Ar–H), 7.55 (d, 1H, J = 7.7 Hz, Ar–H), 7.46–6.7 (m, 12H, H2″, Ar–H), 5.97 (d, 1H, J = 15.7 Hz, H1″), 5.44 (d, 1H, J = 7.7 Hz, H2′), 4.72 (d, 1H, J = 7.7 Hz, H3′), 3.82 (s, 6H, (OMe)$_2$), 2.68 (s, 1H, OH). FAB–MS (m/e): 778 (M$^+$, 3), 761 (M$^+$-OH, 5), 750 (M$^+$-CO, 3), 666 (M$^+$-4CO, 100).

The isomer of **7a** (10%) was extracted from the silica as a yellow oil that did not crystallize. From ^{1}H NMR this appeared to be identical with **7a** in respect of the stereochemistry of the indanol ring. It could be the 4-methoxyphenyltetracarbonylmanganese analog of **7a**; or alternatively the 4-methoxyindanyl analog of **7a**. (Similar uncertainty over regioisomerism exists with the by-products formed (see below) from the manganation of the *meta*-chlorochalcone.) IR: ν(CO) 2082 (m), 1993 (vs, br), 1947 (s) cm^{-1}. ^{1}H NMR: δ 7.80–6.70 (m, 15H, H2″, Ar–H), 6.02 (d, 1H, J = 15.7 Hz, H1″), 5.44 (d, 1H, J = 7.7 Hz, H2′), 4.71 (d, 1H, J = 7.7 Hz, H3′), 3.80 (s, 6H, (OMe)$_2$), 2.80 (s, 1H, OH). FAB–MS (m/e): 778 (M$^+$, 2), 761 (M$^+$-OH, 3), 750 (M$^+$-CO, 2), 666 (M$^+$-4CO, 100).

(k) Manganation of (E)-1-(3-chlorophenyl)-3-(2-trifluoromethylphenyl)prop-2-en-1-one. Reflux was continued for 7 h, and PLC (with dichloromethane/petroleum spirit 1:2) then gave four bands, at R_f 0.95, 0.90, 0.45 and 0.2, from which were obtained [6-chloro-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl] phenyl-κC^1]tetracarbonylmanganese (**4k**), [4-chloro-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl] phenyl-κC^1]tetracarbonylmanganese (**4k′**), and two dichloro analogs **7b** of the dimethoxy compound **7a** discussed above.

[6-Chloro-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl] phenyl-κC^1]tetracarbonylmanganese **4k** (44%) was crystallized from petroleum spirit as small dark red crystals, m.p. 132°C. IR: ν(CO) 2085 (m), 1995 (vs, br), 1949 (s) cm^{-1}. ^{1}H NMR: δ 8.20 (dq, 1H, J = 15.4/2.0 Hz, H3′), 7.91 (d, 1H, J = 7.6 Hz, H3), 7.84 (d, 1H, J = 7.6 Hz, H6″), 7.77 (d, 1H, J = 7.6 Hz, H3″), 7.64 (t, 1H, J = 7.6 Hz, H4″), 7.57 (d, 1H, J = 7.6 Hz, H5), 7.56 (t, 1H, J = 7.6 Hz, H5″), 7.45 (d, 1H, J = 15.4 Hz, H2′), 7.18 (t, 1H, J = 7.6 Hz, H4). FAB–MS (m/e): 476 (M$^+$, 44), 392 (M$^+$-3CO, 80), 364 (M$^+$-4CO, 100). Anal. Found: C, 50.61; H, 2.06. $C_{20}H_9F_3ClO_5$Mn. Calc.: C, 50.40; H, 1.90.

[4-Chloro-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese **4k′** (20%) was crystallized from petroleum spririt as small dark red crystals, m.p. 140 °C. IR: ν(CO) 2084 (m),

1997 (vs, br), 1942 (s) cm^{-1}. ^1H NMR: δ 8.23 (dq, 1H, $J = 15.4/2.0$ Hz, H3′), 8.10 (d, 1H, $J = 7.9$ Hz, H6), 7.98 (s, 1H, H3), 7.88 (d, 1H, $J = 7.7$ Hz, H6″), 7.78 (d, 1H, $J = 7.7$ Hz, H3″), 7.64 (t, 1H, $J = 7.7$ Hz, H4″), 7.57 (t, 1H, $J = 7.7$ Hz, H5″), 7.44 (d, 1H, $J = 15.4$ Hz, H2′), 7.43 (d, 1H, $J = 7.9$ Hz, H5). FAB–MS (m/e): 476 (M^+, 8), 392 (M^+-3CO, 24), 364 (M^+-4CO, 100). Anal. Found: C, 50.40; H, 2.10. $C_{21}H_{12}F_3O_6Mn$. Calc.: C, 50.40; H, 1.90.

Compound **7b** (20%) crystallized as small yellow crystals, m.p. 108°C. From the similarities between the ^1H NMR spectra (especially the coupling between H2 and H3) of **7b** and **7a**, it is assumed that the stereochemistry of the indanyl ring for this compound (**7b**), is the same as that found for **7a**. IR: ν(CO) 2085 (m), 1999 (vs, br), 1943 (s) cm^{-1}. ^1H NMR: δ 8.24–6.73 (m, 15H, H2″, Ar–H), 5.93 (d, 1H, $J = 15.9$ Hz, H1″), 5.48 (d, 1H, $J = 7.8$ Hz, H2′), 4.75 (d, 1H, $J = 7.8$ Hz, H3′), 2.99 (s, 1H, OH). FAB–MS (m/e): 786 (M^+, 10), 769 (M^+-OH, 10), 674 (M^+-4CO, 100).

The other isomer of **7b** (15%) was crystallized as small yellow crystals, m.p. 90°C. IR: ν(CO) 2087 (m), 2000 (vs, br), 1951 (s) cm^{-1}. ^1H NMR: δ 8.06–6.76 (m, 15H, H2″, Ar–H), 5.89 (d, 1H, $J = 15.3$ Hz, H1″), 5.48 (d, 1H, $J = 7.2$ Hz, H2′), 4.71 (d, 1H, $J = 7.2$ Hz, H3′), 2.82 (s, 1H, OH). FAB-MS (m/e): 786 (M^+, 2), 769 (M^+-OH, 8), 674 (M^+-4CO, 100).

(l) Manganation of (E)-3-(2-trifluoromethylphenyl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one. PLC (with dichloromethane/petroleum spirit 2:1) gave bands at R_f 0.35 and R_f 0.1. The first gave a mixture of [4,5,6-trimethoxy-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese (**4l**) and [[1-(2-trifluoromethylphenyl)-2-(3,4,5-trimethoxyphenyl)carbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese (**3l**) as a red oil. When the oil was crystallized, **4l** separated first as small ruby-red crystals (52%), m.p. 134°C. IR: ν(CO) 2080 (m), 1992 (vs, br), 1943 (s) cm^{-1}. ^1H NMR: δ 8.12 (dq, 1H, $J = 15.4/2.0$ Hz, H3′), 7.82 (d, 1H, $J = 7.6$ Hz, H6″), 7.76 (d, 1H, $J = 7.6$ Hz, H3″), 7.64 (t, 1H, $J = 7.6$ Hz, H4″), 7.54 (t, 1H, $J = 7.6$ Hz, H5″), 7.40 (s, 1H, H3), 7.32 (d, 1H, $J = 15.4$ Hz, H2′), 4.08 (s, 3H, 6-OMe), 3.93 (s, 3H, 5-OMe), 3.91 (s, 3H, 4-OMe). FAB–MS (m/e): 532 (M^+, 5), 504 (M^+-CO, 2), 448 (M^+-3CO, 9), 420 (M^+-4CO, 100). Anal. Found: C, 52.17; H, 3.15. $C_{23}H_{16}F_3O_8Mn$. Calc.: C, 51.90; H, 3.03.

A second fraction, [[1-(2-trifluoromethylphenyl)-2-(3,4,5-trimethoxyphenyl)carbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese (**3l**) crystallized as chunky orange crystals (35%), m.p. 127°C. IR: ν(CO) 2088 (m), 1996 (vs, br), 1949 (m) cm^{-1}. ^1H NMR: δ 7.73 (d, 1H, $J = 7.4$ Hz, H3″), 7.63 (s, 1H, H2), 7.59 (t, 1H, $J = 7.4$ Hz, H5″), 7.35 (t, 1H, $J = 7.4$ Hz, H4″), 7.34 (d, 1H, $J = 7.4$ Hz, H6″), 7.24 (s, 2H, H2′, 6′), 3.94 (s, 3H, 4′-OMe), 3.93 (s, 6H, 3′, 5′-$(OMe)_2$). FAB–MS (m/e): 532 (M^+, 20), 504 (M^+-CO, 20), 448 (M^+-3CO, 30), 420 (M^+-4CO, 100). Anal. Found: C, 52.40; H, 3.28. $C_{23}H_{16}F_3O_8Mn$. Calc.: C, 51.90; H, 3.03.

The band at R_f 0.1 gave [2-(1-hydroxy-1-((*E*)-2-(2-trifluoromethylphenyl)-ethenyl)-3-(2-trifluoromethylphenyl)-4,5,6-trimethoxy-2-indanylcarbonyl-κO)-4,5,6-trimethoxyphenyl-κC^1]tetracarbonylmanganese (**7c**) as a yellow oil (12%). This was crystallized as small yellow crystals, m.p. 110°C. The stereochemistry in the indanyl ring is not defined. IR: ν(CO) 2082 (m), 1995 (vs, br), 1944 (s) cm^{-1}. ^1H NMR: δ 7.66 (d, 1H, $J = 7.8$ Hz, Ar–H), 7.40 (m, 7H, Ar–H), 7.01 (d, 1H, $J = 15.7$ Hz, H2″), 6.54 (s, 1H, Ar–H), 5.70 (d, 1H, $J = 15.7$ Hz, H1″), 5.51 (d, 1H, $J = 7.5$ Hz, H2′), 4.36 (d, 1H, $J = 7.5$ Hz, H3′), 3.99 (s, 3H, OMe), 3.84 (s, 9H, $(OMe)_3$), 3.77 (s, 3H, OMe), 3.48 (s, 3H, OMe), 2.54 (s, 1H, OH). FAB–MS (m/e): 899 (M^+, 2), 882 (M^+-OH, 4), 871 (M^+-CO, 6), 787 (M^+-4CO, 100). Anal. Found: C, 56.21; H, 3.84. $C_{42}H_{33}F_6O_{12}Mn$. Calc.: C, 56.14; H, 3.70.

(m) Manganation of (E)-1-phenyl-3-(2-trifluoromethylphenyl)prop-2-en-1-one. PLC (with dichloromethane/petroleum spirit 2:1) gave two bands at R_f 0.95 and R_f 0.5. The band at R_f 0.95 gave a mixture (3:2 by NMR spectroscopy) of [2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese (**4m**) and [[1-(2-trifluoromethylphenyl)-2-phenylcarbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese (**3m**) as a red oil (57%). Crystallization by the diffusion method (dichloromethane, pentane) gave mostly [2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese (**4m**). The latter, when further purified by recrystallization, gave small red crystals, m.p. 137°C. IR: ν(CO) 2081 (m), 1995 (vs, br), 1938 (s) cm^{-1}. ^1H NMR: δ 8.20 (dq, 1H, $J = 15.2/2.0$ Hz, H3′), 8.19 (d, 1H, $J = 7.3$ Hz, H6), 8.03 (d, 1H, $J = 7.3$ Hz, H3), 7.85 (d, 1H, $J = 7.7$ Hz, H6″), 7.77 (d, 1H, $J = 7.7$ Hz, H3″), 7.64 (t, 1H, $J = 7.7$ Hz, H4″), 7.55 (t, 1H, $J = 7.7$ Hz, H5″), 7.49 (d, 1H, $J = 15.2$ Hz, H2′), 7.45 (t, 1H, $J = 7.3$ Hz, H4), 7.22 (t, 1H, $J = 7.3$ Hz, H5). FAB–MS (m/e): 442 (M^+, 7), 358 (M^+-3CO, 29), 329 (M^+-4CO, 100). Anal. Found: C, 54.34; H, 2.29. $C_{20}H_{10}F_3O_5Mn$. Calc.: C, 54.32; H, 2.28.

[[1-(2-Trifluoromethylphenyl)-2-phenylcarbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese (**3m**) crystallized as a second fraction as chunky orange crystals, m.p. 111°C. IR: ν(CO) 2088 (m), 1997 (vs, br), 1949 (s) cm^{-1}. ^1H NMR: δ 8.01 (d, 2H, $J = 7.4$ Hz, H2′, 6′), 7.73 (d, 1H, $J = 8.0$ Hz, H3″), 7.68 (s, 1H, H2), 7.59 (m, 2H, H4′, H5″), 7.49 (t, 2H, $J = 7.6$ Hz, H3′, 5′), 7.35 (m, 2H, H4″, H6″). FAB–MS (m/e): 442

(M^+, 7), 358 (M^+-3CO, 27), 329 (M^+-4CO, 100). Anal. Found: C, 54.84; H, 2.50. $C_{20}H_{10}F_3O_5Mn$. Calc.: C, 54.32; H, 2.28.

The band at R_f 0.5 gave yellow crystals identified by spectroscopy as [2-(1-hydroxy-1-((*E*)-2-(2-trifluoromethylphenyl)-ethenyl)-3-(2-trifluoromethylphenyl)-2-indanylcarbonyl-κO)phenyl-κC^1]tetracarbonylmanganese **7d** (25%), m.p. 107°C. The stereochemistry in the indanyl ring is not defined. IR: ν(CO) 2083 (m), 1996 (vs), 1993 (sh), 1938 (s) cm^{-1}. ^1H NMR: δ 7.50 (m, 17H, H2″, Ar–H), 5.98 (d, 1H, J = 15.5 Hz, H1″), 5.55 (d, 1H, J = 7.5 Hz, H2′), 4.77 (d, 1H, J = 7.5 Hz, H3′), 2.87 (s, 1H, OH). FAB–MS (*m/e*): 718 (M^+, 3), 701 (M^+-OH, 5), 606 (M^+-4CO, 100).

(n) Manganation of (E)-1-(4-bromophenyl)-3-(2-trifluoromethylphenyl)prop-2-en-1-one. PLC (with dichloromethane/petroleum spirit 2:1) gave two bands at R_f 0.9 and 0.5. The band at R_f 0.9 gave a mixture (3:2 by NMR) of [5-bromo-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese (**4n**) and [[1-(2-trifluoromethylphenyl)-2-(4-bromophenyl)carbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese (**3n**) as a red oil (72%). This oil was crystallized, giving mostly [5-bromo-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]-tetracarbonylmanganese (**4n**) which after further recrystallization gave ruby red crystals, m.p. 139°C. IR: ν(CO) 2085 (m), 1998 (vs, br), 1942 (s) cm^{-1}. ^1H NMR: δ 8.31 (d, 1H, J = 1.8 Hz, H6), 8.21 (dq, 1H, J = 15.4/2.0 Hz, H3′), 7.84 (m, 2H, H3, H6″), 7.79 (d, 1H, J = 7.6 Hz, H3″), 7.64 (t, 1H, J = 7.6 Hz, H4″), 7.56 (t, 1H, J = 7.6 Hz, H5″), 7.42 (d, 1H, J = 15.4 Hz, H2′), 7.36 (dd, J = 8.3/1.8 Hz, H4). FAB–MS (*m/e*): 521 (M^+, 20), 437 (M^+-3CO, 80), 408 (M^+-4CO, 100). Anal. Found: C, 46.43; H, 1.84. $C_{20}H_9F_3BrO_5Mn$. Calc.: C, 46.10; H, 1.74.

[[1-(2-Trifluoromethylphenyl)-2-(4-bromophenyl)carbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese (**3n**) crystallized as a second fraction as chunky orange crystals, m.p. 130°C. IR: ν(CO) 2088 (m), 1998 (vs, br), 1951 (s) cm^{-1}. ^1H NMR: δ 7.86 (d, 2H, J = 8.6 Hz, H2′, 6′), 7.73 (d, 1H, J = 7.5 Hz, H3″), 7.64 (s, 1H, H2), 7.63 (d, 2H, J = 8.6 Hz, H3′, 5′), 7.59 (t, 1H, J = 7.5 Hz, H5″), 7.35 (m, 2H, H4″, H6″). FAB–MS (*m/e*): 521 (M^+, 10), 437 (M^+-3CO, 30), 408 (M^+-4CO, 100). Anal. Found: C, 45.81; H, 1.71. $C_{20}H_9F_3BrO_5Mn$. Calc.: C, 46.10; H, 1.74.

The band at R_f 0.5 gave [2-(1-hydroxy-1-((*E*)-2-(2-trifluoromethylphenyl)-ethenyl)-3-(2-trifluoromethylphenyl)-5-bromo-2-indanylcarbonyl-κO)-5-bromophenyl-κC^1]tetracarbonylmanganese (**7e**) as a yellow oil (23%), which was crystallized to give small yellow crystals, m.p. 167°C. IR: ν(CO) 2086 (m), 1999 (vs, br), 1944 (s) cm^{-1}. ^1H NMR: δ 8.17 (s, 1H, Ar–H), 7.94 (d, 1H, J = 8.3 Hz, Ar–H), 7.69 (d, 1H, J = 7.5 Hz, Ar–H), 7.40 (m, 10H, Ar–H), 7.00 (s, 1H, Ar–H), 6.82 (d, 1H, J = 15.7 Hz, H2″), 5.89 (d, 1H, J = 15.7 Hz, H1″), 5.48 (d, 1H, J = 7.9 Hz, H2′), 4.66 (d, 1H, J = 7.9 Hz, H3′), 2.76 (s, 1H, OH). FAB–MS (*m/e*): 876 (M^+, 6), 859 (M^+-OH, 16), 764 (M^+-4CO, 100). Anal. Found: C, 49.46; H, 2.41. $C_{36}H_{19}F_6Br_2O_6Mn$. Calc.: C, 49.34; H, 2.19.

(o) Manganation of (E)-1-(4-bromophenyl)-3-(4-trifluoromethylphenyl)prop-2-en-1-one. PLC (with dichloromethane/petroleum spirit 2:1) gave two bands at R_f 0.95 and R_f 0.3, which yielded [[1-(4-trifluoromethylphenyl)-2-(4-bromophenyl)carbonyl-κO]-ethenyl-κC^1]tetracarbonylmanganese (**3o**) and (1S*,4S*,5R*)-5-(4-bromobenzoyl)-1-(4-bromophenyl)-3,4-di-(4-trifluoromethylphenyl)cyclopent-2-en-1-ol (**8**) respectively.

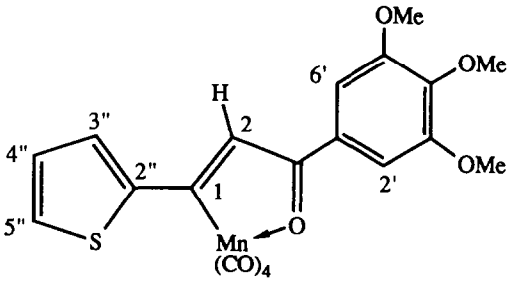
[[1-(4-Trifluoromethylphenyl)-2-(4-bromophenyl)carbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese **3o** (72%) was crystallized as small red crystals, m.p. 103°C. IR: ν(CO) 2085 (m), 2000 (vs, br), 1947 (s) cm^{-1}. ^1H NMR: δ 7.89 (d, 2H, J = 8.7 Hz, H2′, 6′), 7.70 (d, 2H, J = 8.1 Hz, H3″, 5″), 7.67 (s, 1H, H2), 7.65 (d, 2H, J = 8.7 Hz, H3′, 5′), 7.49 (d, 2H, J = 8.1 Hz, H2″, 6″). FAB–MS (*m/e*): 521 (M^+, 20), 437 (M^+-3CO, 40), 409 (M^+-4CO, 100). Anal. Found: C, 46.50; H, 1.94. $C_{20}H_9F_3BrO_5Mn$. Calc.: C, 46.10; H, 1.74.

(1S*, 4S*, 5R*)-5-(4-Bromobenzoyl)-1-(4-bromophenyl)-3,4-di-(4-trifluoro-methylphenyl)cyclopent-2-en-1-ol **8** (10%) was crystallized as colorless chunky crystals, m.p. 176°C. ^1H NMR: δ 7.49 (m, 8H, Ar–H), 7.26 (m, 8H, Ar–H), 6.34 (d, 1H, J = 2.0 Hz, H2), 5.51 (dd, 1H, J = 6.9/2.0 Hz, H4), 4.21 (d, 1H, J = 6.9 Hz, H5), 2.89 (s, 1H, OH). ^{13}C NMR: δ 197.6 (s, CO), 146.6 (s), 145.9 (s), 143.4 (s), 137.1 (s), 135.7 (s), 134.5 (d, C4), 131.7 (d), 130.2 (d), 129.1 (s, C3), 127.8 (d), 127.3 (d), 126.3 (d, J = 3.3 Hz), 125.7 (d, J = 4.1 Hz), 121.9 (s), 85.8 (s, C5), 68.9 (d, C1), 52.6 (d, C2). This compound was further characterized by a single-crystal X-ray structure determination (see below).

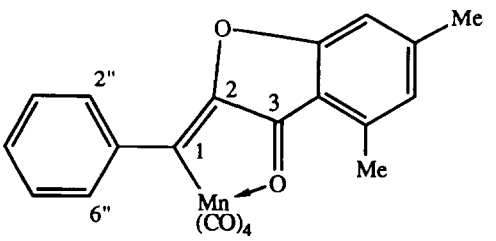
(p) Manganation of (E)-3-(4-trifluoromethylphenyl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one. PLC (with dichloromethane/petroleum spirit 2:1) gave one major band at R_f 0.6, from which crude [[1-(4-trifluoromethylphenyl)-2-(3,4,5-trimethoxyphenyl)carbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese (**3p**) was obtained as a red oil (75%). Crystallization gave small orange crystals, m.p. 120°C. IR: ν(CO) 2084 (m), 1997 (vs), 1946 (s) cm^{-1}. ^1H NMR: δ 7.70 (d, 2H, J = 8.0 Hz, H3″, 5″), 7.65 (s, 1H, H2), 7.50 (d, 2H, J = 8.0 Hz, H2″, 6″), 7.26 (s, 2H, H2′, 6′), 3.95 (s, 3H, 4′-OMe), 3.94 (s, 6H, 3′, 5′-$(OMe)_2$). FAB–MS (*m/e*): 532 (M^+, 4), 504 (M^+-CO, 4), 448 (M^+-3CO, 15), 420 (M^+-4CO, 100). Anal. Found: C, 52.28; H, 3.19; F, 10.60. $C_{23}H_{16}F_3O_8Mn$. Calc.: C, 51.90; H, 3.03; F, 10.71.

Also evident from the NMR spectrum of the red oil was a small amount (about 10%) of the ring-manganated product [4,5,6-trimethoxy-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl]phenyl-κC^1]tetracarbonylmanganese (**4p**). A few small red crystals (m.p. 136°C) were obtained on crystallization, but the amount was too small to allow full characterization.

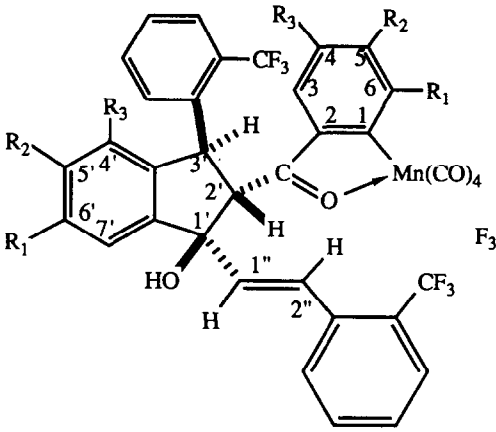
(q) Manganation of (E)-1-(4-chlorophenyl)-3-(4-trifluoromethylphenyl)prop-2-en-1-one. Column chromatography gave as a red oil [[1-(4-trifluoromethylphenyl)-2-(4-chlorophenyl)carbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese **3q** (94%), which crystallized from petroleum spirit as dark orange crystals, m.p. 115°C. IR: ν(CO) 2085 (m), 2000 (vs, br), 1947 (s) cm^{-1}. ^1H NMR: δ 7.97 (d, 2H, $J = 8.5$ Hz, H2′, 6′), 7.72 (s, 1H, H2), 7.71 (d, 2H, $J = 8.3$ Hz, H3″, 5″), 7.67 (s, 1H, H2), 7.49 (d, 2H, $J = 8.3$ Hz, H2″, 6″), 7.48 (d, 2H, $J = 8.5$ Hz, H3′, 5′). Anal. Found: C, 50.47; H, 1.87. $C_{20}H_9F_3ClO_5Mn$. Calc.: C, 50.40; H, 1.90.



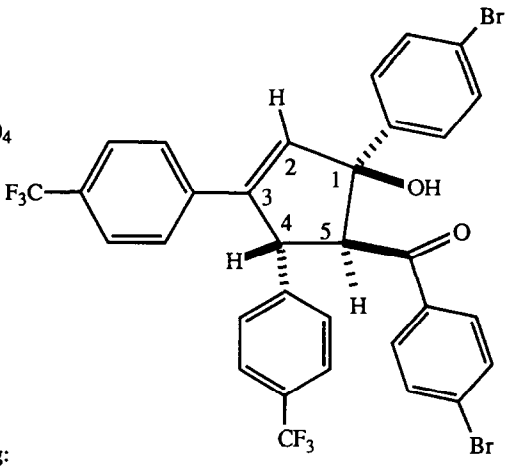
5



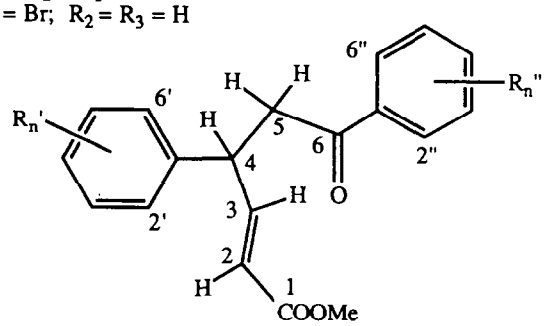
6



7a R_1 = OMe; $R_2 = R_3$ = H
Stereochemistry undefined for the following:
7b R_1 = Cl, $R_2 = R_3$ = H
7c $R_1 = R_2 = R_3$ = OMe
7d $R_1 = R_2 = R_3$ = H
7e R_1 = Br; $R_2 = R_3$ = H



8



9a R_n' = 4′-OMe R_n'' = 3″,4″,5″-$(OMe)_3$
9b R_n' = 3′,4′,5′-$(OMe)_3$ R_n'' = 4″-Cl
9d R_n' = 4′-CF_3 R_n'' = H

(r) Manganation of (E)-1-phenyl-3-(4-trifluoromethylphenyl)prop-2-en-1-one. Column chromatography gave as a red oil [[1-(4-trifluoromethylphenyl)-2-(4-chlorophenyl)carbonyl-κO]ethenyl-κC^1]tetracarbonylmanganese **3r** (88%), which crystallized from petroleum spirit as small orange crystals, m.p. 125°C. IR: ν(CO) 2085 (m), 1999 (vs, br), 1947 (s) cm^{-1}. ^1H NMR δ 8.04 (d, 2H, $J = 7.4$ Hz, H2′, 6′), 7.72 (s, 1H, H2), 7.71 (d, 2H, $J = 8.2$ Hz, H3″, 5″), 7.61 (d, 1H, $J = 7.4$ Hz, H4′), 7.51 (m, 4H, H3′, 5′, H2″, 6″). Anal. Found: C, 54.37; H, 2.28. $C_{20}H_{10}F_3O_5Mn$. Calc.: C, 54.32; H, 2.28.

(s) Manganation of (E)-3-(2-thienyl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one. PLC (with dichloromethane/petroleum spirit 2:1) gave one major band at R_f 0.6 from which was obtained [[1-(2-thienyl)-2-(3,4,5-trimethoxyphenyl)carbonyl-κO]ethenyl κC^1]tetracarbonylmanganese (**5**) as a red oil (57%), which was recrystallized as small orange crystals, m.p. 137°C. IR: ν(CO) 2085 (m), 2000 (vs), 1939 (s) cm^{-1}. ^1H NMR: δ 7.79 (s, 1H, H2), 7.73 (dd, 1H, $J = 3.8/1.0$ Hz, H3″ or H5″), 7.56 (dd, 1H, $J = 5.1/1.0$ Hz, H3″ or H5″), 7.22 (s, 2H, H2′, 6′), 7.20 (m, 1H, H4″), 3.96 (s, 6H, 3′, 5′-$(OMe)_2$), 3.93 (s, 3H, 4′-OMe). FAB–MS (*m/e*): 470 (M^+, 7), 442 (M^+-CO, 3), 386 (M^+-3CO, 17), 358 (M^+-4CO, 100). Anal. Found: C, 51.29; H, 3.09; S, 6.51. $C_{20}H_{15}SO_8Mn$. Calc.: C, 51.08; H, 3.21; S, 6.80.

(t) Manganation of (Z)-4,6-dimethylbenzylidenecoumaranone. PLC (with dichloromethane/petroleum spirit 1:3) gave one major band at R_f 0.5, from which [[4,6-dimethylbenzo[d]furan-3(5H)-on-κO-2-ylidene]-phenyl]methyl]tetracarbonylmanganese **6** (58%) was obtained. Crystallization from petroleum spirit gave small orange crystals, m.p. 139°C. IR: ν(CO) 2086 (m), 2003 (vs, br), 1944 (s) cm^{-1}. ^1H NMR: δ 7.63 (d, 2H, $J = 7.6$ Hz, H2″, 6″), 7.48 (t, 2H, $J = 7.6$ Hz, H3″, 5″), 7.36 (d, 1H, $J = 7.6$ Hz, H4″), 6.85 (s, 1H, H5), 6.74 (s, 1H, H7), 2.57 (s, 3H, 4-Me), 2.41 (s, 3H, 6-Me). Anal. Found: C, 60.70; H, 3.13. $C_{21}H_{13}O_6Mn$. Calc.: C, 60.59; H, 3.15.

2.3. Reactions of cyclomanganated chalcones with alkenes

Reaction of [[1-(4-methoxyphenyl)-2-(3,4,5-trimethoxyphenylcarbonyl-κO)]ethenyl-κC^1]tetracarbonylmanganese 3e with methyl acrylate in carbon tetrachloride. A solution of **3e** (0.218 g, 0.44 mmol) and methyl acrylate (0.22 ml, 2.44 mmol) in nitrogen-saturated carbon tetrachloride (20 ml) was refluxed for 5 h. Carbon tetrachloride was removed under vacuum and the residual oil was chromatographed (PLC, ethyl acetate/petroleum spirit 0.9:1) to give one major band at R_f 0.7. This gave methyl (*E*)-4-(4-methoxyphenyl)-6-oxo-6-(3,4,5-trimethoxyphenyl)hex-2-enoate (**9a**) as a pale yellow oil (0.176 g, 96%), which was crystallized from pentane as fibrous white crystals, m.p. 77°C. IR: 1721 (s, CO), 1711 (s, COOMe) cm^{-1}. ^1H NMR: δ 7.16 (d, 2H, $J = 8.7$ Hz, H2′, 6′), 7.15 (s, 2H, H2″, 6″), 7.14 (dd, 1H, $J = 15.7/6.9$ Hz, H3), 6.85 (d, 2H, $J = 8.7$ Hz, H3′, 5′), 5.78 (dd, 1H, $J = 15.7/1.4$ Hz, H2), 4.24 (ddd, 1H, $J = 7.0/6.9/1.4$ Hz, H4), 3.89 (s, 9H, 4′, 3″, 5″-$(OMe)_3$), 3.77 (s, 3H, 4″-OMe), 3.69 (s, 3H, COOMe), 3.38 (d, 2H, $J = 7.0$ Hz, CH_2). ^{13}C NMR: δ 196.0 (s, C1), 166.9 (s, C6), 158.7 (s, C4′), 153.1 (s, C3″, 5″), 150.8 (d, C3), 142.9 (s, C4″), 133.2 (s, C1′), 132.1 (s, C1″), 128.9 (d, C2′, 6′), 120.8 (d, C2), 114.3 (d, C3′, 5′), 105.7 (d, C2″, 6″), 60.9 (q, 4″-OMe), 56.4 (q, 3″, 5″-$(OMe)_2$), 55.3 (q, 4′-OMe), 51.44(q, COOMe), 43.4 (t, C5), 42.4 (d, C4). MS (*m/e*): 414 (M^+, 7), 340 (M^+-Me-COOMe, 30), 195 ($(MeO)_3C_6H_2CO^+$ (100). Anal. Found: C, 66.64; H, 6.47. $C_{23}H_{26}O_7$. Calc: C, 66.65; H, 6.32.

Reaction of [[1-(4-methoxyphenyl)-2-(3,4,5-trimethoxyphenylcarbonyl-κO)]ethenyl-κC^1]tetracarbonylmanganese (3e) with methyl acrylate in acetonitrile. A solution of **3e** (0.258 g, 0.52 mmol) and methyl acrylate (0.25 ml, 2.78 mmol) in nitrogen-saturated acetonitrile (20 ml) was refluxed for 2 h. Acetonitrile was removed under vacuum and the residual oil was chromatographed (PLC., ethyl acetate/petroleum spirit (1:1)) to give two bands at R_f 0.7 and R_f 0.5. The first gave methyl (*E*)-4-(4-methoxyphenyl)-6-oxo-6-(3,4,5-trimethoxyphenyl)hex-2-enoate (**9a**) (0.054 g, 25%), while the band at R_f 0.5 gave the butenolide 5-(2-methoxycarbonylethyl)-3-(4-methoxyphenyl)-5-(3,4,5-trimetho xyphenyl)furan-2(5H)-one (**10a**) as a colorless oil, which crystallized (ether/pentane) as small translucent crystals, m.p. 106°C. IR: 1758 (vs, CO), 1735 (s, COOMe) cm^{-1}. ^1H NMR: δ 7.79 (d, 2H, $J = 8.3$ Hz, H2″, 6″), 7.57 (s, 1H, H4), 6.89 (d, 2H, $J = 8.3$ Hz, H3″, 5″), 6.62 (s, 2H, H2‴, 6‴), 3.86 (s, 6H, 3‴, 5‴-$(OMe)_2$), 3.80 (s, 6H, 4″, 4‴-$(OMe)_2$), 3.56 (s, 3H, COOMe), 2.40 (m, 4H, CH_2CH_2). ^{13}C NMR: δ 173.3 (s, C3′), 171.0 (s, C2), 160.3 (s, C4″), 153.7 (s, C3‴, 5‴), 148.1 (d, C4), 137.9 (s, C4‴), 134.5 (s, C1″), 129.4 (s, C1‴), 128.6 (d, C2″, 6″), 121.6 (s, C3), 114.1 (d, C3″, 5″), 102.2 (d, C2‴, 6‴), 87.3 (s, C5), 60.9 (q, 4‴-OMe), 56.4 (q, 3‴, 5‴-$(OMe)_2$), 55.4 (q, 4″-OMe), 51.8 (q, COOMe), 35.2 (t, C1′), 28.5 (t, C2′). MS (*m/e*): 442 (M^+, 7), 355 (M^+-CH_2CH_2COOMe, 45), 327 (M^+-CH_2CH_2COOMe-CO, 44), 299 (M^+-CH_2CH_2COOMe-2CO, 48) 195 ($(MeO)_3C_6H_2CO^+$, 100). Anal. Found: C, 65.15; H, 5.95. $C_{24}H_{26}O_8$. Calc.: C, 65.15; H, 5.93.

Reaction of [[1-(3,4,5-trimethoxyphenyl)-2-(4-chlorophenylcarbonyl-κO)]ethenyl-κC^1]tetracarbonylmanganese (3i) with methyl acrylate in carbon tetrachloride. Similarly, **3i** (0.102 g, 0.20 mmol) and methyl acrylate

(0.1 ml, 1.11 mmol) were dissolved in nitrogen-saturated carbon tetrachloride (20 ml) and the solution was refluxed overnight. PLC (with ethyl acetate/petroleum spirit 2:3) gave one major band at R_f 0.7, from which methyl (*E*)-6-(4-chlorophenyl)-6-oxo-4-(3,4,5-trimethoxyphenyl)hex-2-enoate **9b** (0.037 g, 43%) was obtained. It crystallized from pentane as cream crystals, m.p. 101°C, and was identified by spectral correlation with **9a**. IR: 1726 (s, CO), 1712 (s, COOMe) cm^{-1}. ^1H NMR: δ 7.85 (d, 2H, $J = 6.8$ Hz, H2″, 6″), 7.42 (d, 2H, $J = 6.8$ Hz, H3″, 5″), 7.10 (dd, 1H, $J = 15.7/7.0$ Hz, H3), 6.42 (s, 2H, H2′, 6′), 5.81 (dd, 1H, $J = 15.7/1.4$ Hz, H2), 4.20 (ddd, 1H, $J = 7.0/6.9/1.4$ Hz, H4), 3.82 (s, 6H, 3′, 5′-$(OMe)_2$), 3.80 (s, 3H, 4′-OMe), 3.70 (s, 3H, COOMe), 3.39 (d, 2H, $J = 6.9$ Hz, CH_2). ^{13}C NMR: δ 196.0 (s, C1), 166.9 (s, C6), 153.6 (s, C3′, 5′), 150.0 (d, C3), 139.9 (s, C4″), 137.3 (s, C4′), 136.7 (s, C1′), 135.1 (s, C1″), 129.5 (d, C2″, 6″ or C3″, 5″), 129.1 (d, C2″, 6″ or C3″, 5″), 121.2 (d, C2), 104.9 (d, C2′, 6′), 60.9 (q, 4′-OMe), 56.2 (q, 3′, 5′-$(OMe)_2$), 51.6 (q, COOMe), 43.5 (t, C5), 43.3 (d, C4). MS (*m/e*): 418 (M^+, 20), 344 (M^+-MeCOOMe, 35), 205 (45), 139 ($ClC_6H_4CO^+$, 100).

Reaction of [[1-(3,4,5-trimethoxyphenyl)-2-(4-chlorophenylcarbonyl-κO)]ethenyl-κC¹]tetracarbonylmanganese (3i) with methyl acrylate in acetonitrile. Similarly, a solution of **3i** (0.115 g, 0.23 mmol) and methyl acrylate (0.1 ml, 1.11 mmol) in nitrogen-saturated acetonitrile (20 ml) was refluxed for 3 h. PLC (with ethyl acetate/petroleum spirit 2:3) gave two bands at R_f 0.7 and R_f 0.5. From the band at R_f 0.7, methyl (*E*)-6-(4-chlorophenyl)-6-oxo-4-(3,4,5-trimethoxyphenyl)hex-2-enoate (**9b**) was obtained as a pale yellow oil (0.014 g, 14%), as confirmed by ^1H NMR. The band at R_f 0.5 gave the butenolide 5-(4-chlorophenyl)-5-(2-methoxycarbonylethyl)-3-(3,4,5-trimethoxyphenyl)furan-2(5H)-one (**10b**) as a colorless oil (0.037 g, 36%), which crystallized (ether/pentane) as small white fibrous crystals, m.p. 63 °C. IR: 1762 (vs, CO), 1735 (s, COOMe) cm^{-1}. ^1H NMR: δ 7.58 (s, 1H, H4), 7.39 (s, 4H, H2‴, 6‴, H3‴, 5‴), 7.09 (s, 2H, H2″, 6″), 3.89 (s, 6H, 3″, 5″-$(OMe)_2$), 3.86 (s, 3H, 4″-OMe), 3.60 (s, 3H, COOMe), 2.44 (m, 4H, CH_2-2, 3). ^{13}C NMR: δ 173.1 (s, C3′), 170.4 (s, C2), 153.4 (s, C3″, 5″), 149.1 (d, C4), 139.6 (s, C4‴), 137.2 (s, C4″), 134.5 (s, C1″), 129.9 (s, C1‴), 129.3 (d, C2‴, 6‴), 126.4 (d, C3‴, 5‴), 124.3 (s, C3), 104.6 (d, C2″, 6″), 86.8 (s, C5), 61.0 (q, 4″-OMe), 56.3 (q, 3″, 5″-OMe), 51.9 (q, COOMe), 34.2 (t, C1′), 28.4 (t, C2′). MS (*m/e*): 446 (M^+, 60), 359 (M^+-CH_2CH_2COOMe, 45), 303 (M^+-CH_2CH_2COOMe-2CO, 48), 139 ($ClC_6H_4CO^+$, 100).

Reaction of [[1-(3,4,5-trimethoxyphenyl)-2-(4-chlorophenylcarbonyl-κO)]ethenyl-κC¹]tetracarbonylmanganese (3i) with acrolein in acetonitrile. Similarly, **3i** (0.145 g, 0.29 mmol) and acrolein (0.15 ml, 2.27 mmol) were dissolved in nitrogen-saturated acetonitrile (20 ml) and the solution was refluxed for 1 h. PLC (ethyl acetate/petroleum spirit (1:2)) gave one major band at R_f 0.3, which yielded 5-(4-chlorophenyl)-5-(2-formylethyl)-3-(3,4,5-trimethoxyphenyl)furan-2(5H)-one **10c** (0.055 g, 46%). This crystallized (ether/pentane) as white needles, m.p. 62°C. IR: 1762 (vs, CO), 1735 (s, CHO). ^1H NMR: δ 9.71 (s, 1H, H3′), 7.58 (s, 1H, H4), 7.38 (s, 4H, H2‴, 6‴, H3‴, 5‴), 7.09 (s, 2H, H2″, 6″), 3.88 (s, 6H, 3″, 5″-$(OMe)_2$), 3.85 (s, 3H, 4″-OMe), 2.50 (m, 4H, CH_2-2, 3). ^{13}C NMR: δ 200.2 (d, C3′), 171.1 (s, C2), 153.4 (s, C3″, 5″), 149.3 (d, C4), 139.6 (s, C4‴), 137.1 (s, C4″), 134.5 (s, C1″), 129.7 (s, C1‴), 129.3 (d, C2‴, 6‴), 126.4 (d, C3‴, 5‴), 124.2 (s, C3), 104.6 (d, C2″, 6″), 86.7 (s, C4), 60.4 (q, 4″-OMe), 56.3 (q, 3″, 5″-$(OMe)_2$), 38.2 (t, C1′), 31.6 (t, C2′). MS (*m/e*): 416 (M^+, 58), 359 (M^+-CH_2CH_2CHO, 79), 303 (M^+-CH_2CH_2COOMe-2CO, 75), 139 ($ClC_6H_4O^+$, 100).

Reaction of [[1-(4-trifluoromethylphenyl)-2-phenylcarbonyl-κO]ethenyl-κC¹]tetracarbonylmanganese (3r) with methyl acrylate in carbon tetrachloride. A solution of **3r** (0.17 g, 0.38 mmol) and methyl acrylate (0.1 ml, 1.11 mmol) in carbon tetrachloride (20 ml) was heated under reflux for 6 h. The major PLC band was methyl (*E*)-6-oxo-6-phenyl-4-(4-trifluoromethylphenyl)hex-2-enoate **9d** (0.037 g, 43%), which crystallized from pentane as small white fibrous crystals, m.p. 62°C. IR: 1721 (s, CO), 1688 (s, COOMe) cm^{-1}. ^1H NMR: δ 7.92 (d, 2H, $J = 8.0$ Hz, H2″, 6″), 7.58 (m, 3H, H3′, 5′, H4″), 7.45 (t, 2H, $J = 8.0$ Hz, H3″, 5″), 7.38 (d, 2H, $J = 8.1$ Hz, H2′, 6′), 7.13 (dd, 1H, $J = 15.7/7.0$ Hz, H3), 5.81 (dd, 1H, $J = 15.7/1.3$ Hz, H2), 4.39 (ddd, 1H, $J = 7.0/7.0/1.3$ Hz, H4), 3.71 (s, 3H, COOMe), 3.50 (d, 2H, $J = 7.0$ Hz, CH_2). ^{13}C NMR: δ 196.5 (s, C1), 166.7 (s, C6), 149.4 (d, C3), 145.3 (s, C1′), 136.6 (s, C1″), 133.6 (d, C4″), 129.4 (s, $J_{C-F} = 12.7$ Hz, C4′), 128.8 (d, C3″, 5″), 128.4 (d, C2′, 6′), 128.0 (d, C2″, 6″), 125.8 (d, $J_{C-F} = 3.7$ Hz, C3′, 5′), 121.8 (d, C2), 51.7 (q, COOMe), 43.2 (t, C5), 42.7 (d, C4). MS (*m/e*): 362 (M^+, 1), 288 (M^+-MeCOOMe, 15), 105 ($PhCO^+$, 100). Anal. Found: C, 65.92; H, 4.77. $C_{20}H_{17}F_3O_3$. Calc.: C, 66.30; H, 4.73.

Reaction of [[1-(4-trifluoromethylphenyl)-2-phenylcarbonyl-κO]ethenyl-κC¹]tetracarbonylmanganese (3r) with methyl acrylate in acetonitrile. The corresponding reaction of **3r** (0.21 g, 0.47 mmol) and methyl acrylate (0.15 ml, 1.67 mmol) in refluxing acetonitrile (20 ml) for 1.5 h gave on chromatography (PLC, diethyl ether/petroleum spirit 1:2) two bands at R_f 0.5 and R_f 0.4. The band at R_f 0.5 gave methyl (*E*)-6-oxo-6-phenyl-4-(4-trifluoromethylphenyl)hex-2-enoate (**9d**) as a light yellow oil (0.053 g, 31%). The band at R_f 0.4 gave

5-(2-methoxycarbonylethyl)-3-phenyl-5-(4-trifluoromethylphenyl)furan-2(5H)-one (**10d**) as a colorless oil (0.092 g, 49%), which crystallized (ether/pentane) as small white fibrous crystals, m.p. 55°C. IR: 1763 (vs, CO), 1736 (s, COOMe) cm^{-1}. ^1H NMR: δ 7.96 (d, 2H, $J = 8.3$ Hz, H2″, 6″), 7.85 (s, 1H, H3), 7.65 (d, 2H, $J = 8.3$ Hz, H3″, 5″), 7.42 (m, 5H, H2‴, 6‴, H3‴, 5‴, H4‴), 3.58 (s, 3H, COOMe), 2.46 (m, 4H, CH_2-2, 3). ^{13}C NMR: δ 173.1 (s, C3′), 170.1 (s, C1), 152.5 (d, C3), 138.2 (s, C1″), 132.5 (s, C1‴), 129.2 (d, C3‴, 5‴), 128.9 (s, C2), 128.6 (d, C4‴), 127.7 (d, C2″, 6″), 125.5 (d, $J_{C-F} = 3.7$ Hz, C3″, 5″), 124.6 (d, C2‴, 6‴), 87.8 (s, C4), 51.9 (q, COOMe), 34.8 (t, C1′), 28.4 (t, C2′). MS (*m/e*): 390 (M^+, 11), 358 (M^+-MeOH, 22), 331 (M^+-COOMe, 34), 303 (M^+-CH_2CH_2COOMe, 75), 105 ($PhCO^+$, 100).

*Reaction of [4,5,6-trimethoxy-2-[3-(2-trifluoromethylphenyl)prop-2-en-1-on-κO-yl]phenyl-κC¹]tetracarbonylmanganese (**4l**) with methyl acrylate in carbon tetrachloride.* Similarly a solution of **4l** (0.13 g, 0.24 mmol) and methyl acrylate (0.15 ml, 1.67 mmol) in carbon tetrachloride (20 ml) was heated under reflux for 3 h. PLC (with diethyl ether/petroleum spirit 1:1) gave one major band at R_f 0.4, which was 2-methoxycarbonyl-1-(2-(2-trifluoromethylphenyl)ethenyl)-4,5,6-trimethoxyindan-1-ol **11** (0.075 g, 68%). It crystallized as small white fibrous crystals, m.p. 112°C. The stereochemistry at C1 and C2 was undetermined. IR: 1737 cm^{-1} (s, COOMe). ^1H NMR: δ 7.58 (d, 1H, $J = 7.7$ Hz, H3″), 7.43 (m, 2H, H5″, H6″), 7.30 (m, 1H, H4″), 7.00 (dq, 1H, $J = 15.6/2.4$ Hz, H2′), 6.61 (s, 1H, H7), 6.15 (d, 1H, $J = 15.6$ Hz, H1′), 3.91 (s, 3H, 4-OMe), 3.82 (s, 3H, 6-OMe), 3.81 (s, 3H, 5-OMe), 3.72 (s, 3H, COOMe), 3.48 (t, 1H, $J = 9.0$ Hz, H2), 3.20 (m, 2H, CH_2), 3.08 (s, 1H, OH). ^{13}C NMR: δ 172.2 (s, C=O), 154.2 (s, C4), 149.6 (s, C6), 142.0 (s, C5), 139.7 (s, C7a), 136.0 (s, C1″), 134.6 (d, C2′), 131.9 (d, C5″), 127.9 (d, C6″), 127.4 (d, C4″), 125.7 (d, $J_{C-F} = 5.4$ Hz, C3″), 124.8 (d, C1′), 123.8 (s, C3a), 101.9 (d, C7), 85.3 (s, C1), 61.0 (q, 5-OMe), 60.6 (q, 4-OMe), 58.8 (d, C2), 56.1 (q, 6-OMe), 52.0 (q, COOMe), 28.4 (t, C3). MS (*m/e*): 434 (M^+-OH, 100), 375 (M^+-OH-COOMe, 16), 344 (40), 279 (52), 201 (8), 119 (32), 91 (48). Anal. Found: C, 61.20; H, 5.20. $C_{23}H_{23}F_3O_6$. Calc.: C, 61.20; H, 4.91.

*Reaction of [[1-(4-methoxyphenyl)-2-(3,4,5-trimethoxyphenylcarbonyl-κO)]ethenyl-κC¹]tetracarbonylmanganese (**3e**) with methyl vinyl ketone in acetonitrile.* [[1-(4-Methoxyphenyl)-2-(3,4,5-trimethoxyphenylcarbonyl-κO)]ethenyl-κC¹]tetracarbonylmanganese **3e** (0.13 g, 0.26 mmol) and methyl vinyl ketone (0.15 ml, 1.80 mmol) were dissolved in nitrogen-saturated acetonitrile (20 ml) and the solution was refluxed for 1.5 h. PLC (with ethyl acetate/petroleum spirit 1:2) gave two bands at R_f 0.4 and R_f 0.2. The band at R_f 0.2 gave 3-(4-methoxyphenyl)-5-(3-oxobutyl)-5-(3,4,5-trimethoxyphenyl)furan-2(5H)-one (**10e**) as a yellow oil (0.028 g, 24%) which did not crystallize. IR: 1757 (vs, CO), 1715 (s, COMe) cm^{-1}. ^1H NMR: δ 7.78 (d, 2H, $J = 8.8$ Hz, H2″, 6″), 7.53 (s, 1H, H4), 6.91 (d, 2H, $J = 8.8$ Hz, H3″, 5″), 6.61 (s, 2H, H2‴, 6‴), 3.87 (s, 6H, 3‴, 5‴-$(OMe)_2$), 3.82 (s, 6H, 4″, 4‴-$(OMe)_2$), 2.44 (m, 4H, CH_2-2, 3), 2.06 (s, 3H, Me). ^{13}C NMR: δ 207.4 (s, C3′), 171.7 (s, C2), 160.6 (s, C4″), 153.6 (s, C3‴, 5‴), 148.7 (d, C4), 137.9 (s, C4‴), 134.7 (s, C1″), 128.9 (s, C1‴), 128.6 (d, C2″, 6″), 121.6 (s, C3), 114.1 (d, C3″, 5″), 102.1 (d, C2‴, 6‴), 87.5 (s, C5), 60.9 (q, 4‴-OMe), 56.4 (q, 3‴, 5‴-$(OMe)_2$), 55.7 (q, 4″-OMe), 37.6 (t, C1′), 33.6 (t, C2′), 30.2 (q, Me). MS (*m/e*): 426 (M^+, 33), 355 (M^+-CH_2CH_2COMe, 45), 327 (M^+-CH_2CH_2COMe-CO, 55), 299 (M^+-CH_2CH_2COMe-2CO, 80), 195 ($(MeO)_3C_6H_2CO^+$, 100).

The band at R_f 0.4 yielded an unidentified yellow oil (0.03 g) which did not crystallize. IR: 1734 cm^{-1}. ^1H NMR: δ 7.74 (d, 1H, $J = 15.2$ Hz), 7.54 (d, 2H, $J = 7.5$ Hz), 7.20 (d, 1H, $J = 15.2$ Hz), 7.14 (s, 1H), 6.94 (d, 2H, $J = 7.5$ Hz), 4.03 (s, 3H), 3.93 (s, 3H), 3.91 (s, 3H), 3.85 (s, 3H), 3.77 (s, 2H), 2.47 (s, 3H). ^{13}C NMR: δ 210.3 (s), 196.2 (s), 160.2 (s), 153.8 (s), 148.8 (s), 138.9 (s), 137.6 (s), 135.9 (s), 129.7 (s), 128.4 (d), 120.9 (d), 114.3 (d), 102.8 (d), 61.2 (q), 60.5 (q), 56.5 (q), 55.4 (q), 36.9 (t), 30.2 (q).

*Reaction of [[1-(3,4,5-trimethoxyphenyl)-2-(4-chlorophenylcarbonyl-κO)]ethenyl-κC¹]tetracarbonylmanganese (**3i**) with methyl vinyl ketone in acetonitrile.* Similarly **3i** (0.2 g, 0.40 mmol) and methyl vinyl ketone (0.2 ml, 2.40 mmol) in refluxing acetonitrile (20 ml) for 2 h. PLC (with ethyl acetate/petroleum spirit 1.5:1) gave two bands at R_f 0.4 and R_f 0.3. The band at R_f 0.3 gave 5-(4-chlorophenyl)-5-(3-oxobutyl)-3-(3,4,5-trimethoxyphenyl)furan-2(5H)-one (**10f**) as a reddish oil (0.122 g, 71%) which did not crystallize. IR: 1762 (s, CO), 1716 (s, COMe) cm^{-1}. ^1H NMR: δ 7.56 (s, 1H, H4), 7.36 (s, 4H, H2‴, 6‴, H3‴, 5‴), 7.07 (s, 2H, H2″, 6″), 3.87 (s, 6H, 3″, 5″-$(OMe)_2$), 3.84 (s, 3H, 4″-OMe), 2.40 (m, 4H, CH_2-2, 3), 2.05 (s, 3H, Me). ^{13}C NMR: δ 207.1 (s, C3′), 171.2 (s, C2), 153.4 (s, C3″, 5″), 149.9 (d, C4), 139.5 (s, C4‴), 137.4 (s, C4″), 134.4 (s, C1″), 129.4 (s, C1‴), 129.2 (d, C2‴, 6‴), 126.4 (d, C3‴, 5‴), 124.4 (s, C3), 104.5 (d, C2″, 6″), 87.0 (s, C5), 60.9 (q, 4″-OMe), 56.3 (q, 3″, 5″-$(OMe)_2$), 38.0 (t, C1′), 33.1 (t, C2′), 30.2 (q, Me). MS (*m/e*): 430 (M^+, 87), 372 (M^+-MeCOMe, 100), 359 (M^+-CH_2CH_2COMe, 61), 139 ($ClC_6H_4CO^+$, 83).

The band at R_f 0.4 gave 5-acetyl-1-(4-chlorophenyl)-3-(3,4,5-trimethoxyphenyl)cyclopent-2-en-1-ol (**12**) as a colorless oil (0.017 g, 11%) which crystallized as white fibrous crystals, m.p. 155°C. The stereochemistry at C1 and C5 was not established. ^1H NMR:

δ 7.50 (d, 2H, $J = 8.6$ Hz, H3′, 5′), 7.36 (d, 2H, $J = 8.6$ Hz, H2′, 6′), 6.71 (s, 2H, H2″, 6″), 5.92 (dd, 1H, $J = 2.0/1.0$ Hz, H2), 3.86 (s, 6H, 3″, 5″-$(OMe)_2$), 3.85 (s, 3H, 4″-OMe), 3.65 (t, 1H, $J = 8.1/7.4$ Hz, H5), 3.47 (ddd, 1H, $J = 16.4/7.4/2.0$ Hz, H4a), 2.90 (ddd, 1H, $J = 16.4/8.1/1.0$ Hz, H4b), 2.80 (s, 1H, OH), 2.04 (s, 3H, COMe). ^{13}C NMR: δ 207.5 (s, CO), 153.3 (s, C3″, 5″), 145.3 (s, C1″), 144.5 (s, C3), 138.9 (s, C4″), 133.2 (s, C4′), 130.3 (s, C1′), 128.8 (d, C2), 128.5 (d, C2′, 6′), 126.9 (d, C3′, 5′), 103.6 (d, C2″, 6″), 86.4 (s, C1), 63.0 (d, C5), 61.0 (q, 4″-OMe), 56.2 (q, 3″, 5″-$(OMe)_2$), 33.4 (t, C4), 31.2 (q, $COCH_3$). MS (*m/e*): 402 (M^+, 67), 384 (M^+-H_2O, 35), 34 (M^+-H_2O-COMe, 100). Anal. Found: C, 65.00; H, 5.75. $C_{22}H_{23}O_5Cl$. Calc.: C, 65.59; H, 5.75.

Table 2
Final positional parameters for the cyclomanganated indanyl phenyl ketone **7a**

Atom	x	y	z
Mn(1)	0.8187(1)	0.1889(1)	0.1110(1)
C(1)	0.8203(6)	0.3246(5)	0.2616(5)
C(2)	0.8125(6)	0.3526(6)	0.3611(4)
C(3)	0.6813(6)	0.3582(5)	0.4367(5)
C(4)	0.8934(6)	0.2648(6)	0.4039(4)
C(5)	0.6153(7)	0.2617(6)	0.4304(5)
C(6)	0.5002(7)	0.2704(6)	0.4422(5)
C(7)	0.8273(9)	0.1645(6)	−0.0090(6)
C(8)	0.6566(7)	0.2428(7)	0.1418(6)
C(9)	0.8036(8)	0.0339(7)	0.1484(5)
C(10)	0.9884(8)	0.1633(6)	0.0658(5)
C(11)	0.8305(6)	0.3644(6)	0.0987(5)
C(12)	0.8321(6)	0.4110(6)	0.1828(5)
C(13)	0.8390(7)	0.5305(6)	0.1917(5)
C(14)	0.8464(7)	0.6059(6)	0.1130(5)
C(15)	0.8429(7)	0.5636(6)	0.0287(5)
C(16)	0.8347(7)	0.4456(6)	0.0223(5)
C(17)	0.821(1)	0.4797(8)	−0.1356(6)
C(21)	1.0256(6)	0.2885(5)	0.3695(4)
C(22)	1.0478(7)	0.3978(6)	0.3901(5)
C(23)	1.1646(7)	0.4253(6)	0.3615(5)
C(24)	1.2624(7)	0.3474(6)	0.3108(5)
C(25)	1.2438(7)	0.2387(6)	0.2890(5)
C(26)	1.1270(7)	0.2085(6)	0.3180(5)
C(27)	1.1124(7)	0.0881(6)	0.2979(5)
C(31)	0.8273(6)	0.2823(5)	0.5110(4)
C(32)	0.7084(6)	0.3373(5)	0.5301(5)
C(33)	0.6271(7)	0.3572(6)	0.6241(5)
C(34)	0.6683(7)	0.3218(6)	0.6987(5)
C(35)	0.7865(7)	0.2656(6)	0.6819(5)
C(36)	0.8684(7)	0.2464(5)	0.5872(5)
C(37)	0.4726(9)	0.390(1)	0.8166(6)
C(41)	0.4396(7)	0.1684(6)	0.4388(5)
C(42)	0.5012(7)	0.0819(6)	0.3707(5)
C(43)	0.4461(8)	−0.0127(6)	0.3629(6)
C(44)	0.3291(8)	−0.0236(6)	0.4237(6)
C(45)	0.2674(8)	0.0580(6)	0.4938(6)
C(46)	0.3203(7)	0.1534(6)	0.5026(5)
C(47)	0.2533(7)	0.2381(7)	0.5822(5)
F(1)	1.2172(4)	0.0223(4)	0.2514(3)
F(2)	1.0421(4)	0.0898(4)	0.2449(3)
F(3)	1.0589(4)	0.0280(3)	0.3802(3)
F(4)	0.3161(4)	0.2494(4)	0.6391(3)
F(5)	0.2248(4)	0.3479(4)	0.5509(3)
F(6)	0.1475(4)	0.2067(5)	0.6415(4)
O(1)	0.8136(4)	0.2215(4)	0.2460(3)
O(3)	0.6151(4)	0.4711(4)	0.4281(3)
O(7)	0.8326(7)	0.1429(5)	−0.0857(4)
O(8)	0.5577(7)	0.2818(6)	0.1564(5)
O(9)	0.7906(7)	−0.0608(5)	0.1733(4)
O(10)	1.0911(6)	0.1513(5)	0.0343(4)
O(17)	0.8298(6)	0.3997(4)	−0.0581(4)
O(37)	0.5996(5)	0.3375(5)	0.7945(3)
Cl(1)	0.4699(9)	0.003(1)	−0.0931(8)
Cl(2)	0.414(1)	0.171(1)	0.0292(8)
Cx(1)	0.453(5)	0.045(3)	−0.023(3)

2.4. X-Ray crystal structures

2.4.1. X-ray crystal structure of [2-((1S*,2R*,3S*)-1-hydroxy-1-((E)-2-(2-trifluoromethylphenyl)-ethenyl)-3-(2-trifluoromethylphenyl)-6-methoxy-2-indanylcarbonyl-κO)-6-methoxyphenyl-κC¹]tetracarbonylmanganese (7a)

Yellow plate crystals were obtained by vapor diffusion of pentane into a saturated dichloromethane solution of **7a** at 4°C. Preliminary precession photography suggested a triclinic lattice. Intensity data were collected on a Nicolet R3 four-circle diffractometer at −110°C using monochromated Mo Kα radiation ($\lambda = 0.7107$ Å).

Crystal data: $C_{38}H_{25}F_6MnO_8.CH_2Cl_2$, M 863.48, triclinic, $P\bar{1}$, $a = 11.872(6)$, $b = 11.549(7)$, $c = 14.887(8)$Å, $\alpha = 85.42(4)$, $\beta = 68.87(4)$, $\gamma = 80.65°$, $U = 1878.08$ Å^3. D_c 1.53 g cm^{-3} for $Z = 2$. F(000) 876, μ(Mo Kα) 6.00 cm^{-1}.

A total of 4913 unique reflections in the range $2° < 2\theta < 45°$ were collected. These were corrected for Lorentz and polarization effects, and for linear absorption by a Ψ scan method. Of these, 3333 had $I \geqslant 2\sigma(I)$ and were used in all calculations. The coordinates of the manganese atom were found by analysis of the Patterson map using SHELXS-86 [11]. All other non-hydrogen atoms were revealed by a subsequent difference map phased on the manganese atom. In the final cycle of blocked full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic temperature factors, while hydrogen atoms were included in calculated positions with tied temperature factors, except for the hydroxy H(3), which was located and refined. A penultimate difference map showed residual electron density which could be assigned to a disordered molecule of dichloromethane, so this was included in the refinement, which converged at $R = 0.0637$, $R_w = 0.0632$, where $w = [\sigma(F^2) + 0.000993F^2]^{-1}$. In the last cycle of refinement, the largest parameter shift (Δ/σ) was 0.25, and a final difference map showed no feature greater than $|0.61|\ e$ Å^{-3}. Refined coordinates are listed in Table 2.

2.4.2. X-Ray crystal structure of (1S,4S*,5R*)-5-(4-bromobenzoyl)-1-(4-bromophenyl)-3,4-di-(4-trifluoromethylphenyl)cyclopent-2-en-1-ol (8)*

Translucent rectangular crystals were obtained by vapor diffusion of pentane into a saturated chloroform solution of **8** at 4°C. Preliminary precession photography indicated a triclinic lattice. Intensity data were collected on a Nicolet R3 four-circle diffractometer at −110°C, using monochromated Mo Kα radiation (λ = 0.7107Å).

Crystal data: $C_{32}H_{20}Br_2F_6O_2.CHCl_3$, $M = 829.69$, triclinic, $P\bar{1}$, $a = 10.666(8)$, $b = 12.485(9)$, $c = 12.828(10)$ Å, $\alpha = 103.58(6)$, $\beta = 90.44(6)$, $\gamma = 101.32(6)°$, $U = 1625.6\ 2$ Å^3, $D_c = 1.69$ g cm^{-3} for $Z = 2$, F(000) 820, μ(Mo Kα) = 29.6 cm^{-1}.

A total of 4245 unique reflections in the range $4° < 2\theta < 45°$ were collected on a crystal of dimensions 0.80 mm × 0.40mm × 0.22 mm. These were corrected for Lorentz and polarization effects, and for linear absorption by a Ψ scan method. Of these, 2195 had $I \geqslant 3\sigma(I)$ and were used in all calculations. The structure was solved by Patterson methods and routinely developed. A penultimate difference map revealed a molecule of $CHCl_3$ in the lattice, so this was included in the refinement. In the final cycle of full-matrix least-squares refinement, chlorine and bromine atoms were assigned anisotropic temperature factors, while all other non-hydrogen atoms were treated isotropically. The CF_3 group with F(1)–F(3) was disordered over two orientations, so was modeled by six half-F atoms with a common isotropic temperature factor. Hydrogen atoms were included in calculated positions with tied temperature factors, except for the hydroxy H(1), which was located in a penultimate difference map and was included but not refined. Refinement converged at $R = 0.0705$, $R_w = 0.0686$, where $w = [\sigma(F^2) + 0.000993F^2]^{-1}$. In the last cycle of refinement, no parameter shifted by more than a Δ/σ of 0.02, and the largest feature in a final difference map of 1.3 e Å^{-3} was associated with the CF_3 group. Refined coordinates are given in Table 3.

Table 3
Final positional parameters for the cyclopentenol **8**

Atom	x	y	z
Br(1)	1.0074(2)	−0.1384(1)	−0.2634(1)
Br(2)	0.3813(2)	−0.0640(1)	−0.2082(1)
F(1)	0.779(2)	1.003(2)	0.440(2)
F(1a)	0.613(2)	0.875(2)	0.535(2)
F(2)	0.582(2)	0.932(2)	0.444(2)
F(2a)	0.799(2)	0.961(2)	0.531(2)
F(3)	0.729(2)	0.911(2)	0.560(2)
F(3a)	0.642(2)	0.975(2)	0.428(2)
F(4)	0.8426(9)	0.2120(7)	0.5878(7)
F(5)	0.653(1)	0.2419(9)	0.5876(8)
F(6)	0.8108(9)	0.3719(7)	0.6655(7)
O(1)	1.0862(9)	0.3731(8)	0.0900(7)
O(3)	0.8728(8)	0.3965(7)	−0.0801(6)
C(1)	0.984(1)	0.309(1)	0.054(1)
C(2)	0.856(1)	0.338(1)	0.0901(9)
C(3)	0.780(1)	0.365(1)	−0.004(1)
C(4)	0.734(1)	0.469(1)	0.055(1)
C(5)	0.779(1)	0.511(1)	0.156(1)
C(6)	0.870(1)	0.444(1)	0.1866(9)
C(11)	0.985(1)	0.198(1)	−0.019(1)
C(12)	1.092(1)	0.190(1)	−0.081(1)
C(13)	1.097(1)	0.090(1)	−0.154(1)
C(14)	0.996(1)	0.000(1)	−0.164(1)
C(15)	0.893(1)	0.005(1)	−0.103(1)
C(99)	0.304(2)	0.349(1)	0.273(1)
C(16)	0.882(1)	0.104(1)	−0.030(1)
C(21)	0.680(1)	0.268(1)	−0.060(1)
C(22)	0.695(1)	0.200(1)	−0.161(1)
C(23)	0.608(1)	0.102(1)	−0.205(1)
C(24)	0.503(1)	0.070(1)	−0.149(1)
C(25)	0.481(1)	0.135(1)	−0.050(1)
C(26)	0.571(1)	0.235(1)	−0.006(1)
C(31)	0.760(1)	0.613(1)	0.233(1)
C(32)	0.647(1)	0.657(1)	0.222(1)
C(33)	0.631(1)	0.753(1)	0.296(1)
C(34)	0.719(1)	0.805(1)	0.377(1)
C(35)	0.833(2)	0.768(1)	0.388(1)
C(36)	0.848(1)	0.671(1)	0.314(1)
C(37)	0.705(2)	0.912(2)	0.464(2)
C(41)	0.843(1)	0.407(1)	0.2915(9)
C(42)	0.719(1)	0.372(1)	0.319(1)
C(43)	0.697(1)	0.333(1)	0.412(1)
C(44)	0.796(1)	0.326(1)	0.477(1)
C(45)	0.920(1)	0.362(1)	0.449(1)
C(46)	0.942(1)	0.402(1)	0.358(1)
C(47)	0.774(2)	0.288(1)	0.577(1)
Cl(1)	0.3754(4)	0.2292(3)	0.2422(3)
Cl(2)	0.2870(5)	0.3874(4)	0.4114(3)
Cl(3)	0.3958(5)	0.4580(4)	0.2270(5)
H(1)	0.878	0.480	0.904

3. Results and discussion

3.1. Cyclomanganation reactions

The reaction of $PhCH_2Mn(CO)_5$ with chalcones proceeded smoothly in refluxing petroleum spirit (b.p. 60–80°C) to give either the alkene-manganated (**3**) or the ring-manganated (**4**) isomers or both. The reaction conditions are a little milder than those used for aryl ketones (refluxing heptane: b.p. 98°C), and were the best compromise for cleanest reaction within a reasonable time. Reactions were generally complete after 5 h, and the products were readily purified by chromatography. Results are summarized in Table 1. Prepared similarly were **3a**, **5** and **6** from the corresponding benzylidene-acetone, thienyl chalcone analog and coumaranone respectively. Overall yields were reasonable for most substrates, with lower yields in some cases attributable to subsequent reaction of the cyclometallated complex with another molecule of chalcone (see below).

The direct metallation complements the insertion methods used by Booth and Hargreaves [7] to produce compounds **3**. Their methods are experimentally more complicated and require expensive alkynes, while the

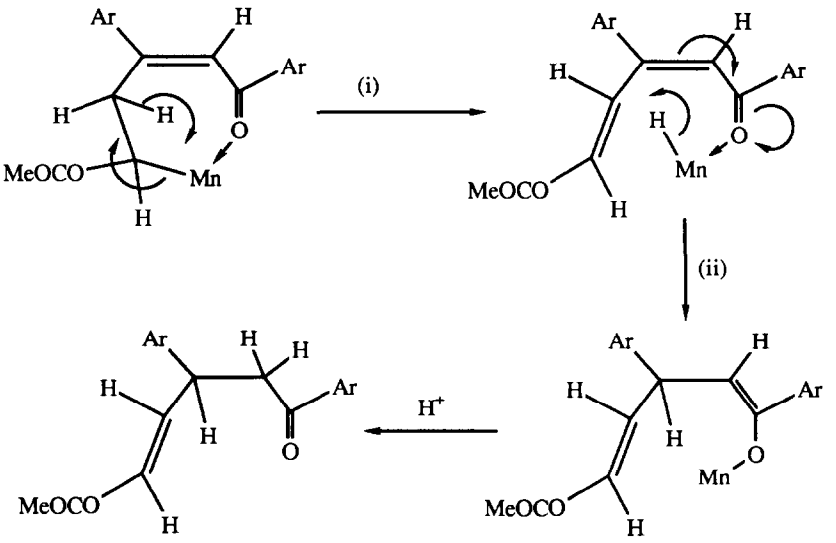
direct metallation starts from chalcones readily prepared from a variety of accessible acetophenones and benzaldehydes, thereby allowing more flexibility in substituent variation than the limited number of commercially available alkynes permits. On the other hand, the direct approach may give mixtures of alkene- and ring-metallated isomers, although this varies with substituents (see below). Where such isomers were formed, their complete separation was not always possible by chromatography, in which cases they were characterized by NMR spectroscopy of the mixtures. Separation could also sometimes be achieved by fractional crystallization using dichloromethane/petroleum spirit, when the ring-manganated product tended to crystallize first. The cyclomanganated products were yellow to red, with the ring-manganated species darker in color. All are readily handled in air without significant decomposition, can be chromatographed, and are soluble in common organic solvents.

In the solution infrared spectrum of a *cis*-$LL'Mn(CO)_4$ molecule, four absorption bands are expected in the $\nu(CO)$ region, but the cyclomanganated species prepared in this study generally showed only three, at about 2080, 1995 and 1940 cm^{-1}, with the middle of these containing two coincidental vibrations. There was no systematic difference between the infrared spectra of the alkene- and ring-manganated compounds, so this technique could not be used for distinguishing them. The similarity of the carbonyl stretching vibration patterns suggests that the five-membered ring in the metallated non-aromatic compounds (**3**) is similar electronically and geometrically to those formed in orthometallated aromatic substrates (e.g. **4**, and orthometallated acetophenones generally). This is also the conclusion from comparison of the reported [8b,12] structure of **3a** with those of numerous aromatic examples of type **1**, all of which have very similar Mn–C and Mn–O distances and O–Mn–C angles [1].

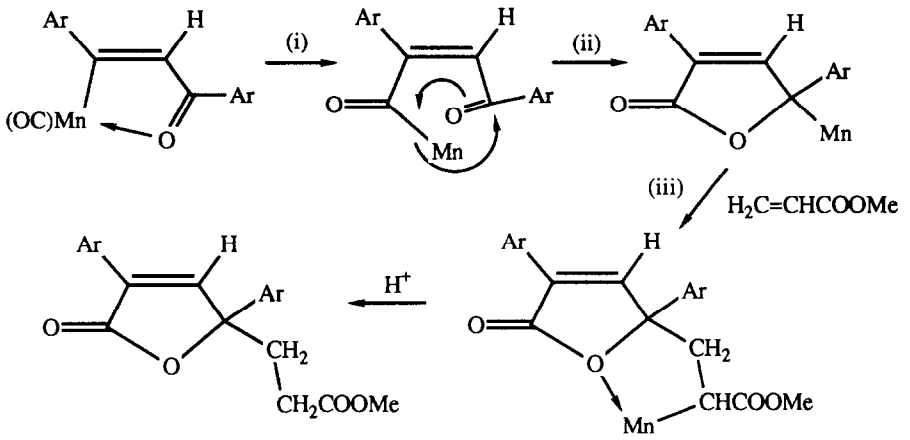
The alkene- and ring-manganated isomers can be readily distinguished by ^1H NMR, since alkene manganation eliminates the alkene H3 signal, and converts the H2 doublet to a singlet which moves dramatically down field. On the other hand, the ring-manganated compounds show predictable changes in the aromatic H pattern, and the alkene H signals (H2′ and H3′ in **4**) remain as doublets moved only slightly downfield.

The range of chalcones with different substituents on the α-phenyl and benzoyl rings allowed study of electronic effects of substituents on the selectivity between the alternative metallation sites. Little is known about the mechanism of cyclomanganation reactions in general, but early work by Takahashi and Tsuji [13] and by Bennett et al. [14] suggested that cyclopalladiation of unsymmetrically substituted azobenzenes was electrophilic, while cyclomanganation of similar substrates was nucleophilic. The results of the present study, listed in Table 1, do not allow such a clear conclusion. Alkene manganation is favored by a CF_3 group in the para position of the β-phenyl ring bonded to the manganation site, though it is less favored by the same group in the ortho position, presumably for steric reasons. Methoxy substituents on the β-phenyl ring have a weaker directing influence.

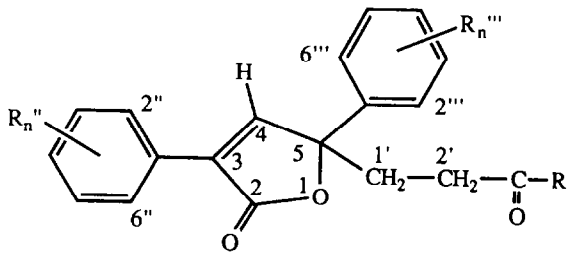
By contrast, in the benzoyl ring a para-chloro or -trifluoromethyl group (meta to the potential site of ring manganation) directs manganation away preferentially to the alkene center. Overall there appears to be a general preference for alkene manganation, but ring-manganation is only marginally less favored. Interpretations of substituent effects in terms of electrophilic or nucleophilic mechanisms are not justified with the present lack of knowledge of mechanism. Nevertheless



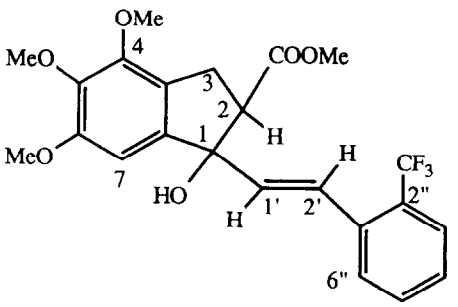
Scheme 1. Possible mechanisms for formation of products of type **9** subsequent to insertion of methyl acrylate into the C–Mn bond of alkene-manganated chalcones. Metal carbonyl ligands are omitted for clarity.



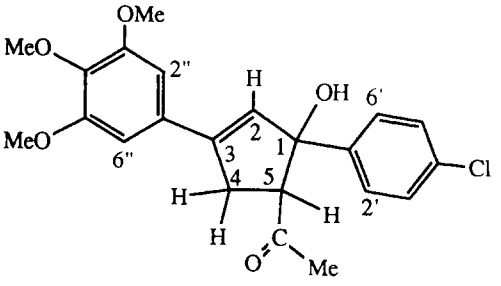
Scheme 2. Possible mechanism of formation of butenolides (**10**) by coupling of alkene-manganated chalcones with methyl acrylate. Metal ligands are omitted for clarity.



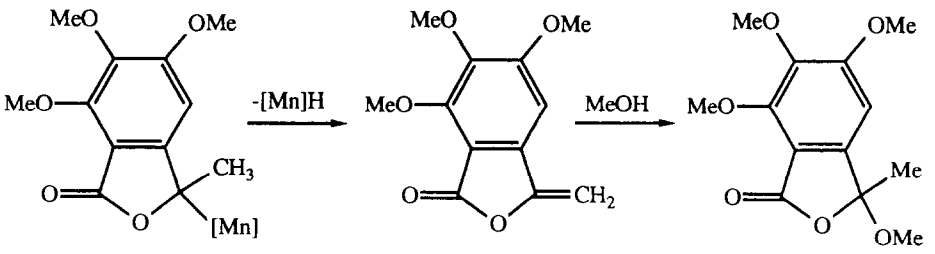
	R	R_n''	R_n'''
10a	OMe	4''-OMe	3''',4''',5'''-$(OMe)_3$
10b	OMe	3'',4'',5''-$(OMe)_3$	4'''-Cl
10c	H	3'',4'',5''-$(OMe)_3$	4'''-Cl
10d	OMe	4''-CF_3	H
10e	Me	4''-OMe	3''',4''',5'''-$(OMe)_3$
10f	Me	3'',4'',5''-$(OMe)_3$	4'''-Cl



11



12



13 14 15

specificity, or at least high selectivity, for alkene manganation can be achieved if required (a) by having no aromatic ring on the carbonyl carbon, as in **3a**, (b) by blocking the ortho sites on the benzoyl ring, as in **3c**, or (c) by including a $-CF_3$ substituent in the para position on the β-phenyl ring (**3o–3r**).

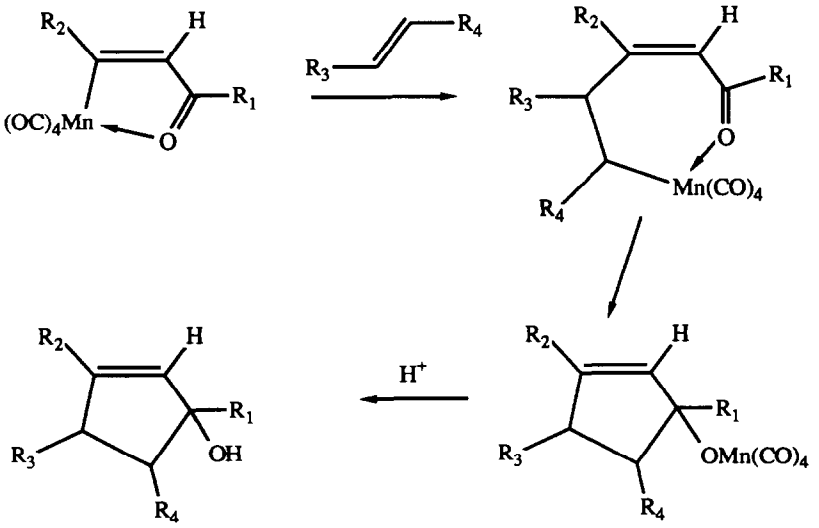
For chalcones with a meta group in the benzoyl ring, two different manganation sites are available. This accounts for the formation of the isomeric pairs **4j–4j'** and **4k–4k'**, in which Mn is bonded either ortho or para to the substituent (MeO and Cl, respectively). The ortho isomers (**4j** and **4k**) were formed in greater than twofold excess in each case. Similar directive effects promoting orthomanganation in the sterically crowded position have been noted more generally with 3-substituted acetophenones [1,15].

3.2. Reactions of cyclomanganated chalcones with alkenes

Orthomanganated acetophenones and related species react with alkenes to give a variety of products, although promotion with Li_2PdCl_4 or Me_3NO has often been employed [1,16]. We have therefore investigated similar reactions with the cyclometallated chalcones made available by the reactions discussed above. Thus, cyclometallated chalcone **3e** reacted with methyl acrylate in refluxing CCl_4, in the absence of any promoter, to give a high yield of the α,β-unsaturated ester **9a**. Substrates **3i** and **3r** gave the corresponding compounds **9b** and **9d** similarly. In these products, conjugation across the chalcone system has been lost with saturation of the α,β double bond. Such saturation is unknown in analogous coupling reactions of orthomanganated acetophenones, the α,β double bond in those cases, however, being part of an aromatic ring.

Shown in Scheme 1 is one possible pathway to product subsequent to insertion of alkene into the C–Mn bond. It involves hydride migration via β-metal-hydride elimination (i), followed by δ-metal-hydride addition (ii), with the subsequent protonation possibly occurring on work-up. There are many possible variations on and alternatives to this tentative proposal.

The reactions are of synthetic interest in that they result in carbon–carbon bond formation between the electrophilic β-carbons of two α,β-unsaturated carbonyl (enone) systems. Transition-metal catalysis of analogous tail-to-tail dimerization of methyl acrylate to dimethyl hexanedioates is receiving considerable current attention as a potential industrial route to adipic acid for use in the Nylon-6,6 industry as an alternative to routes based on cyclohexane-based feedstocks [17]. The product shown in Scheme 1 is also formed in acetonitrile as solvent, but in lower yield and with substituted furan-2(5H)-ones (α,β-butenolides) formed as well, such as **10a** from **3e**. Butenolide formation is presumably initiated by carbonyl insertion induced by the donor MeCN molecule (step (i) of the postulated sequence of steps in Scheme 2). Step (ii) involves cyclization and concomitant Mn transfer to form an alkyl-Mn species, which then (step (iii)) reacts with alkene to form an insertion product. This, on protonation (step (iv)) — again possibly during work-up — gives the butenolide. If the rearrangement (step (ii)) is too stereoelectronically restricted to occur, a concerted cyclization and insertion may somehow occur. There is only indirect support for the formation of such an alkyl-Mn species: in the unsuccessful attempted coupling of orthomanganated 2',3',4'-trimethoxyacetophenone with methyl acrylate and with methyl vinyl ketone in methanol containing Li_2PdCl_4, a common though very minor by-product, not incorporating alkene,



Scheme 3. Possible route from alkene-manganated chalcones and alkenes to cyclopentenol products **8** (R_1 = 4-bromophenyl; $R_2 = R_3$ = 4-trifluoromethylphenyl; R_4 = 4-bromobenzoyl) and **12** (R_1 = 4-chlorophenyl; R_2 = 3,4,5-trimethoxyphenyl; R_3 = H; $R_4 = COCH_3$).

was identified [18] as the methanol adduct **15** of the methenyl α,β-butenolide **14**, the latter possibly formed from the corresponding alkylmanganese precursor **13** by β-hydride elimination. In this case, the low yield of **14** may simply represent uncompetitive carbonyl insertion.

DeShong et al. have shown [8a] that butenolides related to **10** but with only one substituent at C(5) are formed when cyclomanganated enones are demetallated by H^+ or by H^-, so the reactions with alkenes reported here extend the range of butenolides that can be prepared from organomanganese reagents.

Other activated alkenes, methyl vinyl ketone or acrolein, also reacted with **3i** or **3e** in acetonitrile to give related lactones **10f** and **10e**, although reactions were less specific and yields were lower. The only other product identified from these reactions was from the reaction of **3i** with methyl vinyl ketone in acetonitrile, where a substituted cyclopentenol **12** was found. This last species presumably forms as outlined in Scheme 3. Initially there is an insertion of the C=C of the alkene into the Mn–C bond of the cyclomanganated enone to give a seven-membered metallocyclic ring. The new Mn–C bond then adds across the C=O bond to form the cyclopentene ring and a manganese alkoxide which would give the alcohol on protonation. This cyclization reaction has precedence in reactions of alkynes [1,15,19] and alkenes [1,16] with orthomanganated aromatic ketones, and a new example of this type came from the reaction of ring-manganated chalcone **4l** with methyl acrylate, which gave a high yield of an undefined stereoisomer of the substituted indanol **11**. This is the expected product based on comparisons with other orthometallated aryl ketones, so the chalcone side chain is having no influence on the course of reaction.

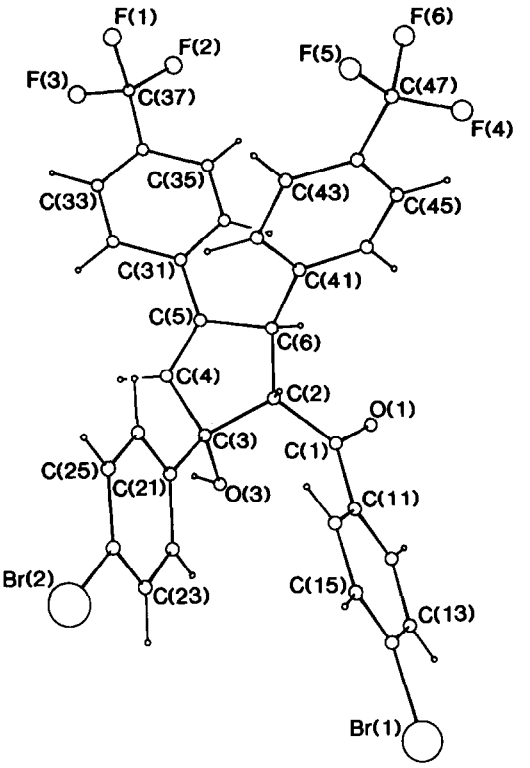


Fig. 2. Structure of (1S*,4S*,5R*)-5-(4-Bromobenzoyl)-1-(4-bromophenyl)-3,4-di-(4-trifluoromethylphenyl)cyclopent-2-en-1-ol (**8**) formed during cyclometallation of 1-(4-bromophenyl)-3-(4-trifluoromethylphenyl)prop-2-en-1-one. Only one of the orientations of the disordered CF_3 group at C(37) is shown.

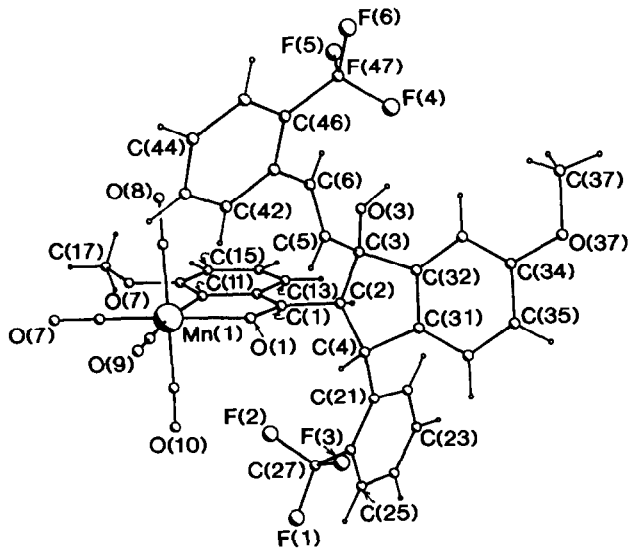


Fig. 1. Structure of [2-((1S*,2R*,3S*)-1-hydroxy-1-((*E*)-2-(2-trifluoromethylphenyl)ethenyl)-3-(2-trifluoromethylphenyl)-6-methoxy-2-indanylcarbonyl-κO)-6-methoxyphenyl-κC^1]tetracarbonylmanganese (**7a**), formed during cyclomanganation of 1-(3-methoxyphenyl)-3-(2-trifluoromethylphenyl)prop-2-en-1-one. Selected bond parameters: Mn–C(11), 2.043(7) Å; Mn–O(1), 2.052(5) Å; C(1)–O(1), 1.251(8) Å, C(11)–Mn–O(1), 79.0°. Other bond lengths and angles fall within expected ranges.

Chalcones themselves are activated alkenes, and the reaction type just described explains some of the high-molecular-mass products detected as by-products in the metallation reactions described earlier. For example, from the preparation of **4j**, 26% of **7a** was also isolated. The compound was identified by an X-ray crystal structure determination (Fig. 1) which highlights the extensive substitution in the five-membered ring by bulky groups, including an orthomanganated acetophenone. This product is clearly a more complicated example of the alkene-coupled product **11** formed (see above) from the ring-manganated species **4l**. Similar products are to be expected, and are found (**7b–7e**), in 12–28% yields, in all of the metallation reactions of chalcones where ring metallation is favored.

Similarly, with substrates which are not ring-manganated, a different type of product is expected, related to those formed by reaction of alkene-manganated complexes with alkenes. Indeed, a cyclopentenol **8** was isolated in 10% yield from the manganation reaction forming **3o**, and was structurally char-

acterized by X-ray crystallography as shown in Fig. 2. The crystal consists of molecules linked via O(3)–H(1)....O(1) hydrogen bonds. The five-membered ring of **8** is highly substituted, but otherwise the geometry is unremarkable. The formation of **8** can be envisaged to parallel the route given in Scheme 3 for the preparation of **12**.

Acknowledgements

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References

[1] L. Main and B.K. Nicholson, *Adv. Met.-Org. Chem., 3* (1994) 1.
[2] A.W. Cabral, *Ph.D. Thesis*, University of California, Los Angeles, 1981.
[3] N.P. Robinson, *D.Phil. Thesis*, University of Waikato, New Zealand, 1989.
[4] W. Tully, *M.Sc. Thesis*, University of Waikato, New Zealand, 1991.
[5] R.C. Cambie, M.R. Metzler, C.E.F. Rickard, P.S. Rutledge and P.D. Woodgate, *J. Organomet. Chem., 425* (1992) 59.
[6] D.A. Harbourne and F.G.A. Stone, *J. Chem. Soc. A* (1968) 1765.
[7] B.L. Booth and R.G. Hargreaves, *J. Chem. Soc. A* (1969) 2766; *J. Chem. Soc. A* (1970) 308.
[8] (a) P.D. DeShong, D.R. Sidler and G.A. Slough, *Tetrahedron Lett., 28* (1987) 2233; (b) P.D. DeShong, D.R. Sidler, P.J. Rybczynski, G.A. Slough and A.L. Rheingold, *J. Am. Chem. Soc., 110* (1988) 2575.
[9] (a) R.D. Closson, J. Kozikowski and T.H. Coffield, *J. Org. Chem., 22* (1957) 598; (b) M.I. Bruce, M.J. Liddell and G.N. Parr, *Inorg. Synth., 26* (1989) 172.
[10] N.P. Robinson, *D.Phil. Thesis*, University of Waikato, New Zealand, 1989.
[11] SHELXS-86, G.M. Sheldrick, University of Göttingen, Germany, 1986; SHELX-76, G.M. Sheldrick, University of Cambridge, UK, 1976.
[12] P. DeShong, G.A. Slough, D.R. Sidler, P.J. Rybczynski, W. von Philipsborn, R.W. Kunz, B.E. Bursten and T.W. Clayton, *Organometallics, 8* (1989) 1381.
[13] H. Takahashi and J. Tsuji, *J. Organomet. Chem., 10* (1967) 511.
[14] R.L. Bennett, M.I. Bruce and I. Matsuda, *Aust. J. Chem., 28* (1975) 1265; M.I. Bruce, *Angew. Chem., Int. Edn. Engl., 16* (1977) 73; and references therein.
[15] L.S. Liebeskind, J.R. Gasdaska, J.S. McCallum and S.J. Tremont, *J. Org. Chem., 54* (1989) 669.
[16] L.H.P. Gommans, L. Main and B.K. Nicholson, *J. Chem. Soc., Chem. Commun.* (1987) 761.
[17] E. Hauptman, S. Sabo-Etienne, P.S. White, M. Brookhart, J.M. Garner, P.J. Fagan and J.C. Calabrese, *J. Am. Chem. Soc., 116* (1994) 8038, and references therein.
[18] J.M. Cooney, *D.Phil. Thesis*, University of Waikato, New Zealand, 1994.
[19] N.P. Robinson, L. Main and B.K. Nicholson, *J. Organomet. Chem., 364* (1989) C37.