Synthesis and reactions
of [(((η^6) -2-acylaryl) -C,O) tetracarbonylmanganese]-tricarbonylchromium complexes: enhancement of diastereoselection during cyclopentaannulation

George R. Clark, Michael R. Metzler, Giles Whitaker, Paul D. Woodgate *

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand

Abstract

Cyclomanganation reactions of [(η^6)-acylaryl]tricarbonylchromium complexes have been investigated. Three novel heterobimetallic complexes have been synthesised in moderate to good yield, with one being characterised by X-ray crystallography. Several modes of activating these bimetallic complexes towards coupling reactions with substituted alkenes and alkynes were investigated, including oxidative decarbonylation at room temperature, and thermal promotion. The stereochemistry of one of the cyclopentaannulated adducts has been established by X-ray crystallography. Thermal displacement of one of the CO ligands of the bimetallic complex **27** in the presence of PPh$_3$ afforded a single adduct, the structure of which was established by X-ray crystallography. The chemistry of this novel bimetallic system was investigated.

Keywords: Manganese; Carbonyl; Chromium; Crystal structure; Cyclopentaannulation; Stereoselection

1. Introduction

The synthesis and chemistry of bimetallic complexes is a research area that is currently very active. The complexes may be expected to exhibit interesting spectroscopic or structural features owing to possible interaction between the two metal centres. Moreover, coordination of two different metals to a single hydrocarbon may activate the ligand in a cooperative fashion which would allow novel synthetic transformations in high diastereoselectivity. Bimetallic complexes containing a Cr(CO)$_3$ unit and group 14 elements (Si, Ge and Sn) σ-bound to the aromatic ring have been prepared by Poeth et al. [1]. Hunter and co-workers [2,3] have synthesised biphenyl-, terphenyl-, naphthalene- and anthracene-bridged bi- and tri-metallic complexes of iron and chromium in which Cr(CO)$_3$ is η^6-bound to the aryl ligand and (η^5-C$_5$H$_5$)Fe(CO)$_2$ groups are directly σ-bound to the aromatic rings. These complexes were synthesised by thermal treatment of the appropriate acyl-bridged iron complexes with an excess of Cr(CO)$_6$, resulting in coordination of chromium and decarboxylation, leaving the iron atom(s) directly bonded to the aromatic ring(s). Benzene-bridged heterobimetallic complexes containing both σ-bound gold and σ-bound titanium have been reported by Lotz and co-workers [4]; they have also prepared bimetallic complexes of chromium and manganese with bridging σ,π-benzene and benzoyl ligands [5]. These acyl-bridged compounds were prepared by reacting lithiated (η^6-arene)Cr(CO)$_3$ complexes with bromopentacarbonylmanganese. Heterobimetallic complexes of thiophene containing both σ-bound Mn and η^6-Cr have also been reported [6,7]. To our knowledge, a bimetallic complex of benzoquinoline in which the Mn is N-bound is the only reported example of an ortho manganated (η^6-arene)tricarbonylchromium complex [8]. This complex was prepared in low yield by ortho manganation of the η^6-tricarbonylchromium complex of benzoquinoline with CH$_3$Mn(CO)$_5$.

The synthesis and chemistry of (η^6-arene)tricarbonylchromium complexes [9] and of ortho man-

* Corresponding author.
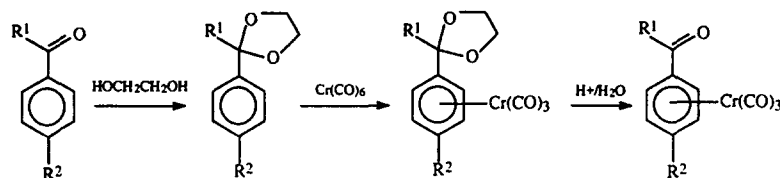
	R^1	R^2			
1	H	H	5 (97%)	9 (67%)	13 (76%)
2	Me	H	6 (89%)	10 (49%)	14 (76%)
3	Et	H	7 (98%)	11 (68%)	15 (89%)
4	Me	OMe	8 (78%)	12 (77%)	16 (95%)

Scheme 1.

ganated aryl ketones [10–20] has been well studied. However, the effect of combining these coordinated metal systems with a view to obtaining enhanced diastereoselectivity in insertion–cyclisation sequences leading to cyclopentaannulation has not been investigated previously. Given that alkene or alkyne insertion could still be induced in an electron-poor heptacarbonyl bimetallic complex, then the cyclisation step to give a 1-indanol should be controlled stereochemically by the desire of the larger incipient C-1 substituent to be anti to the $Cr(CO)_3$ group. The present work was undertaken to investigate this possibility. Since either the bimetallic

Table 1
Products from complexation reactions of **13**, **14**, **15** and **16** with $PhCH_2Mn(CO)_5$

Reagent (g)	$PhCH_2Mn(CO)_5$ (g)	Solvent, ml	Time	Products (%)	
Complex 13				**13**	**25**
0.10	0.15	heptane, 10	30 min	60	0
0.10	0.45	octane, 10	30 min	50	0
0.10	0.15	heptane, 10	1.0 h	40	0
Complex 14				**14**	**26**
0.50	0.67	heptane, 55	45 min	86	2
0.50	0.92	heptane, 50	1.5 h	46	30
0.50	0.79	heptane, 50	2.0 h	54	34
0.50	0.79	heptane, 50	2.5 h	42	32
1.10	1.75	heptane, 110	2.0 h	58	22
0.87	1.16	heptane, 40	1.5 h	43	38
0.87	1.16	cyclohexane, 40	3.75 h	79	5
0.10	0.14	acetonitrile, 5	2.0 h	80	0
Complex 15				**15**	**27**
0.50	0.64	heptane, 50	2.0 h	42	53
0.50	0.64	heptane, 100	1.5 h	92	5
0.87	1.10	heptane, 40	1.5 h	48	45
0.87	1.10	heptane, 40	4.0 h	31	68
0.87	1.10	heptane, 40	2.0 h	31	64
0.87	1.10	cyclohexane, 40	2.0 h	54	45
Complex 16				**16**	**28**
0.10	0.12	heptane, 10	1.5 h	60	18
0.10	0.18	heptane, 20	2.0 h	53	19
0.10	0.06	heptane, 12	4.5 h	25	1
0.20	0.24	heptane, 20	1.0 h	84	8
0.10	0.12	heptane, 10	35 min	36	32
0.10	0.12	heptane, 10	17 min	83	6
0.50	0.10	heptane, 32	30 min	94	2
0.05	0.06	DMF, 5	2.5 h	70	0
0.10	0.12	1,2-dichloroethane, 15	2.0 h	85	0
0.10	0.12	dibutyl ether–heptane, 15	1.0 h	60	0

complex or an (η^6-Cr(CO)$_3$) 1-indanol product could be optically resolved, the diastereoselectivity induced in the cyclisation step could be transformed into enantioselectivity in the decomplexed cyclopentaannulated ligand.

2. Results and discussion

A number of [(η^6)-acylaryl]tricarbonylchromium complexes were synthesised in a three step reaction sequence from their parent aryl ketones via their dioxolane derivatives, in the yields indicated (Scheme 1) [21].
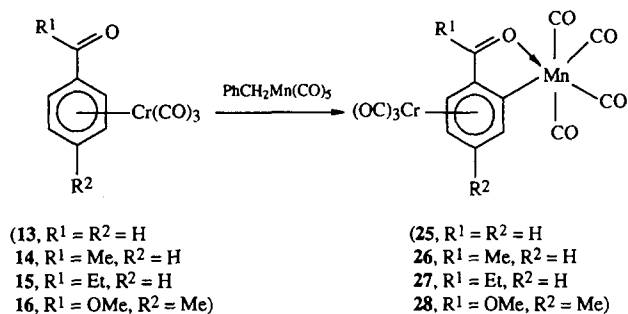
It has been suggested [12,22] that, as an empirical guide, carbonyl-containing substrates with ν_{max}(C=O) < 1700 cm^{-1} should be amenable to cyclomanganation, with the additional requirement that an sp^2 carbon be ortho to the organic carbonyl group to enable σ

bonding to the manganese. Complexes **13**, **14**, **15** and **16** all satisfy this requirement, ν_{max}(C=O) being observed between 1682–1689 cm^{-1}. Optimised conditions for ortho manganation of a number of acylarenes involve refluxing a solution of the aromatic compound with PhCH$_2$Mn(CO)$_5$ (1.2 molar equiv.) in heptane (30 ml/0.2 g of ligand) for 1–6 h under positive nitrogen pressure [16]. In the present work, treatment of the tricarbonylchromium complexes **13**, **14**, **15** and **16** under a variety of conditions afforded the product distributions summarised in Table 1.

For ligands **14**, **15** and **16**, optimised yields for the corresponding bimetallic complexes of **26** (38%), **27** (68%) and **28** (32%) were obtained under conditions similar to those reported [16]. In all three cases a typical reaction initially formed a bright red solution, with significant precipitation developing after about 5 min of heating under reflux. As the reaction proceeded, more precipitate formed. Several attempts were made to

Table 2
Crystal data and structure refinement for **26** and **29**

	26	29
Empirical formula	$C_{15}H_7CrMnO_8$	$C_{33}H_{24}CrMnO_7P$
Formula weight	422.15	670.43
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.710694	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions (Å)	$a = 14.204(3)$	$a = 14.751(6)$
	$b = 7.369(3)$	$b = 14.168(5)$
	$c = 16.482(4)$	$c = 16.320(2)$
	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 111.67(2)°$	$\beta = 115.53(2)°$
	$\gamma = 90°$	$\gamma = 90°$
Volume (Å^3)	1603.2(8)	3078(2)
Z	4	4
Density (calculated (Mg m^{-3})	1.749	1.447
Absorption coefficient (mm^{-1})	1.506	0.862
F(000)	840	1368
Crystal size (mm)	$0.18 \times 0.23 \times 0.28$	$0.45 \times 0.25 \times 0.25$
θ range for data collection	1.62 to 27.01°	1.56 to 24.99°
Index ranges	$-18 \leq h \leq 16$	$-15 \leq h \leq 17$
	$-9 \leq k \leq 0$	$-16 \leq k \leq 0$
	$0 \leq l \leq 20$	$-19 \leq l \leq 0$
Reflections collected	3743	5599
Independent reflections	3491 [R(int) = 0.0289]	5400 [R(int) = 0.0555]
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/Restraints/Parameters	3491/0/254	5400/0/407
Goodness-of-fit on F^2	1.032	0.988
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0318$	$R1 = 0.0572$
	$wR2 = 0.0713$	$wR2 = 0.1188$
R indices (all data)	$R1 = 0.0637$	$R = 0.1826$
	$wR2 = 0.0847$	$wR2 = 0.1608$
Largest difference max. (e Å^{-3})	0.287	0.378
Largest difference min. (e Å^{-3})	-0.307	-0.478
$\omega = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$	$a = 0.0371$	$a = 0.0613$
	$b = 0.85$	$b = 0.76$
Number of observed reflections [$I > 2\sigma(I)$]	2512	2491

Scheme 2.

(13, R¹ = R² = H
14, R¹ = Me, R² = H
15, R¹ = Et, R² = H
16, R¹ = OMe, R² = Me)

(25, R¹ = R² = H
26, R¹ = Me, R² = H
27, R¹ = Et, R² = H
28, R¹ = OMe, R² = Me)

maintain a homogeneous mixture by employing a number of alternative solvents and co-solvents (DMF, acetonitrile, 1,2-dichloroethane, dibutyl ether, cyclohexane). The only solvent apart from heptane that gave limited success was cyclohexane, which afforded the bimetallic complex **27** in 45% yield after 4 h. Several attempts were made to isolate and identify the precipitate which formed during the course of reaction. Unfortunately, however, the material proved to be too unstable for ^{1}H NMR analysis, giving only very broad signals. The infrared spectrum of the crude precipitate showed a number of ν_{max} 1950–1800 cm^{-1}, consistent with metal C≡O absorptions. Attempted purification by chromatography on either silica gel or alumina resulted in decomposition of the material.

The data reported in Table 1 show that ortho manganation of [(η^6)-acylaryl]tricarbonylchromium complexes is a very sensitive process, the yields being affected by concentration, solvent, and reaction time. The optimum reaction conditions for formation of the heterobimetallic compounds involve heating a concentrated solution of the starting tricarbonylchromium complex (100 mg/5 ml of heptane) with a slight excess of PhCH$_2$Mn(CO)$_5$
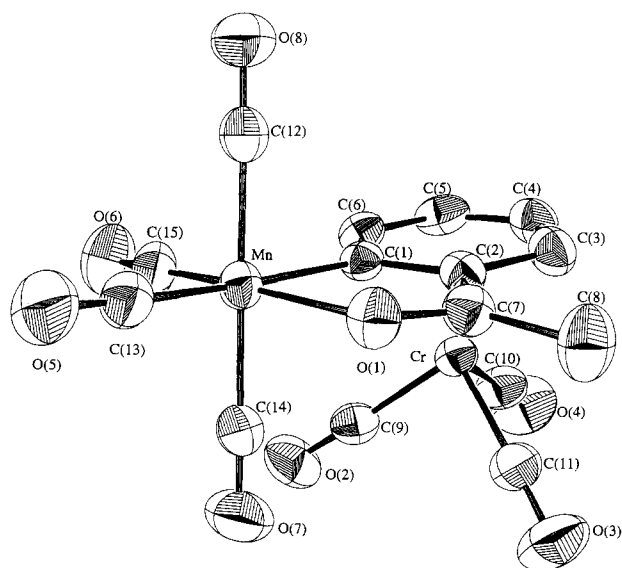
Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for **26**; U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	x	y	z	U_{eq}
Mn	5325(1)	2093(1)	2082(1)	37(1)
Cr	2526(1)	156(1)	903(1)	35(1)
O(1)	4781(1)	3493(3)	925(1)	43(1)
O(2)	3829(2)	−3120(3)	1477(2)	70(1)
O(3)	2525(2)	−348(5)	−900(2)	80(1)
O(4)	755(2)	−2371(4)	488(2)	86(1)
O(5)	7488(2)	2935(4)	2398(2)	75(1)
O(6)	5773(2)	−270(4)	3608(2)	78(1)
O(7)	5383(2)	−1116(4)	981(2)	73(1)
O(8)	5209(2)	5180(4)	3213(2)	76(1)
C(1)	3801(2)	1927(4)	1801(2)	33(1)
C(2)	3232(2)	2854(4)	1015(2)	35(1)
C(3)	2151(2)	3074(4)	720(2)	44(1)
C(4)	1642(2)	2328(5)	1216(2)	47(1)
C(5)	2178(2)	1358(5)	1978(2)	47(1)
C(6)	3230(2)	1160(4)	2259(2)	40(1)
C(7)	3949(2)	3603(4)	555(2)	39(1)
C(8)	3400(3)	4498(6)	−317(2)	56(1)
C(9)	3324(2)	−1858(4)	12541(2)	45(1)
C(10)	1425(2)	−1385(5)	637(2)	53(1)
C(11)	2509(2)	−142(5)	−216(2)	48(1)
C(12)	5257(2)	4060(5)	2762(2)	48(1)
C(13)	6663(2)	2613(5)	2259(2)	48(1)
C(14)	5350(2)	68(5)	1398(2)	45(1)
C(15)	5623(2)	667(5)	3016(2)	51(1)

(1.2 molar equiv.) for about 2 h under positive nitrogen pressure.

[(((1,2,3,4,5,6-η)-2-Acetylphenyl)-C,O)tetracarbonylmanganese]tricarbonylchromium (**26**) crystallised from diethyl ether as red rods and showed six C≡O stretching absorptions in its infrared spectrum (2093, 2010, 1965, 1037, 1894 and 1866 cm^{-1}). It analysed correctly for C$_{15}$H$_7$CrMnO$_8$ and showed a molecular ion at m/z 422 in the mass spectrum. The ^{1}H NMR spectrum showed two sets of triplet × doublets and broadened doublets, at δ 5.5–6.0 ppm, consistent with ortho disubstitution on the aromatic ring. The 2 ppm upfield shift relative to the free ligand is also consistent with the retention of the Cr(CO)$_3$ complexed system. A single crystal X-ray structure analysis of **26** was undertaken in order to investigate the spatial arrangement of the ligands about the manganese moeity (Fig. 1, Tables 2–4).

Treatment of **14** in refluxing heptane also afforded a number of side products of which only hexacarbonyl[μ-(η^6:^{6}-2,4-diphenylbut-2-en-3-one)]dichromium (**30**) could be isolated pure. This compound crystallised as bright red rods, analysed correctly for C$_{22}$H$_{14}$Cr$_2$MnO$_7$, and showed a molecular ion at m/z 494 in the mass spectrum. The ^{1}H NMR and ^{13}C NMR spectra were consistent with the proposed structure. This homobimetallic complex is clearly the result of an aldol condensation reaction between two molecules of **14**.

Fig. 1. The atomic arrangement in **26**.

The expected anti disposition of the $Cr(CO)_3$ groups was confirmed by a single crystal X-ray diffraction experiment (Figs. 2 and 3, Tables 5–7).

Attempted cyclomanganation of $(\eta^6$-benzaldehyde)-tricarbonylchromium (13) did not give rise to any bimetallic derivatives, or to any other identifiable complexes. Although some of the starting material clearly decomposed as the reaction proceeded, significant amounts of 13 were recovered after work-up. This observation is similar to that observed by Cambie et al. [16] who reported that direct ortho manganation of non-complexed substituted benzaldehydes afforded mixtures, only low yields of the expected tetracarbonylmanganese derivatives being generated. These low yields were attributed more to the susceptibility of the CHO group towards side reactions rather than to the inherent inability of the ortho manganated complex to form.

In an attempt to increase the solubility of the starting [(η^6)-acylaryl]tricarbonylchromium ligands in non-polar solvents such as heptane, a series of derivatives were prepared in which a CO ligand was replaced with either Ph_3P (18) (19), or Bu_3P (20), or $(O^iPr)_3P$ (21). Photolytically-promoted displacement of CO ligands by R_3P is a facile process and is well documented in the literature [23]. Thus, treatment of the precursor tricarbonylchromium complex with R_3P (1.2 molar equiv.) in cyclohexane–diethyl ether under irradiation for 2 h gave the R_3P-containing adducts 18 (40%) [24], 19 (69%), 20 (55%), and 21 (62%).

Attempted ortho manganation of 18, 19, 20 or 21 using the optimum conditions established earlier led only to the formation of small amounts of chromium-free arene, unreacted starting η^6 complex making up most of the recovered material. That is, although 18–21 were easily soluble in heptane as anticipated, the coordination of a phosphine ligand significantly decreased the rate of the desired cyclomanganation reaction.

Coupling reactions of ortho manganated complexes with alkenes or alkynes have been reported extensively in the literature [10–20]. There are three main methods of activating simple tetracarbonylmanganese complexes towards coupling reactions with unsaturated hydrocarbons. Firstly, transmetallation with lithium tetrachloropalladate, followed by reaction with a suitably substituted alkene gives the expected Heck-type insertion product, generally in very good yield [10]. Secondly, oxidative activation of aryltetracarbonylmanganese complexes by treatment with Me_3NO in acetonitrile to effect decarbonylation (as CO_2), followed by insertion of an alkene [18] or alkyne [14,19] and cyclisation involving a suitable ortho substituent may lead directly to indanols or indenols in a one-pot reaction sequence. Thirdly, thermally-promoted decarbonylation in a suitable solvent (usually benzene) can lead to the corresponding indanols and indenols in excellent yields [14,18,19].

One of the aims of this project was to study the influence of the η^6 $Cr(CO)_3$ unit on the stereoselection during formation of the isomeric 1-indanol products resulting from an insertion–cyclisation sequence involving carbon–manganese bonds. It was anticipated that the $Cr(CO)_3$ tripod would favour the formation of some diastereoisomers over others. Since an initial transmetallation would replace the σ-bound manganese, only the oxidative or thermal activation methods were suitable pathways for this sequence.

In the event, treatment of the heterobimetallic complexes 26 and 27 with methyl propenoate in refluxing benzene for 24 h afforded the products shown in Scheme 3. A small amount of benzenetricarbonylchromium (17)
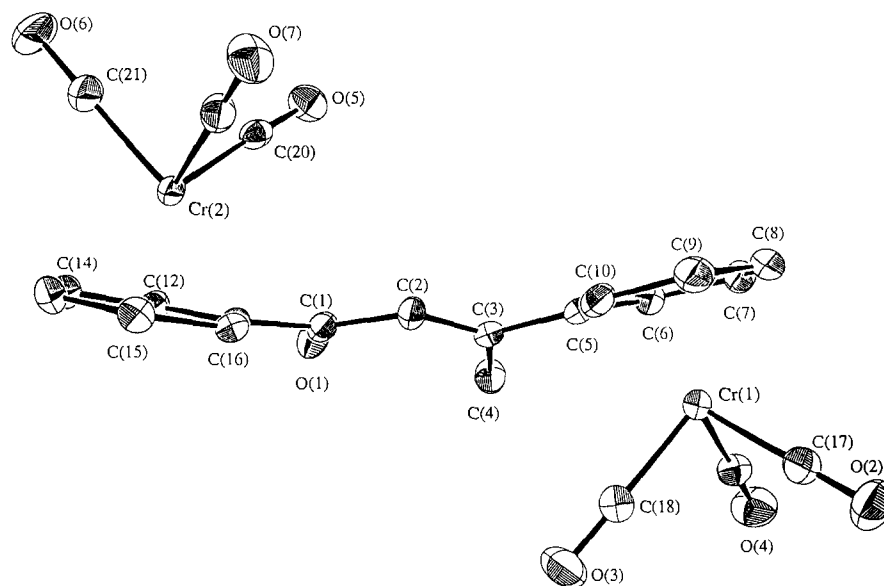

Fig. 2. The atomic arrangement in 30.

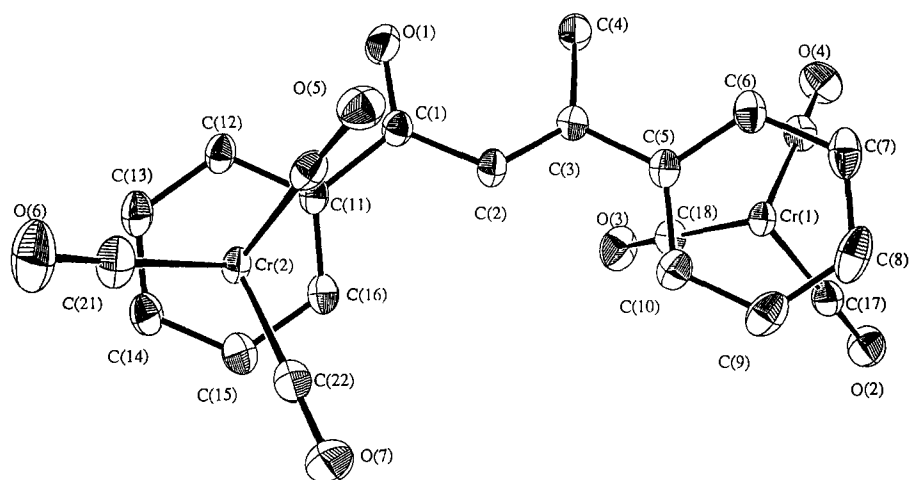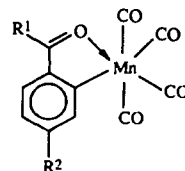Fig. 3. The atomic arrangement in **30**.

(3–5%) was also isolated from both reactions. Clearly, this compound has formed via transfer of 'Cr(CO)₃' from the starting complex to the solvent medium. This type of intermolecular transfer is well documented in the literature [25].
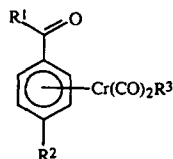
Complex **26** afforded the product of cyclisation followed by dehydration, indene **48** (26%), together with a small amount of demanganated starting material, **14** (13%). The cyclised 1-indanol complexes were isolated after chromatography as an inseparable mixture (4:1,
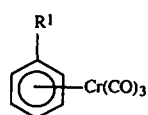
(17, R = H
35, R = COCHCH(Me)CH₂CH₂CO₂Me)

(18, R¹ = R² = H, R³ = PPh₃
19, R¹ = Me, R² = OMe, R³ = PPh₃
20, R¹ = Me, R² = OMe, R³ = PBu₃
21, R¹ = Me, R² = OMe, R³ = P(OⁱPr)₃)
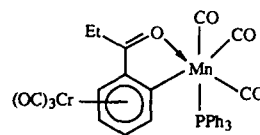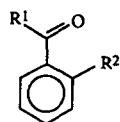
(32, R¹ = CH(Me)CH₂CH₂CO₂Me, R² = H
33, R¹ = CH(Me)CH₂CH₂CO₂CMe₃, R² = H
34, R¹ = Et, R² = CH₂CH₂CO₂Me)

(22, R¹ = Me, R² = H
23, R¹ = Me, R² = OMe
24, R¹ = Et, R² = H)

(29)
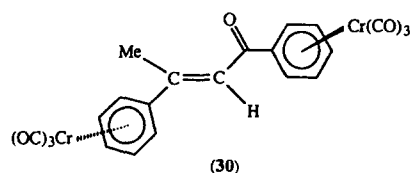
(30)
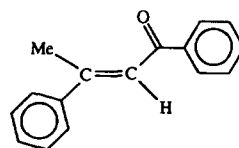
(31)

56%) of two diastereoisomers. The major stereoisomer was then purified by repetitive crystallisation from diethyl ether as yellow rod-shaped crystals. The stereochemistry of this complex was established by single crystal X-ray analysis, which showed it to be the α diastereoisomer **36** (Fig. 4, Tables 5, 8 and 9). The structure of the minor product was assigned as **38**. The relative stereochemistry at C1 and C2 of **38** was established by decomplexation (diethyl ether, $h\nu$, O_2) and comparison of the NMR data of the resulting free ligand (assigned as **41**) with that obtained when complex **36** was decomplexed to give **40**. The ^{1}H NMR spectrum of compound **40** showed the 1-CH_3 resonance at δ 1.76 ppm and the methyl ester resonance at δ 3.78 ppm, whereas in stereoisomer **41** these signals were observed at δ 1.38 ppm and at δ 3.81 ppm respectively. These spectral data led directly to the indicated assignments. The observed relative chemical shift values are in good agreement with those reported [18] for pairs of isomeric 1-indanols formed from $Mn(CO)_4$ complexes derived from podocarpic acid. Owing to significant overlap of signals in the ^{1}H NMR spectrum of (**36, 38**) the stereochemistry of the $Cr(CO)_3$ unit in the minor product **38** could not be assigned.

Similarly, complex **27** afforded **51** (16%), **15** (2%), **37** (59%), and **39** (3%) (Scheme 3). Also isolated from this reaction was tricarbonyl[(3a,3,4,5,6,7,7a-η)-3-ethyl-1H-indene]chromium (**49**) (12%). This yellow oil
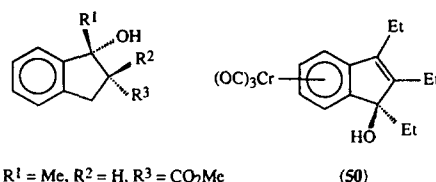
(**40**, R¹ = Me, R² = H, R³ = CO₂Me)   (**50**)
41. R¹ = Me, R² = CO₂Me, R³ = H
42. R¹ = Et, R² = H, R³ = CO₂Me
43. R¹ = Et, R² = CO₂Me, R³ = H
44. R¹ = Me, R² = H, R³ = CO₂CMe₃
45. R¹ = Me, R² = CO₂CMe₃, R³ = H
46. R¹ = Et, R² = H, R³ = CO₂CMe₃
47. R¹ = Et, R² = CO₂CMe₃, R³ = H)
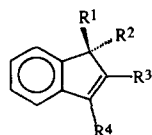
(52. R¹ = Me, R² = OH, R³ = R⁴ = Ph
53. R¹ = R² = H, R³ = CO₂Me, R⁴ = Me
54. R¹ = R² = H, R³ = CO₂CMe₃, R⁴ = Me
55. R¹ = Et, R² = OH, R³ = R⁴ = Ph
56. R¹ = R² = R³ = H, R⁴ = Et
57. R¹ = R² = H, R³ = CO₂Me, R⁴ = Et
58. R¹ = R² = H, R³ = CO₂CMe₃, R⁴ = Et
59. R¹ = CO₂Me, R² = H, R³ = CO₂Me, R⁴ = Et
60. R¹ = Et, R² = OH, R³ = CO₂Me, R⁴ = Me
61. R¹ = Et, R² = OH, R³ = R⁴ = Et)

Table 4
Bond lengths (Å) and angles (deg) for **26**

Mn–C(15)	1.781(3)	C(11)–Cr–C(1)	115.47(12)
Mn–C(13)	1.853(3)	C(10)–Cr–C(1)	154.87(12)
Mn–C(12)	1.856(3)	C(1)–Cr–C(5)	66.84(10)
Mn–C(14)	1.878(3)	C(1)–Cr–C(2)	36.96(9)
Mn–C(1)	2.043(3)	C(1)–Cr–C(3)	67.98(10)
Mn–O(1)	2.052(2)	C(1)–Cr–C(4)	79.50(10)
Cr–C(9)	1.825(3)	C(1)–Cr–C(6)	36.69(9)
Cr–C(11)	1.849(3)	C(7)–C(2)–Mn	117.2(2)
Cr–C(10)	1.850(3)	C(1)–C(2)–C(6)	122.6(2)
Cr–C(5)	2.194(3)	C(6)–C(2)–C(7)	114.0(2)
Cr–C(2)	2.204(3)	C(6)–C(2)–C(7)	123.5(3)
Cr–C(3)	2.209(3)	C(1)–C(2)–Cr	74.4(2)
Cr–C(4)	2.209(3)	C(6)–C(2)–Cr	71.2(2)
Cr–C(6)	2.211(3)	C(7)–C(1)–Cr	129.7(2)
Cr–C(1)	2.279(3)	C(6)–C(1)–C(2)	115.6(2)
O(1)–C(7)	1.239(3)	C(6)–C(1)–Mn	132.2(2)
O(2)–C(9)	1.152(4)	C(2)–C(1)–Mn	112.1(2)
O(3)–C(11)	1.146(3)	C(6)–C(1)–Cr	69.0(2)
O(4)–C(10)	1.149(4)	C(2)–C(1)–Cr	68.7(2)
O(5)–C(13)	1.133(4)	Mn–C(1)–Cr	134.70(12)
O(6)–C(15)	1.149(4)	C(5)–C(6)–C(1)	122.4(3)
O(7)–C(14)	1.122(4)	C(5)–C(6)–Cr	70.8(2)
O(8)–C(12)	1.130(4)	C(1)–C(6)–Cr	74.3(2)
C(1)–C(2)	1.423(4)	C(6)–C(5)–C(4)	120.7(3)
C(2)–C(3)	1.439(4)	C(6)–C(5)–Cr	72.1(2)
C(2)–C(7)	1.461(4)	C(4)–C(5)–Cr	72.0(2)
C(1)–C(6)	1.414(4)	C(10)–Cr–C(3)	115.16(13)
C(5)–C(6)	1.399(4)	C(5)–Cr–C(3)	66.58(13)
C(4)–C(5)	1.401(5)	C(2)–Cr–C(3)	38.06(10)
C(3)–C(4)	1.389(4)	C(9)–Cr–C(4)	149.39(13)
C(7)–C(8)	1.494(4)	C(11)–Cr–C(4)	121.29(14)
C(15)–Mn–C(13)	94.77(14)	C(10)–Cr–C(4)	89.81(13)
C(15)–Mn–C(12)	89.3(2)	C(5)–Cr–C(4)	37.11(12)
C(13)–Mn–C(12)	91.27(13)	C(2)–Cr–C(4)	66.88(11)
C(15)–Mn–C(14)	89.9(2)	C(3)–Cr–C(4)	36.64(11)
C(13)–Mn–C(14)	90.78(13)	C(9)–Cr–C(6)	88.05(13)
C(12)–Mn–C(14)	177.88(13)	C(11)–Cr–C(6)	151.92(12)
C(15)–Mn–C(1)	93.15(12)	C(10)–Cr–C(6)	118.18(12)
C(13)–Mn–C(1)	170.77(13)	C(5)–Cr–C(6)	37.02(11)
C(12)–Mn–C(1)	84.09(11)	C(2)–Cr–C(6)	65.90(10)
C(14)–Mn–C(1)	93.96(11)	C(3)–Cr–C(6)	78.97(12)
C(15)–Mn–O(1)	171.02(11)	C(4)–Cr–C(6)	66.79(12)
C(13)–Mn–O(1)	93.15(11)	C(3)–C(4)–C(5)	120.1(3)
C(12)–Mn–O(1)	94.72(12)	C(3)–C(4)–Cr	71.7(2)
C(14)–Mn–O(1)	85.72(12)	C(5)–C(4)–Cr	70.9(2)
C(1)–Mn–O(1)	79.34(9)	C(4)–C(3)–C(2)	118.6(3)
C(9)–Cr–C(11)	89.15(14)	C(4)–C(3)–Cr	71.7(2)
C(9)–Cr–C(10)	87.1(2)	C(2)–C(3)–Cr	70.8(2)
C(11)–Cr–C(10)	89.55(14)	O(1)–C(7)–C(2)	117.1(2)
C(9)–Cr–C(5)	112.46(13)	O(1)–C(7)–C(8)	120.0(3)
C(11)–Cr–C(5)	158.38(14)	C(2)–C(7)–C(8)	122.8(3)
C(10)–Cr–C(5)	90.95(13)	O(2)–C(9)–Cr	178.1(3)
C(9)–Cr–C(2)	119.69(12)	O(4)–C(10)–Cr	178.3(3)
C(11)–Cr–C(2)	91.62(13)	O(3)–C(11)–Cr	178.1(3)
C(10)–Cr–C(2)	153.22(13)	O(8)–C(12)–Mn	175.6(3)
C(2)–Cr–C(5)	78.44(11)	O(5)–C(13)–Mn	177.7(3)
C(9)–Cr–C(3)	157.56(12)	O(7)–C(14)–Mn	178.0(3)
C(11)–Cr–C(3)	93.75(14)	O(6)–C(15)–Mn	177.1(3)
C(9)–Cr–C(1)	90.70(12)		

showed a molecular ion at m/z 280 in the mass spectrum, accurate mass measurement of which was correct for $C_{14}H_{12}CrO_3$. The absence of a methyl reso-

nance at δ 3.8 ppm in the ^{1}H NMR spectrum, and of an absorption due to an ester carbonyl in the infrared spectrum, confirmed that decarbonylation had occurred. Decomplexation of **49** in diethyl ether–$h\nu$–O_2 afforded **56** as a clear oil, the molecular ion of which had a correct accurate mass measurement for $C_{11}H_{12}$. The ^{1}H NMR spectrum of this compound was in very good agreement with that published for the congener, 3-methylindene [26,27].

Also isolated from reaction of **27** with methyl propenoate was tricarbonyl[methyl(1,2,3,4,5,6-η)-4-methyl-5-oxo-5-phenylpentanoate]chromium (**35**), as a mixture with **15** and the two 1-indanol complexes **37** and **39**. Photolytically-induced decomplexation afforded methyl 4-methyl-5-oxo-5-phenylpentanoate (**32**) (1%) as a clear oil. Accurate mass measurement of the molecular ion of **32** was correct for $C_{13}H_{16}O_3$, and the infrared spectrum showed two carbonyl absorption

bands, due to an ester and to a benzylic ketone (1736 and 1682 cm^{-1}). The ^{1}H and ^{13}C NMR data were also consistent with the structure.

In order to determine whether the heterobimetallic complexes afforded better chemical yields (alkenes, alkynes) and/or enhanced stereocontrol (alkenes) during the formation of the cyclised insertion products (indenol/indanol), a comparative study was undertaken, the results of which are listed in Table 10. Thermally-promoted reactions of the aryltetracarbonylmanganese complex **24** with disubstituted symmetrical alkynes (PhC≡CPh, EtC≡CEt) generally gave very high chemical yields (92%) of the insertion–cyclisation products **55** and **61**. This is much higher than the yields (25%) of indenols isolated from similar reactions of the heterobimetallic complexes **26** and **27**. Insertion of phenylacetylene was unprofitable for both the mono- and bi-metallic systems, complicated mixtures of prod-

Table 5
Crystal data and structure refinement for **30** and **36**

	30	36
Empirical formula	$C_{22}H_{14}Cr_2O_7$	$C_{15}H_{14}CrO_6$
Formula weight	494.35	553.20
Temperature (K)	193(2)	193(2)
Wavelength (Å)	0.71069	0.71069
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	C_2/c
Unit cell dimensions (Å)	$a = 7.214(6)$	$a = 13.207(6)$
	$b = 10.563(5)$	$b = 10.099(7)$
	$c = 13.984(7)$	$c = 21.554(6)$
	$\alpha = 104.17(4)°$	$\alpha = 90°$
	$\beta = 100.86(5)°$	$\beta = 100.33(3)°$
	$\gamma = 100.30(5)°$	$\gamma = 90°$
Volume (Å^3)	986.0(11)	2828(3)
Z	2	8
Density (calculated) Mg m^{-3}	1.665	1.608
Absorption coefficient (mm^{-1})	1.146	0.836
$F(000)$	500	1408
Crystal size (mm)	$0.25 \times 0.35 \times 0.37$	$0.23 \times 0.38 \times 0.25$
θ range for data collection	1.55 to 26.97°	1.92 to 29.98°
Index ranges	$-9 \leq h \leq 0$	$0 \leq h \leq 18$
	$-13 \leq k \leq 13$	$-8 \leq k \leq 14$
	$-17 \leq l \leq 17$	$-30 \leq l \leq 29$
Reflections collected	4675	4864
Independent reflections	4272 [R(int) = 0.0232]	4119 [R(int) = 0.0546]
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/Restraints/Parameters	4271/0/336	4119/0/205
Goodness-of-fit on F^2	0.813	1.000
Final R indices [$I > 2\sigma(I)$]	$R = 0.0382$	$R1 = 0.0357$
	$wR2 = 0.1066$	$wR2 = 0.0911$
R indices (all data)	$R1 = 0.0509$	$R1 = 0.0591$
	$wR2 = 0.1197$	$wR2 = 0.1022$
Largest difference max. (e Å^{-3})	0.798	0.418
Largest difference min. (e Å^{-3})	-0.760	-0.474
$\omega = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$	$a = 0.990$	$a = 0.0648$
	$b = 1.56$	$b = 0.06$
Number of observed reflections [$I > 2\sigma(I)$]	3561	3131

ucts being formed in both reactions. This result is attributed to the reactivity of the acidic hydrogen of PhC≡CH.

In contrast, thermally-promoted coupling not only of **24** but also of **26** and **27** with monosubstituted alkenes, in particular with those having an electron-withdrawing substituent, in general gave very good chemical yields (70–95%) of the insertion–cyclisation product. However, the use of electron-donating substituted alkenes led either to complicated mixtures (triethoxyvinylsilane) or to recovery of decomplexed starting material (vinyl acetate, ethyl vinyl ether).

The formation of 1-indanols, and therefore of the label necessary to determine the diastereoselectivity of cyclisation, was complicated by the significant amount (3–37%) of dehydration to indenes that followed the annulation reactions. In general, the $(1\beta,2\beta):(1\beta,2\alpha)$ 1-indanol diastereoisomers were formed in a 3:1 ratio from the heterobimetallic complexes **26** and **27**, the corresponding indenes being formed in relatively low (3–14%) yield. For the monometallic tetracarbonylmanganese complex **24**, however, the amounts of indene formed were too high (30–37%) to allow valid compar-

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **30**; U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	x	y	z	U_{eq}
Cr(1)	685(1)	−2569(1)	4230(1)	22(1)
Cr(2)	4202(1)	2865(1)	1446(1)	19(1)
O(1)	2872(3)	−1213(2)	423(2)	34(1)
O(2)	−1816(3)	−2608(3)	5719(2)	40(1)
O(3)	−2704(3)	−2424(3)	2686(2)	45(1)
O(4)	−539(4)	−5576(2)	3437(2)	44(1)
O(5)	7289(3)	1443(2)	2028(2)	32(1)
O(6)	7283(4)	4805(3)	1009(2)	49(1)
O(7)	5158(4)	4601(2)	3601(2)	36(1)
C(1)	2553(4)	−373(3)	1109(2)	23(1)
C(2)	2629(4)	−509(3)	2136(2)	24(1)
C(3)	2562(4)	−1671(3)	2390(2)	22(2)
C(4)	2294(5)	−3014(3)	1641(2)	28(1)
C(5)	2793(4)	−1635(3)	3476(2)	23(1)
C(6)	3476(4)	−2648(3)	3825(2)	27(1)
C(7)	3715(4)	−2640(3)	4854(2)	33(1)
C(8)	3232(5)	−1640(4)	5535(2)	37(1)
C(9)	2541(5)	−601(3)	5209(2)	34(1)
C(10)	2304(4)	−620(3)	4188(2)	27(1)
C(11)	2151(4)	901(3)	907(2)	22(1)
C(12)	2681(4)	1213(3)	41(2)	24(1)
C(13)	2490(4)	2427(3)	−144(2)	29(1)
C(14)	1728(4)	3332(3)	495(2)	29(1)
C(15)	1143(4)	3009(3)	1324(2)	28(1)
C(16)	1359(4)	1793(3)	1532(2)	24(1)
C(17)	−869(4)	−2610(3)	5141(2)	28(1)
C(18)	−1403(4)	−2487(3)	3279(2)	29(1)
C(19)	−76(4)	−4419(3)	3751(2)	29(1)
C(20)	6123(4)	2003(3)	1796(2)	23(1)
C(21)	6081(4)	4083(3)	1176(2)	32(1)
C(22)	4803(4)	3931(3)	2775(2)	26(1)

isons of the initial cyclisation diastereoselectivity to be made.

In summary, aryltetracarbonylmanganese complexes afford better chemical yields when coupled with alkynes under thermal activation. However, the heterobimetallic complexes couple with alkenes to give a slightly higher yield of insertion products, and, by minimising the subsequent reaction to form indenes, a significantly higher yield of 1-indanols.

Activation of **24** by oxidative decarbonylation with Me_3NO-MeCN afforded the stereoisomeric 1-indanols **42** (45%) and **43** (23%), and the saturated adduct **34** (15%). This product distribution is consistent with that observed from related systems [18]. Treatment of the bimetallic complexes **26** and **27** under similar conditions afforded (after decomplexation) only the starting ligands **2** (74%) and **3** (73%) respectively.

In an attempt to determine if the diastereoselectivity of formation of the 1-indanols could be improved by increasing the ligand size around the active metal centre tricarbonyl[(((1,2,3,4,5,6-η)-2-(1-oxopropyl)phenyl)-C,O)tricarbonylmanganese(triphenylphosphine)]chromium (**29**) was synthesised (99%) from **27** and PPh_3 via thermally-promoted displacement of CO. The deep red solid analysed correctly for $C_{33}H_{24}CrMnO_7P$ and showed the molecular ion at m/z 670 in the mass spectrum. The infrared spectrum showed three metal–C≡O absorption bands, at 2014, 1957 and 1892 cm^{-1}, and the ^{1}H and ^{13}C NMR data were in agreement with the structure. The position of the PPh_3 ligand was established by single crystal X-ray analysis, which showed it to be axial and anti to the $Cr(CO)_3$ unit (Fig. 5, Tables 5, 11 and 12).

Treatment of **29** with methyl propenoate in refluxing benzene for 23 h afforded only recovered starting material. Treatment of **29** with *tert*-butyl propenoate in refluxing toluene afforded only a small amount of the indene **58** (8%), the decomplexed starting material **3** (41%) and the conjugated addition product **33** (37%) comprising most of the product mixture. Similarly, activation with Me_3NO in MeCN followed by treatment with methyl propenoate afforded only **3** (80%) and **33** (10%).

In summary, a number of heterobimetallic complexes have been synthesised and coupled with several substituted alkynes and alkenes. Optimum conversions were observed when substituted alkenes were coupled under thermal conditions, giving better chemical yields and diastereoselectivity of cyclopentaannulation than their tetracarbonylmanganese analogues.

2.1. X-ray crystal structures for 26, 29, 30 and 36

Crystals suitable for data collection were mounted on glass fibres and positioned on a Nonius CAD-4 diffractometer. Unit cell dimensions were derived from least

Table 7
Bond lengths (Å) and angles (deg) for **30**

|			
Cr(2)–C(22)	1.845(3)	C(21)–Cr(2)–C(13)	88.52(13)
Cr(2)–C(20)	1.845(3)	C(11)–Cr(2)–C(13)	67.32(11)
Cr(2)–C(21)	1.856(3)	C(16)–Cr(2)–C(13)	78.96(12)
Cr(2)–C(11)	2.186(3)	C(14)–Cr(2)–C(13)	36.80(12)
Cr(2)–C(16)	2.198(3)	C(12)–Cr(2)–C(13)	36.55(11)
Cr(2)–C(14)	2.223(3)	C(15)–Cr(2)–C(13)	66.25(12)
Cr(2)–C(12)	2.221(3)	C(18)–Cr(1)–C(19)	88.61(14)
Cr(2)–C(15)	2.217(3)	C(18)–Cr(1)–C(17)	89.42(14)
Cr(2)–C(13)	2.223(3)	C(19)–Cr(1)–C(17)	89.29(14)
Cr(1)–C(18)	1.842(3)	C(18)–Cr(1)–C(10)	90.27(14)
Cr(1)–C(19)	1.846(3)	C(19)–Cr(1)–C(10)	151.47(12)
Cr(1)–C(17)	1.852(3)	C(17)–Cr(1)–C(10)	119.22(13)
Cr(1)–C(10)	2.198(3)	C(18)–Cr(1)–C(6)	119.72(13)
Cr(1)–C(6)	2.202(3)	C(19)–Cr(1)–C(6)	89.38(13)
Cr(1)–C(8)	2.210(3)	C(17)–Cr(1)–C(6)	150.79(12)
Cr(1)–C(9)	2.215(4)	C(10)–Cr(1)–C(6)	66.62(12)
Cr(1)–C(7)	2.218(3)	C(18)–Cr(1)–C(8)	152.63(12)
Cr(1)–C(5)	2.231(3)	C(19)–Cr(1)–C(8)	118.66(14)
O(1)–C(1)	1.225(3)	C(17)–Cr(1)–C(8)	88.73(14)
O(2)–C(17)	1.151(4)	C(10)–Cr(1)–C(8)	67.09(13)
O(3)–C(18)	1.152(4)	C(6)–Cr(1)–C(8)	66.56(13)
O(4)–C(19)	1.155(4)	C(18)–Cr(1)–C(9)	115.37(14)
O(5)–C(20)	1.154(4)	C(19)–Cr(1)–C(9)	156.02(13)
O(6)–C(21)	1.146(4)	C(17)–Cr(1)–C(9)	91.21(13)
O(7)–C(22)	1.150(4)	C(10)–Cr(1)–C(9)	36.99(11)
C(1)–C(2)	1.469(4)	C(6)–Cr(1)–C(9)	78.66(13)
C(1)–C(11)	1.507(4)	C(8)–Cr(1)–C(9)	37.41(11)
C(2)–C(3)	1.354(4)	C(18)–Cr(1)–C(7)	157.00(12)
C(3)–C(5)	1.486(4)	C(19)–Cr(1)–C(7)	91.53(14)
C(3)–C(4)	1.499(4)	C(17)–Cr(1)–C(7)	113.58(13)
C(5)–C(6)	1.407(4)	C(10)–Cr(1)–C(7)	78.77(13)
C(5)–C(10)	1.418(4)	C(6)–Cr(1)–C(7)	37.31(11)
C(6)–C(7)	1.414(4)	C(8)–Cr(1)–C(7)	36.38(14)
C(7)–C(8)	1.382(5)	C(9)–Cr(1)–C(7)	66.39(14)
C(8)–C(9)	1.419(5)	C(18)–Cr(1)–C(5)	91.88(13)
C(9)–C(10)	1.400(4)	C(19)–Cr(1)–C(5)	114.19(12)
C(11)–C(16)	1.399(4)	C(17)–Cr(1)–C(5)	156.50(12)
C(11)–C(12)	1.430(4)	C(10)–Cr(1)–C(5)	37.35(11)
C(12)–C(13)	1.394(4)	C(6)–Cr(1)–C(5)	37.01(10)
C(13)–C(14)	1.403(5)	C(8)–Cr(1)–C(5)	79.46(12)
C(14)–C(15)	1.402(4)	C(9)–Cr(1)–C(5)	67.11(12)
C(15)–C(16)	1.413(4)	C(7)–Cr(1)–C(5)	67.16(11)
C(22)–Cr(2)–C(20)	89.49(13)	O(1)–C(1)–C(2)	123.7(3)
C(22)–Cr(2)–C(21)	89.40(14)	O(1)–C(1)–C(11)	118.3(2)
C(20)–Cr(2)–C(21)	87.33(14)	C(2)–C(1)–C(11)	117.9(2)
C(22)–Cr(2)–C(11)	122.86(12)	C(3)–C(2)–C(1)	125.3(3)
C(20)–Cr(2)–C(11)	87.78(12)	C(2)–C(3)–C(5)	119.1(2)
C(21)–Cr(2)–C(11)	147.31(12)	C(2)–C(3)–C(4)	124.0(3)
C(22)–Cr(2)–C(16)	93.54(13)	C(5)–C(3)–C(4)	116.9(2)
C(20)–Cr(2)–C(16)	111.52(12)	C(6)–C(5)–C(10)	117.6(3)
C(21)–Cr(2)–C(16)	160.92(12)	C(6)–C(5)–C(3)	120.1(3)
C(11)–Cr(2)–C(16)	37.21(11)	C(10)–C(5)–C(3)	122.32(2)
C(22)–Cr(2)–C(14)	111.37(13)	C(6)–C(5)–Cr(1)	70.4(2)
C(20)–Cr(2)–C(14)	159.07(12)	C(10)–C(5)–Cr(1)	70.1(2)
C(21)–Cr(2)–C(14)	94.33(14)	C(3)–C(5)–Cr(1)	129.5(2)
C(11)–Cr(2)–C(14)	79.57(12)	C(5)–C(6)–C(7)	121.4(3)
C(16)–Cr(2)–C(14)	67.05(12)	C(5)–C(6)–Cr(1)	72.6(2)
C(22)–Cr(2)–C(12)	160.14(12)	C(7)–C(6)–Cr(1)	71.9(2)
C(20)–Cr(2)–C(12)	93.55(12)	C(8)–C(7)–C(6)	120.0(3)
C(21)–Cr(2)–C(12)	110.33(13)	C(8)–C(7)–Cr(1)	71.5(2)
C(11)–Cr(2)–C(12)	37.87(10)	C(6)–C(7)–Cr(1)	70.7(2)
C(16)–Cr(2)–C(12)	67.09(12)	C(7)–C(8)–C(9)	120.0(3)
C(14)–Cr(2)–C(12)	66.29(12)	C(7)–C(8)–Cr(1)	72.1(2)
C(22)–Cr(2)–C(15)	88.69(13)	C(9)–C(8)–Cr(1)	71.5(2)

Table 7 (continued)

C(20)–Cr(2)–C(15)	148.51(11)	C(10)–C(9)–C(8)	119.5(3)
C(21)–Cr(2)–C(15)	124.08(13)	C(10)–C(9)–Cr(1)	70.8(2)
C(11)–Cr(2)–C(15)	67.17(12)	C(8)–C(9)–Cr(1)	71.1(2)
C(16)–Cr(2)–C(15)	37.33(11)	C(9)–C(10)–Cr(1)	121.4(3)
C(14)–Cr(2)–C(15)	36.82(11)	C(9)–C(10)–Cr(1)	72.2(2)
C(12)–Cr(2)–C(15)	78.51(12)	C(5)–C(10)–Cr(1)	72.6(2)
C(22)–Cr(2)–C(13)	147.69(12)	C(16)–C(11)–C(12)	119.4(2)
C(21)–Cr(2)–C(13)	122.59(12)		

squares fits to the observed setting angles of 25 reflections, using monochromated Mo K α radiation. Intensity data collection employed the $2\theta/\omega$ technique with a total peak/background count time of 2:1. Reflections were counted for 60 s or until $(\sigma I)/I$ was 0.02. Crystal alignment and decomposition were monitored throughout data collection by measuring three standard reflections every 100 measurements; no statistical variation was observed. The data were corrected for Lorentz and polarisation effects and equivalent reflections averaged. Computing was carried out using the SDP suite of programs on a PDP-11 for initial data processing, SHELXS-86 [28] and SHELXL-93 [29] on an IBM 4341 or Microvax computer for structure solution and refinement. Details of crystal data and intensity data collection parameters are summarised in Tables 2 and 5.

2.2. Structure solution and refinement

The structures were solved by direct methods using SHELXS-86 [28]. Refinement was by full-matrix least squares [29], minimising the function $\Sigma \omega(\| F_o \|^2 -$
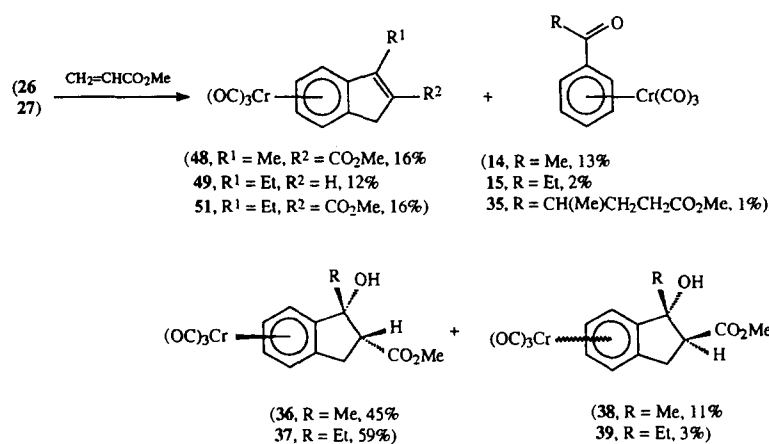
Scheme 3.
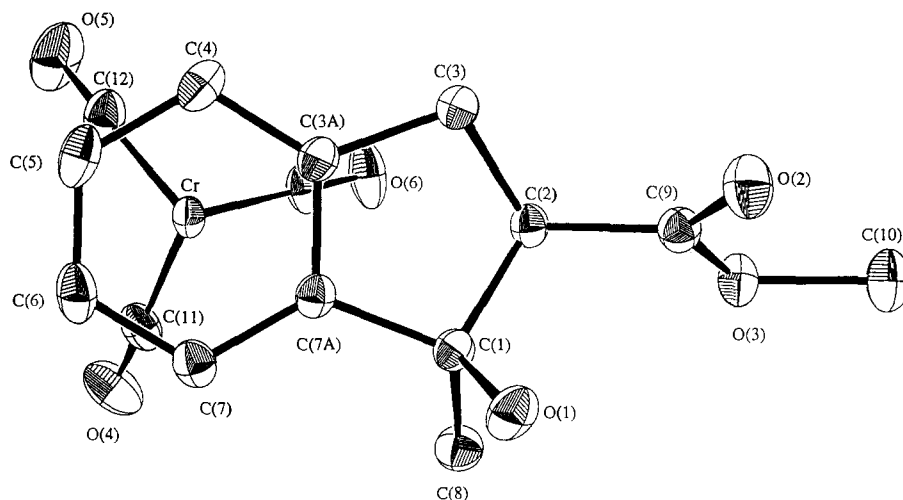
Fig. 4. The atomic arrangement in 36.

Table 8

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for **36**; U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	x	y	z	U_{eq}
Cr(1)	2710(1)	3049(1)	1817(1)	19(1)
O(1)	249(1)	3225(2)	23(1)	25(1)
O(2)	−1424(1)	4880(1)	467(1)	28(1)
O(3)	−1799(1)	2958(1)	884(1)	25(1)
O(4)	3496(2)	275(2)	1969(1)	45(1)
O(5)	4050(1)	3707(2)	3050(1)	55(1)
O(6)	1087(1)	2263(2)	2548(1)	42(1)
C(1)	558(1)	2843(2)	666(1)	19(1)
C(2)	−68(1)	3614(2)	1105(1)	19(1)
C(3)	556(1)	4867(2)	1322(1)	23(1)
C(3a)	1637(1)	4494(2)	1264(1)	19(1)
C(4)	2550(1)	5153(2)	1511(1)	25(1)
C(5)	3492(1)	4630(2)	1388(1)	29(1)
C(6)	3510(1)	3488(2)	1026(1)	29(1)
C(7)	2582(1)	2807(2)	790(1)	23(1)
C(7a)	1646(1)	3329(2)	907(1)	19(1)
C(8)	422(2)	1359(2)	687(1)	26(1)
C(9)	−1153(1)	3909(2)	780(1)	21(1)
C(10)	3191(2)	1335(2)	1909(1)	29(1)
C(11)	−2879(1)	3192(2)	636(1)	33(1)
C(12)	3540(2)	3455(2)	2575(1)	33(1)
C(13)	1703(1)	2583(2)	2264(1)	26(1)

$\| F_c \|^2)^2$. Atomic scattering factors were for neutral atoms. After initial isotropic refinement, anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were located from difference maps and refined with a common thermal parameter. A final electron density map showed no feature greater than 0.5 e $\mathring{A}^{-3}$. Weights used were $\omega = 1/[(\sigma^2(F_o)^2 + (aP)^2 + bP)]$ where $P = [(F_o)^2 + 2(F_c)^2]/3$, and the final values of a and b are given in Tables 2 and 5. Final atomic coordinates and bond distances and bond angles are given in Tables 3, 4, 6–9, 11, 12. Lists of hydrogen coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. The crystal structure determinations established the stereochemistries of the four compounds as described earlier in the text. The figures show the observed geometries, and outline the atomic numbering schemes. Each compound contains the arene–Cr(CO)$_3$ tripodal piano-stool arrangement, and each tripod is in the staggered configuration with respect to its arene ring. The average Cr–CO and Cr–C(arene) distances are consistent at 1.841, 2.227 Å for **26**, 1.848, 2.212 Å for **30**, 1.840, 2.212 Å for **36**, and 1.811, 2.227 Å for **29**. The significantly shorter average Cr–CO value in **29** compared with **26** is presumably a long range consequence of replacing one of the π-acceptor CO groups on the Mn atom with the triphenylphosphine. The geometries at the Mn atoms in **26** and **29** are also of interest. In both complexes the Mn–C(1) and Mn–O(1) bonds are equivalent, but the Mn–CO bonds show distinct differences which reflect the different Mn donor sets. In **26**,

the Mn–C(12) (1.856 Å), Mn–C(13) (1.853 Å) and Mn–C(14) (1.878 Å) distances are all quite long (these carbonyl groups lie trans to carbonyl and arene carbon donors which exhibit strong structural trans influences) whereas Mn–C(15) (1.781 Å) is much shorter, indicating a weaker trans influence of the ketonic oxygen. On substituting an axial carbonyl in **26** for a triphenylphosphine in **29**, the Mn–C(13) bond (1.812 Å, trans to

Table 9

Bond lengths (Å) and angles (deg) for **36**

Cr–C(13)	1.837(2)	C(7)–Cr–C(4)	79.71(7)
Cr–C(11)	1.842(2)	C(6)–Cr–C(4)	67.14(8)
Cr–C(12)	1.842(2)	C(7a)–Cr–C(4)	66.67(7)
Cr–C(5)	2.195(2)	C(13)–Cr–C(3a)	89.85(8)
Cr–C(7)	2.204(2)	C(11)–Cr–C(3a)	147.92(8)
Cr–C(6)	2.207(2)	C(12)–Cr–C(3a)	123.34(9)
Cr–C(7a)	2.218(2)	C(5)–Cr–C(3a)	66.39(8)
Cr–C(4)	2.224(2)	C(7)–Cr–C(3a)	66.87(7)
Cr–C(3a)	2.226(2)	C(6)–Cr–C(3a)	78.51(7)
O(1)–C(1)	1.425(2)	C(7a)–Cr–C(3a)	36.92(6)
O(2)–C(9)	1.206(2)	C(4)–Cr–C(3a)	36.59(6)
O(3)–C(9)	1.330(2)	C(9)–O(3)–C(10)	116.0(2)
O(3)–C(10)	1.449(2)	O(1)–C(1)–C(8)	106.47(14)
O(4)–C(11)	1.143(3)	O(1)–C(1)–C(7a)	109.45(14)
O(5)–C(12)	1.150(3)	C(8)–C(1)–C(7a)	114.9(2)
O(6)–C(13)	1.149(2)	O(1)–C(1)–C(2)	111.17(14)
C(1)–C(8)	1.511(3)	C(8)–C(1)–C(2)	113.27(14)
C(1)–C(7a)	1.519(2)	C(7a)–C(1)–C(2)	101.65(13)
C(1)–C(2)	1.571(2)	C(9)–C(2)–C(3)	113.1(2)
C(2)–C(9)	1.508(2)	C(9)–C(2)–C(1)	112.12(14)
C(2)–C(3)	1.563(3)	C(3)–C(2)–C(1)	106.26(14)
C(3)–C(3a)	1.503(2)	C(3a)–C(3)–C(2)	103.52(14)
C(3a)–C(4)	1.397(2)	C(4)–C(3a)–C(7a)	121.0(2)
C(3a)–C(7a)	1.407(3)	C(4)–C(3a)–C(3)	128.1(2)
C(4)–C(5)	1.420(3)	C(7a)–C(3a)–C(3)	110.9(2)
C(5)–C(6)	1.395(3)	C(4)–C(3a)–Cr	71.62(11)
C(6)–C(7)	1.418(3)	C(7a)–C(3a)–Cr	71.20(10)
C(7)–C(7a)	1.406(2)	C(3)–C(3a)–Cr	129.99(12)
C(13)–Cr–C(11)	88.37(9)	C(3a)–C(4)–C(5)	118.5(2)
C(13)–Cr–C(12)	87.98(9)	C(3a)–C(4)–Cr	71.78(11)
C(11)–Cr–C(12)	88.61(10)	C(5)–C(4)–Cr	70.13(11)
C(13)–Cr–C(5)	147.86(9)	C(6)–C(5)–C(4)	121.0(2)
C(11)–Cr–C(5)	123.34(9)	C(6)–C(5)–Cr	72.00(12)
C(12)–Cr–C(5)	87.78(9)	C(4)–C(5)–Cr	72.40(11)
C(13)–Cr–C(7)	124.44(8)	C(5)–C(6)–C(7)	120.1(2)
C(11)–Cr–C(7)	88.06(8)	C(5)–C(6)–Cr	71.04(11)
C(12)–Cr–C(7)	147.27(8)	C(7)–C(6)–Cr	71.12(10)
C(5)–Cr–C(7)	67.29(8)	C(7a)–C(7)–C(6)	119.0(2)
C(13)–Cr–C(6)	161.49(8)	C(7a)–C(7)–Cr	72.01(10)
C(11)–Cr–C(6)	93.90(8)	C(6)–C(7)–Cr	71.39(10)
C(12)–Cr–C(6)	110.42(9)	C(7)–C(7a)–C(3a)	120.3(2)
C(5)–Cr–C(6)	36.96(8)	C(7)–C(7a)–C(1)	128.7(2)
C(7)–Cr–C(6)	37.50(7)	C(3a)–C(7a)–C(1)	110.86(14)
C(13)–Cr–C(7a)	95.35(8)	C(7)–C(7a)–Cr	70.91(10)
C(11)–Cr–C(7a)	111.45(8)	C(3a)–C(7a)–Cr	71.87(10)
C(12)–Cr–C(7a)	159.71(9)	C(1)–C(7a)–Cr	132.16(11)
C(5)–Cr–C(7a)	78.76(7)	O(2)–C(9)–O(3)	123.1(2)
C(7)–Cr–C(7a)	37.09(6)	O(2)–C(9)–C(2)	125.6(2)
C(6)–Cr–C(7a)	66.72(7)	O(3)–C(9)–C(2)	111.3(2)
C(13)–Cr–C(4)	111.16(8)	O(4)–C(11)–C	179.4(2)
C(11)–Cr–C(4)	160.41(8)	O(5)–C(12)–Cr	179.3(2)
C(12)–Cr–C(4)	93.44(9)	O(6)–C(13)–Cr	178.3(2)
C(5)–Cr–C(4)	37.47(8)		
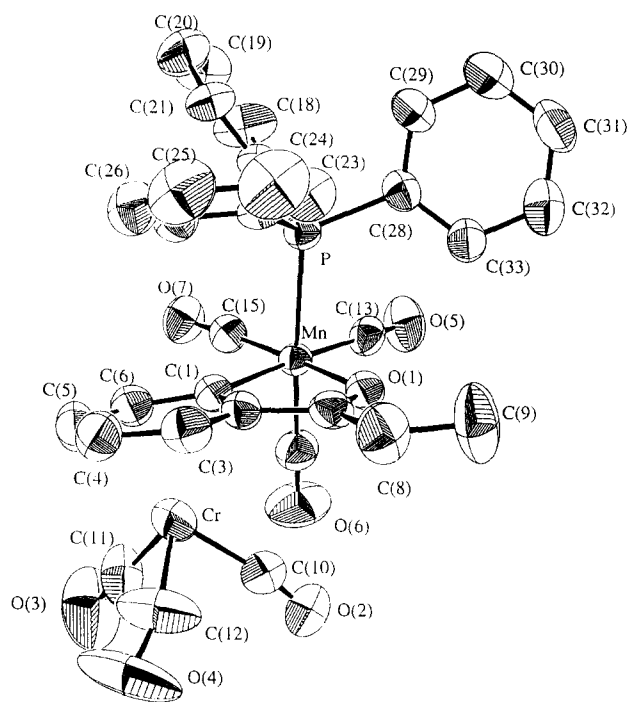
Fig. 5. The atomic arrangement in **29**.

arene carbon) shortens considerably, the Mn–C(14) bond is 1.795 Å (phosphines exhibit weak structural trans influences), and the Mn–C(15) bond is unchanged.

3. Experimental

For general experimental details, see Refs. [30,31]. High field ^{1}H NMR spectra were recorded at 400.13 MHz and ^{13}C NMR spectra at 100.62 MHz on a Bruker AM400 instrument operating at 9.2 T. Multiplicities were determined from DEPT spectra.

3.1. 2-Phenyl-1,3-dioxolane (5) (97%), 2-methyl-2-phenyl-1,3-dioxolane (6) (89%), 2-ethyl-2-phenyl-1,3-dioxolane (7) (98%), 2-methyl-2-(4-methoxyphenyl)-1,3-dioxolane (8) (78%)

These were synthesised from their parent aryl ketones/aldehydes by treatment with ethane-1,2-diol/p-toluenesulfonic acid/benzene [32].

3.2. Tricarbonyl[2-(η^6-phenyl)-1,3-dioxolane]chromium (9)

A nitrogen-degassed mixture of hexacarbonylchromium (4.40 g, 0.020 mol) and **5** (3.50 g, 0.023 mol), in dibutyl ether (130 ml) and THF (15 ml) was heated to reflux for 48 h under positive nitrogen pressure. The cooled reaction mixture was filtered, concentrated and purified by flash chromatography (silica gel, hexanes–diethyl ether, 3:1) to give **9** (3.83 g, 67%) as yellow rods, m.p. 70–72°C (Ref. [24] 70–73 °C). ν_{max} (KBr) 1891 and 1968 cm^{-1} (Cr–C≡O). δ_H 4.02–4.11, m,

Table 10
Product distribution from coupling reactions of complexes **24**, **26** and **27**. Reactions of complex **26** and **27** involved a subsequent photolytic decomplexation step in diethyl ether

Alkene/Alkyne	Conditions	Products (%)			
Complex 24					
PhC≡CPh	benzene, Δ 11.0 h	**55** (92)			
PhC≡CH	benzene, Δ 12.5 h	mixture			
EtC≡CEt	benzene, Δ 12.5 h	**61** (92)			
CH$_2$=CHCO$_2$Me	benzene, Δ 11.5 h	**57** (30)	**42** (2)	**43** (33)	
CH$_2$=CHCO$_2$CMe$_3$	benzene, Δ 11.0 h	**58** (37)	**46** (33)	**47** (12)	
CH$_2$=CHCO$_2$Me	Me$_3$NO–MeCN	**34** (15)	**42** (45)	**43** (23)	
Complex 26					
PhC≡CPh	benzene, Δ 24.0 h	**31** (5)	**52** (24)		
CH$_2$=CHCO$_2$Me	benzene, Δ 11.5 h	**53** (6)	**40** (68)	**41** (21)	
CH$_2$=CHCO$_2$CMe$_3$	benzene, Δ 22.5 h	**54** (14)	**44** (47)	**45** (21)	
CH$_2$=CHSi(OEt)$_3$	benzene, Δ 24.0 h	mixture			
CH$_2$=CHCO$_2$Me	Me$_3$NO–MeCN	**2** (74)			
Complex 27					
PhC≡CPh	benzene, Δ 11.0 h	**55** (25)	**3** (48)		
PhC≡CH	benzene, Δ 10.5 h	mixture			
EtC≡CEt	benzene, Δ 24.0 h	**61** (25)	**3** (70)		
MeO$_2$CC≡CCO$_2$Me	benzene, Δ 12.0 h	**59** (21)	**60** (17)		
CH$_2$=CHCO$_2$Me	benzene, Δ 10.5 h	**57** (3)	**42** (71)	**43** (25)	
CH$_2$=CHCO$_2$CMe$_3$	benzene, Δ 11.5 h	**58** (11)	**33** (15)	**46** (40)	**47** (14)
CH$_2$=CHSi(OEt)$_3$	benzene, Δ 11.0 h	**3** (70)			
CH$_2$=CHOCOMe	benzene, Δ 11.0 h	**3** (65)			
CH$_2$=CHCO$_2$Me	Me$_3$NO–MeCN	**3** (43)			

Table 11

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **29**; U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	x	y	z	U_{eq}
Mn	67(1)	660(1)	7446(1)	38(1)
Cr	−2317(1)	−504(1)	7634(1)	64(1)
P	1560(1)	−250(1)	8075(1)	41(1)
O(1)	−473(3)	−425(3)	6515(3)	48(1)
O(2)	−3203(38)	378(38)	5860(26)	159(18)
O(2')	−3196(38)	81(27)	5647(23)	99(8)
O(3)	−3433(7)	1007(5)	8064(6)	152(4)
O(4)	−4230(24)	−1575(25)	7136(25)	144(15)
O(4')	−4138(27)	−1654(30)	6722(24)	142(12)
O(5)	967(4)	1912(4)	6546(4)	83(2)
O(6)	−1722(5)	1855(5)	6570(4)	115(2)
O(7)	750(4)	1921(4)	9030(3)	71(2)
C(1)	−634(4)	−159(5)	8015(4)	45(2)
C(2)	−977(5)	−1046(5)	7565(4)	47(2)
C(3)	−1380(5)	−1759(5)	7904(5)	58(2)
C(4)	−1525(5)	−1589(6)	8687(5)	62(2)
C(5)	−1308(5)	−711(6)	9083(5)	68(2)
C(6)	−866(5)	−3(5)	8763(4)	58(2)
C(7)	−883(5)	−1101(5)	6706(5)	51(2)
C(8)	−1242(6)	−1930(6)	6090(5)	82(3)
C(9)	−1030(8)	−1954(7)	5313(6)	112(4)
C(10)	−2832(6)	−60(8)	6483(6)	94(3)
C(11)	−3003(7)	423(6)	7896(6)	86(3)
C(12)	−3461(7)	−1187(7)	7226(8)	107(4)
C(13)	633(5)	1375(5)	6871(4)	51(2)
C(14)	−1044(6)	1367(6)	6907(5)	66(2)
C(15)	501(5)	1435(5)	8398(5)	51(2)
C(16)	2620(5)	300(5)	9030(4)	47(2)
C(17)	2820(5)	1228(5)	8930(5)	69(2)
C(18)	3613(6)	1695(6)	9613(7)	92(3)
C(19)	4207(6)	1221(6)	10377(6)	84(3)
C(20)	4027(6)	297(7)	10490(5)	85(3)
C(21)	3227(5)	−160(5)	9814(4)	58(2)
C(22)	1425(4)	−1418(5)	8475(4)	48(2)
C(23)	1427(6)	−2226(5)	8011(5)	67(2)
C(24)	1234(7)	−3109(6)	8276(6)	89(3)
C(25)	1034(6)	−3176(7)	9020(6)	87(3)
C(26)	1037(6)	−2383(6)	9501(5)	72(2)
C(27)	1224(5)	−1513(5)	9223(5)	58(2)
C(28)	2132(5)	−511(4)	7294(4)	47(2)
C(29)	3116(6)	−789(6)	7632(5)	73(2)
C(30)	3561(6)	−1008(6)	7066(6)	84(3)
C(31)	3005(7)	−946(5)	6143(6)	75(2)
C(32)	2036(6)	−643(5)	5787(5)	70(2)
C(33)	1584(5)	−421(5)	6364(4)	52(2)

4H, $-OCH_2CH_2O-$; 5.28–5.37, m, 3H, PhCH(OCH$_2$CH$_2$O) and (H$_{meta}$)$_2$; 5.52–5.55, m, 3H, (H$_{ortho}$)$_2$ and H$_{para}$. δ_c 65.73 (2C), $-OCH_2CH_2O-$; 91.02 (2C), C$_{ortho}$; 91.22 (2C), C$_{meta}$; 92.91, C$_{para}$; 101.37, HC(OR)$_2$; 113.07, C$_{ipso}$; 232.28 (3C), Cr(CO)$_3$.

3.3. Tricarbonyl[2-methyl-2-(η^6-phenyl)-1,3-dioxolane]chromium (10)

A nitrogen-degassed mixture of hexacarbonylchromium (4.40 g, 0.020 mol) and **6** (4.00 g, 0.024 mol), in

dibutyl ether (130 ml) and THF (15 ml) was heated to reflux for 48 h under positive nitrogen pressure. The reaction mixture was filtered, concentrated and purified by flash chromatography (silica gel, hexanes–diethyl ether, 12:1 then 10:1) to give **10** (2.91 g, 49%) as yellow rods, m.p. 85–89°C (Ref. [24] 87–89 °C). ν_{max} (Nujol mull) 1866 and 1965 cm^{-1} (Cr–C≡O stretch). δ_H 1.59, s, 3H, 2-CH$_3$; 3.98–4.20, m, 4H, $-OCH_2CH_2O-$; 5.14, t, J 6.4 Hz, 2H, (H$_{meta}$)$_2$; 5.42, bt, J 6.4 Hz, 1H, H$_{para}$; 5.67, d, J 6.4 Hz, 2H, (H$_{ortho}$)$_2$.

3.4. Tricarbonyl[2-ethyl-2-(η^6-phenyl)-1,3-dioxolane]chromium (11)

A nitrogen-degassed mixture of hexacarbonylchromium (13.75 g, 0.063 mol) and **7** (10.00 g, 0.057 mol) in dibutyl ether (250 ml) and THF (30 ml) was heated to reflux for 45 h under positive nitrogen pressure. The reaction mixture was filtered, concentrated and purified by flash chromatography (silica gel, hexanes–diethyl ether; 10:0, 9:1, then 0:10) to give **11** (11.97 g, 68%) as yellow crystals. An analytical sample was recrystallised from diethyl ether to give **11** as large yellow globular crystals. m.p. 116–119°C. (Found: C, 53.5; H, 4.3. C$_{14}$H$_{14}$CrO$_5$. Calc.: C, 53.5; H, 4.5%). (Found: M^+, 314.0244. C$_{14}$H$_{14}$CrO$_5$. Calc.: M, 314.0246). ν_{max} (KBr) 1966 and 1885 cm^{-1} (Cr–C≡O). δ_H 0.86, t, J 7.3 Hz, 3H, 2-CH$_2$CH_3; 1.82, q, J 7.4 Hz, 2H, 2-CH_2CH$_3$; 4.00–4.24, m, 4H, $-OCH_2CH_2O-$; 5.14, bt, J 6.4 Hz, 2H, (H$_{meta}$)$_2$; 5.47, bt, J 6.2 Hz, 1H, H$_{para}$; 5.68, d, J 6.6 Hz, 2H, (H$_{ortho}$)$_2$. δ_c 7.88, 2-CH$_2$CH_3; 35.38, 2-CH_2CH$_3$; 66.07 (2C), $-OCH_2CH_2O-$; 88.49 (2C), C$_{ortho}$; 93.38 (2C), C$_{meta}$; 95.32, C$_{para}$; 108.45, EtC(OR)$_2$; 113.07, C$_{ipso}$; 232.77 (3C), Cr(CO)$_3$. m/z 314(M^+, 28), 285(M–CH$_2$CH$_3$, 5), 258(M–2CO, 10), 230 (258–CO, 45), 200(20), 186(18), 170(60), 52(Cr$^+$, 100).

3.5. Tricarbonyl[2-methyl-2-((1,2,3,4,5,6-η)-4-methoxyphenyl)-1,3-dioxolane]chromium (12)

A nitrogen-degassed mixture of hexacarbonylchromium (6.23 g, 0.028 mol) and **8** (5.00 g, 0.026 mol) in dibutyl ether (130 ml) and THF (15 ml) was heated to reflux for 32 h under positive nitrogen pressure. The reaction mixture was filtered, concentrated and purified by flash chromatography (silica gel, hexanes–diethyl ether; 10:0, 9:1, then 0:10) to give **12** (6.52 g, 77%) as yellow crystals. An analytical sample was recrystallised from diethyl ether to give **11** as yellow microcrystals, m.p. 114–116°C. (Found: C, 51.9; H, 4.6. C$_{14}$H$_{14}$CrO$_6$ · 1/4C$_4$H$_{10}$O. Calc.: C, 51.7; H, 4.8%). (Found: M^+, 330.0198. C$_{14}$H$_{14}$CrO$_6$. Calc.: M, 330.0196). ν_{max} (CH$_2$Cl$_2$) 1965 and 1883 cm^{-1} (Cr–C≡O). δ_H 1.58, s,

Table 12
Bond lengths (Å) and angles (deg) for **29**

Mn–C(15)	1.781(8)	C(3)–Cr–C(4)	37.2(2)
Mn–C(14)	1.795(8)	C(5)–Cr–C(4)	36.2(2)
Mn–C(13)	1.812(8)	C(12)–Cr–C(6)	151.4(4)
Mn–C(1)	2.026(6)	C(10)–Cr–C(6)	124.4(4)
Mn–O(1)	2.064(4)	C(11)–Cr–C(6)	90.5(4)
Mn–P	2.370(2)	C(2)–Cr–C(6)	65.7(2)
Cr–C(12)	1.805(10)	C(3)–Cr–C(6)	78.2(3)
Cr–C(10)	1.809(10)	C(5)–Cr–C(6)	37.0(2)
Cr–C(11)	1.818(9)	C(4)–Cr–C(6)	65.8(3)
Cr–C(1)	2.335(6)	C(12)–Cr–C(1)	158.1(4)
Cr–C(2)	2.168(6)	C(10)–Cr–C(1)	97.3(3)
Cr–C(3)	2.177(7)	C(11)–Cr–C(1)	114.9(3)
Cr–C(4)	2.224(7)	C(2)–Cr–C(1)	36.9(2)
Cr–C(5)	2.204(7)	C(3)–Cr–C(1)	66.9(2)
Cr–C(6)	2.254(7)	C(5)–Cr–C(1)	66.0(2)
P–C(22)	1.822(7)	C(4)–Cr–C(1)	78.2(2)
P–C(18)	1.839(6)	C(6)–Cr–C(1)	36.0(2)
P–C(28)	1.843(6)	C(22)–P–C(16)	105.4(3)
O(1)–C(7)	1.242(7)	C(22)–P–C(28)	102.6(3)
O(2)–O(2')	0.55(7)	C(16)–P–C(28)	101.3(3)
O(2)–C(10)	1.11(5)	C(22)–P–Mn	115.1(2)
O(2')–C(10)	1.25(4)	C(16)–P–Mn	115.4(2)
O(3)–C(11)	1.146(9)	C(28)–P–Mn	115.3(2)
O(4)–O(4')	0.75(5)	C(7)–O(1)–Mn	117.7(4)
O(4)–C(12)	1.21(3)	O(2')–O(2)–C(10)	91(10)
O(4')–C(12)	1.19(4)	O(2)–O(2')–C(10)	63(9)
O(5)–C(13)	1.152(7)	O(4')–O(4)–C(12)	70(5)
O(6)–C(14)	1.143(8)	O(4)–O(4')–C(12)	74(5)
O(7)–C(15)	1.160(7)	C(3)–C(2)–C(1)	123.1(6)
C(1)–C(6)	1.419(8)	C(3)–C(2)–C(7)	124.7(7)
C(2)–C(1)	1.433(8)	C(1)–C(2)–C(7)	112.2(6)
C(2)–C(3)	1.401(8)	C(3)–C(2)–Cr	71.5(4)
C(2)–C(7)	1.470(8)	C(1)–C(2)–Cr	77.9(4)
C(4)–C(3)	1.405(9)	C(7)–C(2)–Cr	122.1(4)
C(5)–C(4)	1.375(9)	C(6)–C(1)–C(2)	114.5(6)
C(6)–C(5)	1.414(9)	C(6)–C(1)–Mn	131.6(5)
C(7)–C(8)	1.487(9)	C(2)–C(1)–Mn	113.8(4)
C(8)–C(9)	1.432(9)	C(6)–C(1)–Cr	68.9(4)
C(16)–C(21)	1.370(8)	C(2)–C(1)–Cr	65.2(3)
C(16)–C(17)	1.373(8)	Mn–C(1)–Cr	133.8(3)
C(17)–C(18)	1.388(10)	C(5)–C(6)–C(1)	121.8(6)
C(18)–C(19)	1.354(11)	C(5)–C(6)–Cr	69.6(4)
C(19)–C(20)	1.363(11)	C(1)–C(6)–Cr	75.1(4)
C(20)–C(21)	1.381(9)	C(4)–C(5)–C(6)	121.3(7)
C(22)–C(23)	1.373(9)	C(4)–C(5)–Cr	72.7(4)
C(22)–C(27)	1.382(8)	C(6)–C(5)–Cr	73.4(4)
C(23)–C(24)	1.392(10)	C(5)–C(4)–C(3)	119.1(7)
C(24)–C(25)	1.371(11)	C(5)–C(4)–Cr	71.1(4)
C(25)–C(26)	1.369(11)	C(3)–C(4)–Cr	69.6(4)
C(26)–C(27)	1.382(10)	C(4)–C(3)–C(2)	119.5(7)
C(28)–C(29)	1.370(9)	C(4)–C(3)–Cr	73.2(4)
C(28)–C(33)	1.384(8)	C(2)–C(3)–Cr	70.8(4)
C(29)–C(30)	1.380(10)	O(1)–C(7)–C(2)	117.0(6)
C(30)–C(31)	1.372(10)	O(1)–C(7)–C(8)	120.7(6)
C(31)–C(32)	1.360(10)	C(2)–C(7)–C(8)	122.3(7)
C(32)–C(33)	1.404(9)	C(9)–C(8)–C(7)	117.8(7)
C(15)–Mn–C(14)	89.5(3)	O(2)–C(10)–O(2')	26(4)
C(15)–Mn–C(13)	92.0(3)	O(2)–C(10)–Cr	165(2)
C(14)–Mn–C(13)	87.8(3)	O(2')–C(10)–Cr	169(2)
C(15)–Mn–C(1)	90.9(3)	O(3)–C(11)–Cr	179.7(6)
C(14)–Mn–C(1)	90.3(3)	O(4')–C(12)–O(4)	37(3)
C(13)–Mn–C(1)	176.5(3)	O(4')–C(12)–Cr	158(2)
C(15)–Mn–O(1)	168.7(2)	O(4)–C(12)–Cr	165(2)
C(14)–Mn–O(1)	94.2(3)	O(5)–C(13)–Mn	172.6(6)

Table 12 (continued)

C(13)–Mn–O(1)	98.8(2)	O(6)–C(14)–Mn	176.6(8)
C(1)–Mn–O(1)	78.4(2)	O(7)–C(15)–Mn	176.7(6)
C(15)–Mn–P	92.3(2)	C(21)–C(16)–C(17)	118.7(7)
C(14)–Mn–P	176.1(2)	C(21)–C(16)–P	124.4(5)
C(13)–Mn–P	88.7(2)	C(17)–C(16)–P	116.9(5)
C(1)–Mn–P	93.0(2)	C(16)–C(17)–C(18)	120.7(7)
O(1)–Mn–P	84.56(13)	C(19)–C(18)–C(17)	119.4(8)
C(12)–Cr–C(10)	84.0(5)	C(18)–C(19)–C(20)	120.9(8)
C(12)–Cr–C(11)	87.0(4)	C(19)–C(20)–C(21)	119.4(8)
C(10)–Cr–C(11)	88.0(4)	C(16)–C(21)–C(20)	120.8(7)
C(12)–Cr–C(2)	121.3(4)	C(23)–C(22)–C(27)	117.3(7)
C(10)–Cr–C(2)	93.1(3)	C(23)–C(22)–P	122.2(5)
C(11)–Cr–C(2)	151.7(4)	C(27)–C(22)–P	120.2(5)
C(12)–Cr–C(3)	92.7(3)	C(22)–C(23)–C(24)	121.9(8)
C(10)–Cr–C(3)	116.1(4)	C(25)–C(24)–C(23)	119.2(8)
C(11)–Cr–C(3)	155.7(3)	C(26)–C(25)–C(24)	121.7(7)
C(2)–Cr–C(3)	37.6(2)	C(25)–C(26)–C(27)	118.9(6)
C(12)–Cr–C(5)	114.6(4)	C(26)–C(27)–C(22)	121.7(7)
C(10)–Cr–C(5)	161.4(4)	C(29)–C(28)–C(33)	118.9(6)
C(11)–Cr–C(5)	91.8(4)	C(29)–C(28)–P	120.0(5)
C(2)–Cr–C(5)	78.4(3)	C(33)–C(28)–P	121.0(5)
C(3)–Cr–C(5)	66.3(3)	C(28)–C(29)–C(30)	121.5(7)
C(12)–Cr–C(4)	90.6(4)	C(31)–C(30)–C(29)	119.2(8)
C(10)–Cr–C(4)	152.7(4)	C(32)–C(31)–C(30)	120.7(7)
C(11)–Cr–C(4)	118.5(3)	C(31)–C(32)–C(33)	120.0(7)
C(2)–Cr–C(4)	67.0(3)	C(28)–C(33)–C(32)	119.6(7)

3H, 2-CH$_3$; 3.72, s, 3H, OCH$_3$; 3.97–4.15, m, 4H, –OCH_2CH_2O–; 5.03, bt, J 7.0 Hz, 2H, (H$_{ortho}$)$_2$ to OMe; 5.82, bd, J 7.0 Hz, 2H, (H$_{ortho}$)$_2$ to MeC(OR)$_2$. δ_c 29.17, 2-CH$_3$; 55.58, OCH$_3$; 65.46 (2C), –OCH_2CH_2O–; 75.85 (2C), C$_{ortho}$; 93.34 (2C), C$_{meta}$; 106.66 and 107.52, C$_{ipso}$ to MeC(OR)$_2$ and MeC(OR)$_2$; 143.89, C$_{ipso}$ to OMe; 232.93 (3C), Cr(CO)$_3$. m/z 330(M^+, 40), 315(M–CH$_3$, 3), 298(M–MeOH, 10), 274 (M–2CO, 25), 246(274–CO, 90), 218(93), 202(37), 52(Cr$^+$, 100).

3.6. Tricarbonyl[(1,2,3,4,5,6-η)benzaldehyde]chromium (13)

A nitrogen-degassed solution of **9** (2.84 g, 9.90 mmol), p-toluenesulphonic acid (0.17 g, 0.99 mmol) and water (0.72 g, 0.040 mol) in acetone (50 ml) was heated to reflux for 1.0 h under a nitrogen atmosphere. The solvent was removed in vacuo and the residue partitioned between diethyl ether and water. Flash chromatography (silica gel, hexanes–diethyl ether, 3:1) afforded **13** (1.30 g, 76%) as red rods, m.p. 76–78°C (Ref. [33] 76–78°C). ν_{max} (KBr) 1973 and 1886 (Cr–C≡O stretch), 1689 cm^{-1} (CHO). δ_H 5.32, bt, J 6.4 Hz, 2H, (H$_{meta}$)$_2$; 5.72, bt, J 6.3 Hz, 1H, H$_{para}$; 5.95, bd, J 6.6 Hz, 2H, (H$_{ortho}$)$_2$; 9.46, s, 1H, CHO. δ_c 89.02 (2C), C$_{ortho}$; 94.36, C$_{ipso}$; 94.60 (2C), C$_{meta}$; 95.45, C$_{para}$; 187.66, 1-CHO; 229.87 (3C), Cr(CO)$_3$.

3.7. Tricarbonyl[(η⁶-phenyl)ethanone]chromium (14)

A nitrogen-degassed solution of **10** (2.00 g, 6.70 mmol), p-toluenesulphonic acid (0.12 g, 0.70 mmol)

and water (0.13 g, 7.20 mmol) in acetone (50 ml) was heated to reflux for 1.5 h under a nitrogen atmosphere. The solvent was removed in vacuo and the residue partitioned between diethyl ether and water. Flash chromatography (silica gel, hexanes–diethyl ether, 1:1) afforded **14** (1.30 g, 76%) as orange rods, m.p. 84–85°C (Ref. [34] 83.5–84.5°C). ν_{max} (KBr) 1903 and 1965 (Cr–C≡O), 1686 cm^{-1} (R$_2$CO). δ_H 2.43, s, 3H, 1-COCH$_3$; 5.25, tt, J 6.4, 1.3 Hz, 2H, (H$_{meta}$)$_2$; 5.62, tt, J 6.3, 1.0 Hz, 1H, H$_{para}$; 6.03, dd, J 6.8, 1.0 Hz, 2H, (H$_{ortho}$)$_2$. δ_c 25.16, 1-COCH$_3$; 89.25 (2C), C$_{ortho}$; 94.19 (2C), C$_{meta}$; 95.14, C$_{para}$; 95.56, C$_{ipso}$; 194.92, 1-COCH$_3$; 230.50 (3C), Cr(CO)$_3$.

3.8. Tricarbonyl[1-(η^6-phenyl)-1-propanone]chromium (15)

A nitrogen-degassed solution of **11** (10.02 g, 0.032 mol), p-toluenesulphonic acid (0.60 g, 3.49 mmol) and water (1.00 g, 0.056 mol) in acetone (90 ml) was heated under gentle reflux for 2.25 h under a nitrogen atmosphere. The solvent was removed in vacuo and the residue partitioned between diethyl ether and water. Flash chromatography (silica gel, hexanes–diethyl ether, 1:1) afforded: (i) recovered **11** (0.72 g, 7%); (ii) **15** (8.62 g, 89%) as red rods, m.p. 110–112°C [35]. ν_{max} (KBr) 1972 and 1897 (Cr–C≡O) and 1682 cm^{-1} (R$_2$CO). δ_H 1.19, t, J 7.2 Hz, 3H, 1-COCH$_2$CH$_3$; 2.79, q, J 7.2 Hz, 2H, 1-COCH$_2$CH$_3$; 5.28, bt, J 6.6 Hz, 2H, (H$_{meta}$)$_2$; 5.63, tt, J 6.3, 1.1 Hz, 1H, H$_{para}$; 5.63, bdd, J 6.8, 1.0 Hz, 2H, (H$_{ortho}$)$_2$. δ_c 8.03, 1-COCH$_2$CH$_3$; 30.47, 1-COCH$_2$CH$_3$; 89.46 (2C), C$_{ortho}$; 93.86 (2C), C$_{meta}$; 95.09, C$_{para}$; 95.59, C$_{ipso}$; 197.84, 1-COCH$_2$CH$_3$; 230.68 (3C), Cr(CO)$_3$.

3.9. Tricarbonyl[((1,2,3,4,5,6-η)-4-methoxyphenyl)ethanone]chromium (16)

A nitrogen degassed solution of **12** (5.52 g, 0.017 mol), p-toluenesulphonic acid (0.30 g, 1.74 mmol) and water (1.00 g, 0.056 mol) in acetone (30 ml) was heated under gentle reflux for 1.25 h under a nitrogen atmosphere. The solvent was removed in vacuo and the residue partitioned between diethyl ether and water. Flash chromatography (silica gel, hexanes–diethyl ether, 1:1) afforded **16** (4.54 g, 95%) as orange rods. An analytical sample was recrystallised from diethyl ether–dichloromethane to give **16** as large yellow globular crystals, m.p. 87–88°C. (Found: C, 50.1; H, 3.5. C$_{12}$H$_{10}$CrO$_5$. Calc.: C, 50.3; H, 3.5%). (Found: M^+, 285.9923. C$_{12}$H$_{10}$CrO$_5$. Calc.: M, 285.9933). ν_{max} (KBr) 1965 and 1886 (Cr–C≡O), 1681 cm^{-1} (R$_2$CO). δ_H 2.40, s, 3H, 1-COCH$_3$; 3.77, s, 3H, 4-OCH$_3$; 5.14, bd, J 7.2 Hz, 2H, (H3)$_2$; 6.17, bd, J 7.2 Hz, 2H, (H2)$_2$. δ_c 25.22, 1-COCH$_3$; 55.87, 4-OCH$_3$; 76.38 (2C), C3; 91.25, C1; 94.61 (2C), C2; 144.52, C4;

193.92, 1-COCH3; 230.52 (3C), Cr(CO)$_3$. m/z 286(M^+, 18), 258(M–CO, 8), 230(258–CO, 12), 202(230–CO, 91), 135(10), 52(Cr$^+$, 100).

3.10. Dicarbonyl(triphenylphosphine)[(1,2,3,4,5,6-η)-benzaldehyde]chromium (18)

A solution of **13** (0.20 g, 0.83 mmol) and triphenylphosphine (0.26 g, 0.73 mmol) in benzene (50 ml) (quartz tube, medium Hg pressure lamp) was photolysed for 8 h under positive nitrogen pressure. The dark red solution was filtered and purified by flash chromatography (silica gel, hexanes–dichloromethane, 1:1) to give **18** (0.15 g, 40%) as a dark red solid, m.p. 130–131°C (Ref. [24] 134–137°C). ν_{max} (KBr) 1906 and 1850 (Cr–C≡O), 1684 cm^{-1} (CHO). δ_H 4.63, btd, J 6.2, 1.8 Hz, 2H, (H3)$_2$; 4.78, dt, J 6.4, 1.8 Hz, 1H, H4; 5.44, bd, J 6.4 Hz, 2H, (H2)$_2$; 7.30–7.45, m, 15H, PPh$_3$; 9.20, s, 1H, 1-CHO.

3.11. Dicarbonyl(triphenylphosphine)[((1,2,3,4,5,6-η)-4-methoxyphenyl)ethanone]chromium (19)

A solution of **16** (0.20 g, 0.70 mmol) and triphenylphosphine (0.20 g, 0.77 mmol) in cyclohexane–diethyl ether (4:1, 35 ml) was photolysed for 1.5 h (Rayonet Photochemical Reactor, 3000 Å with ten tubes) under positive nitrogen pressure. The dark red solution was filtered and purified by flash chromatography (silica gel, hexanes–diethyl ether, 4:1) to give **19** (0.25 g, 69%) as a dark red solid which was recrystallised from diethyl ether–dichloromethane–hexanes as orange-red needles, m.p. 136–139°C. (Found: C, 66.8; H, 4.9. C$_{29}$H$_{25}$CrO$_4$P. Calc.: C, 66.9; H, 4.8%). (Found: M^+, 520.0896. C$_{29}$H$_{25}$CrO$_4$P. Calc.: M, 520.0884). ν_{max} (KBr) 1893 and 838 (Cr–C≡O), 1669 (R$_2$CO), 1526 cm^{-1} (C=C). δ_H 2.25, s, 3H, 1-COCH$_3$; 3.50, s, 3H, 4-OCH$_3$; 4.36, dd, J 7.0, 1.7 Hz, 2H, (H3)$_2$; 5.53, dd, J 6.9, 3.1 Hz, 2H, (H2)$_2$; 7.30–7.45, m, 15H, PPh$_3$. δ_c 26.08, 1-COCH$_3$; 55.27, 4-OCH$_3$; 73.75 (2C), C3; 89.76, C1; 91.24 (2C), C2; 127.95, d, J 8.9 Hz, 6C, C$_{meta}$ PPh$_3$; 129.15, 3C, C$_{para}$ PPh$_3$; 132.81, d, J 10.9 Hz, 6C, C$_{ortho}$ PPh$_3$; 138.43, d, J 34.4 Hz, 3C, C$_{ipso}$ PPh$_3$; 142.10, C4; 195.99, 1-COCH$_3$; 239.34, d, J 19.7 Hz, 3C, Cr(CO)$_3$. m/z 520(M^+, 3), 464(M–2CO, 13), 314(18), 277(8), 262(PPh$_3^+$, 100), 183(65), 135(20), 108(30), 91(8), 77(12), 52(Cr$^+$, 22).

3.12. Dicarbonyl(tributylphosphine)[((1,2,3,4,5,6-η)-4-methoxyphenyl)ethanone]chromium (20)

A solution of **16** (0.31 g, 1.08 mmol) and tributylphosphine (0.26 g, 1.30 mmol) in cyclohexane–diethyl ether (4:1, 50 ml) was photolysed for 2.5 h (Rayonet Photochemical Reactor, 3000 Å, ten tubes) under positive nitrogen pressure. The dark red solution

was filtered and purified by flash chromatography (silica gel, hexanes–diethyl ether, 4:1) to give **20** (0.27 g, 55%) as a dark red oil. (Found: M^+, 460.1832. $C_{23}H_{37}CrO_4P$. Calc.: M, 460.1835). ν_{max} (KBr) 1888 and 1836 (Cr–C≡O), 1661 (R_2CO), 1522 cm^{-1} (C=C). δ_H 0.92, t, J 7.1 Hz, 9H, $P(CH_2CH_2CH_2CH_3)_3$; 1.20–1.41, m, 12 H, $P(CH_2CH_2CH_2CH_3)_3$; 1.46–1.62, m, 6H, $P(CH_2CH_2CH_2CH_3)_3$; 2.39, s, 3H, 1-COCH$_3$; 3.75, s, 3H, 4-OCH$_3$; 4.65, bdd, J 6.9, 1.5 Hz, 2H, (H3)$_2$; 5.67, bdd, J 6.9, 3.7 Hz, 2H, (H2)$_2$. δ_c 13.82 (3C), $P(CH_2CH_2CH_2CH_3)_3$; 24.28, d, J 11.9 Hz, 3C, $P(CH_2CH_2CH_2CH_3)_3$; 25.53 (4C), 1-COCH$_3$ and $P(CH_2CH_2CH_2CH_3)_3$; 27.99, d, J 20.3 Hz, 3C, $P(CH_2CH_2CH_2CH_3)_3$; 55.15, 4-OCH$_3$; 71.95 (2C), C3; 87.28, C1; 89.99 (2C), C2; 140.33, C4; 195.42, 1-COCH$_3$; 239.40, d, J 20.2 Hz, 3C, Cr(CO)$_3$. m/z 460(M^+, 8), 404(M–2CO, 22), 347(2), 298(3), 254(39), 198(10), 173(8), 150(40), 135(100), 107(20), 92(13), 77(24), 52(Cr$^+$, 12).

3.13. Dicarbonyl(triisopropylphosphite)[((1,2,3,4,5,6-η)-4-methoxyphenyl)ethanone]chromium (21)

A solution of **16** (0.31 g, 1.08 mmol) and triisopropylphosphite (0.25 g, 1.19 mmol) in cyclohexane–diethyl ether (4:1, 50 ml) was photolysed for 2 h (Rayonet Photochemical Reactor, 3000 Å) under positive nitrogen pressure. The dark red solution was concentrated and purified by flash chromatography (silica gel, hexanes–diethyl ether, 4:1) to give **21** (0.33 g, 62%) as a dark red solid which was recrystallised from diethyl ether–dichloromethane–hexanes as orange-red needles, m.p. 136–139°C. (Found: C, 51.7; H, 6.8. $C_{20}H_{31}CrO_7P$. Calc.: C, 51.5; H, 6.8%). (Found: M^+, 466.1210. $C_{20}H_{31}CrO_7P$. Calc.: M, 466.1213). ν_{max} (KBr) 1903 and 1845 (Cr–C≡O), 1673 (R_2CO), 1529 cm^{-1} (C=C). δ_H 1.24, d, J 6.1 Hz, 18H, P[OCH(CH$_3$)$_2$]$_3$; 2.38, s, 3H, 1-COCH$_3$; 3.75, s, 3H, 4-OCH$_3$; 4.51, septet × d, J 6.1, 3.0 Hz, 3H, P[OCH(CH$_3$)$_2$]$_3$; 4.81, bdd, J 6.9, 2.2 Hz, 2H, (H3)$_2$; 5.81, bdd, J 6.9, 3.5 Hz, 2H, (H2)$_2$. δ_c 24.09, d, J 2.7 Hz, 6C, P[OCH(CH$_3$)$_2$]$_3$; 25.60, 1-COCH$_3$; 55.29, 4-OCH$_3$; 67.99, d, J 5.3 Hz, 3C, P[OCH(CH$_3$)$_2$]$_3$; 73.48 (2C), C3; 89.93, C1; 91.71 (2C), C2; 141.20, C4; 195.63, 1-COCH$_3$; 237.47, d, J 30.6 Hz, 3C, Cr(CO)$_3$. m/z (M^+, 20), 410(M–2CO, 30), 309(22), 260(20), 202(20), 135(100), 115(22), 107(10), 52(Cr$^+$, 25).

3.14. [(((1,2,3,4,5,6-η)-2-Acetylphenyl)-C,O)tetracarbonylmanganese]tricarbonylchromium (26)

A nitrogen-degassed solution of **14** (0.87 g, 3.38 mmol) and pentacarbonyl(phenylmethyl)manganese (1.16 g, 4.05 mmol) in heptane (40 ml) was heated to vigorous reflux for 1.5 h under positive nitrogen pressure. During this time a heavy precipitate formed. The

deep red reaction mixture was concentrated in vacuo and was purified by flash chromatography using hexanes–dichloromethane as eluent to give in order of increasing polarity: (i) pentacarbonyl(phenylmethyl)manganese (0.20 g); (ii) tetracarbonyl(2-acetyl-4-methoxyphenyl)manganese (**22**) (60 mg, 6%) [10]; (iii) **26** (0.54 g, 38%) as a red solid which was recrystallised from diethyl ether as red rods, m.p. 130–150°C (dec.). (Found: C, 42.9; H, 1.4. $C_{15}H_7CrMnO_8$. Calc.: C, 42.7; H, 1.7%). (Found: M^+, 421.8928. $C_{15}H_7CrMnO_8$. Calc.: M, 421.8928). ν_{max} (KBr) 2093 (sharp), 2010 (sharp), 1965 (broad), 1937 (broad), 1894 (broad) and 1866 (broad), (Cr–C≡O and Mn–C≡O), 1598 (C=C), 1511 cm^{-1} ($R_2C=O$). δ_H 2.52, s, 3H, 2-COCH$_3$; 5.39, td, J 6.4, 0.9 Hz, 1H, H4; 5.62, td, J 6.2, 0.9 Hz, 1H, H5; 5.70, bd, J 6.5 Hz, 1H, H3; 6.03, dd, J 6.3, 0.7 Hz, H6. δ_c 23.46, 2-COCH$_3$; 91.10, C4; 93.36, C3; 94.55, C5; 102.80, C6; 104.75, C2; 153.26, C1; 207.77, 208.80, 210.54 and 219.94, Mn(CO)$_4$; 218.75, 2-COCH$_3$; 232.68 (3C), Cr(CO)$_3$. m/z 422(M^+, 3), 366(M–2CO, 2), 338(366–CO, 2), 310(338–CO, 5), 282(310–CO, 3), 256(M–Mn(CO)$_4$ + H, 12), 226(10), 200(10), 172(43), 129(5), 105(20), 92(14), 77(20), 52(Cr$^+$, 100); (iv) an unidentified deep purple solid (69 mg); (v) **14** (0.37 g, 43%); (vi) hexacarbonyl[μ-(η^6:η^6-2,4-diphenylbut-2-en-3-one)]dichromium (**30**) (0.11 g, 13%) as a red solid which was recrystallised from diethyl ether–dichloromethane–hexanes as red rods, m.p. 150–153 °C. (Found: C, 53.1; H, 2.5. $C_{22}H_{14}Cr_2O_7$. Calc.: C, 53.5; H, 2.9%). (Found: M^+, 493.9581. $C_{22}H_{14}Cr_2O_7$. Calc.: M, 493.9550). ν_{max} (KBr) 1973 (broad) and 1902 (broad) (Cr–C≡O); 1652 ($R_2C=O$), 1591 cm^{-1} (C=C). δ_H 2.43, d, J 1.2 Hz, 3H, (H1)$_3$; 5.30, bt, J 7.0 Hz, 2H, 4-(H$_{meta}$)$_2$; 5.38, bt, J 6.5 Hz, 2H, 2-(H$_{meta}$)$_2$; 5.49, tt, J 6.2, 0.9 Hz, 1H, 2-(H$_{para}$); 5.67, bd, J 6.6 Hz, 2H, 2-(H$_{ortho}$)$_2$; 5.67, tt, J 6.4, 0.9 Hz, 1H, 4-(H$_{para}$); 6.12, dd, J 6.8, 0.8 Hz, 2H, 4-(H$_{ortho}$)$_2$; 6.85, q, J 1.2 Hz, 1H, H3. δ_c 18.14, C1; 89.36 (2C), 2-(C$_{ortho}$); 90.82 (2C), 2-(C$_{meta}$); 92.24 (2C), 4-(C$_{ortho}$); 93.30, 2-(C$_{para}$); 94.43, 4-(C$_{para}$); 95.20 (2C), 4-(C$_{meta}$); 97.74, 4-(C$_{ipso}$); 107.83, 2-(C$_{ipso}$); 120.29, C3; 151.72, C2; 187.68, C4; 230.71 and 231.93 (3C each), Cr(CO)$_3$. m/z 494(M^+, 8), 438(M–2CO, 3), 410(438–CO, 20), 382(410–CO, 5), 354(382–CO, 5), 326(354–CO, 42), 302(354–Cr, 10), 274(326–Cr, 100), 52(Cr$^+$, 82); (vi) an unidentified deep red oil (10 mg).

3.15. Tricarbonyl[(((1,2,3,4,5,6-η)-2-(1-oxopropyl)-phenyl)-C,O)tetracarbonylmanganese]chromium (27)

A nitrogen-degassed solution of **15** (0.87 g, 3.21 mmol) and pentacarbonyl(phenylmethyl)manganese (1.10 g, 3.85 mmol) in heptane (40 ml) was heated to vigorous reflux for 2.0 h under positive nitrogen pressure. During this time a heavy precipitate formed. The

deep red reaction mixture was concentrated in vacuo and was purified by flash chromatography using hexanes–dichloromethane as eluent to give in order of increasing polarity: (i) pentacarbonyl(phenylmethyl) manganese (0.10 g); (ii) tetracarbonyl[(2-(1-oxopropyl) phenyl)-C,O]manganese (24) (40 mg, 4%) [36]; (iii) 27 (0.95 g, 68%) as a red solid which was recrystallised from diethyl ether–dichloromethane as red rods, m.p. 115–120°C (dec.). (Found: C, 44.1; H, 1.8. $C_{16}H_9CrMnO_8$. Calc.: C, 44.1; H, 2.1%). (Found: $M^{+ \cdot}$, 435.9082. $C_{16}H_9CrMnO_8$. Calc.: M, 435.9083). ν_{max} (KBr) 2094 (sharp), 2014 (sharp), 1992 (broad), 1945 (broad) and 1868 (broad), (Cr–C≡O and Mn–C≡O), 1589 (C=C), 1508 cm^{-1} ($R_2C=O$). δ_H 1.24, t, J 7.2 Hz, 3H, 2-COCH$_2$CH_3; 2.81, dq, J 17.9, 7.2 Hz, 1H, 2-COCH_2CH$_3$; 2.90, dq, J 17.8, 7.2 Hz, 1H, 2-COCH_2CH$_3$; 5.40, td, J 6.4, 1.0 Hz, 1H, H4; 5.61, td, J 6.3, 1.0 Hz, 1H, H5; 5.74, dd, J 6.3, 1.0 Hz, 1H, H3; 6.05, dd, J 6.2, 0.8 Hz, 1H, H6. δ_c 8.13, 2-COCH$_2$CH_3, 30.72, 2-COCH_2CH$_3$; 91.16, C4; 92.78, C3; 94.58, C5; 103.08, C6; 104.58, C2; 152.89, C1; 207.91, 208.96, 210.64 and 220.01, Mn(CO)$_4$; 222.00, 2-COCH$_2$CH$_3$; 232.85 (3C), Cr(CO)$_3$. m/z 436($M^{+ \cdot}$, 14), 380(M–2CO, 12), 352(366–CO, 15), 324(352–CO, 30), 296(324–CO, 10), 268(M–Mn(CO)$_4$ + H, 20), 240(268–CO, 10), 185(100), 55(Mn$^+$, 28), 52(Cr$^+$, 60); (iv) 15 (0.27 g, 31%).

3.16. [(((1,2,3,4,5,6-η)-2-Acetyl-4-methoxyphenyl)-C,O)tetracarbonylmanganese]tricarbonylchromium (28)

A nitrogen-degassed solution of 16 (0.10 g, 0.35 mmol) and pentacarbonyl(phenylmethyl)manganese (0.12 g, 0.42 mmol) in heptane (10 ml) was heated to vigorous reflux with stirring for 35 min under positive nitrogen pressure. During this time a heavy precipitate formed. The deep red reaction mixture was concentrated in vacuo and was purified by flash chromatography using hexanes–diethyl ether as eluent to give in order of increasing polarity: (i) pentacarbonyl(phenylmethyl) manganese (20 mg); (ii) tetracarbonyl(2-acetyl-4-methoxyphenyl)manganese (23) (4 mg, 4%) [10]; (iii) 28 (50 mg, 32%) as a red solid which was recrystallised from diethyl ether as red rods, m.p. 110–119°C. (Found: $M^{+ \cdot}$, 451.9023. $C_{16}H_9CrMnO_9$. Calc.: M, 451.9032). ν_{max} (KBr) 2091 (sharp), 1995 (broad), 1950 (broad) and 1883 (broad), (Cr–C≡O and Mn–C≡O), 1579 (C=C), 1518 cm^{-1} ($R_2C=O$). δ_H 2.46, s, 3H, 2-COCH$_3$; 3.84, s, 3H, 5-OCH$_3$; 5.15, dd, J 7.0, 2.1 Hz, 1H, H4; 5.91, d, J 2.8 Hz, 1H, H6; 5.93, d, J 6.7 Hz, 1H, H3. δ_c 23.75, 2-COCH_3; 55.54, 5-OCH_3; 76.03, C4; 94.25, C3; 99.69, C3; 143.94, C5; 157.16, C1; 207.02, 208.36, 210.14 and 219.62, Mn(CO)$_4$; 215.66, 2-COCH$_3$; 231.07 (3C), Cr(CO)$_3$. m/z 452($M^{+ \cdot}$, 1), 396(M–2CO, 2), 368(396–CO, 1), 340(368–CO, 3), 312(340–CO, 1), 286(M–Mn(CO)$_4$ + H, 5), 266(7),

256(5), 230(5), 202(30), 150(286–Cr(CO)$_3$, 28), 135(100), 107(14), 92(14), 77(25), 52(Cr$^+$, 27); (iv) an unidentified deep violet component (3 mg); (v) 16 (36 mg, 36%); (vi) an unidentified deep red component (4 mg).

3.17. Tetracarbonyl[(2-(1-oxopropyl)phenyl)-C,O]manganese (24)

A nitrogen-degassed solution of 3 (1.00 g, 7.46 mmol) and pentacarbonyl(phenylmethyl)manganese (2.67 g, 9.32 mmol) in heptane (80 ml) was heated to reflux under positive nitrogen pressure for 2 h. The reaction mixture was concentrated in vacuo and purified by flash chromatography using hexanes–diethyl ether as eluent to give 24 (2.53 g) as a yellow solid. Recrystallisation from hexanes–diethyl ether afforded yellow needles (2.12 g, 95%), m.p. 69–73°C [36]. (Found: $M^{+ \cdot}$, 299.9831. $C_{13}H_9MnO_5$. Calc.: M, 299.9830). ν_{max} (KBr) 2082 (sharp), 1992 (broad), and 1938 (broad), Mn–C≡O, 1578 (C=C), 1538 cm^{-1} ($R_2C=O$). δ_H 1.22, t, J 7.4 Hz, 3H, 2-COCH$_2$CH_3; 3.01, q, J 7.4 Hz, 2H, 2-COCH_2CH$_3$; 7.17, td, J 7.3, 1.2 Hz, 1H, H4; 7.41, td, J 7.3, 1.3 Hz, 1H, H5; 7.85, bd, J 7.7 Hz, 1H, H3; 8.09, bdd, J 7.5, 0.4 Hz, 1H, H6. δ_c 8.90, 2-COCH$_2$CH_3; 30.70, 2-COCH_2CH$_3$; 123.69, C4; 130.78, C3; 133.65, C5; 141.52, C6; 144.68, C2; 192.94, C1; 211.61 (2C), 212.99, and 221.11, Mn(CO)$_4$; 219.65, 2-COCH$_2$CH$_3$. m/z 300(M^+, 10), 272(M–CO, 2), 244(272–CO, 3), 216(272–2CO, 11), 188(216–CO, 71), 134(15), 105(100), 77(47), 55(Mn +, 28), 51(15).

3.18. Tricarbonyl[(((1,2,3,4,5,6-η)-2-(1-oxopropyl)-phenyl)-C,O)tricarbonylmanganese(triphenylphosphine)]-chromium (29)

A nitrogen-degassed solution of 27 (1.00 g, 2.29 mmol) and triphenylphosphine (0.60 g, 2.29 mmol) in benzene (90 ml) was heated to vigorous reflux for 45 min under a nitrogen atmosphere. The deep red reaction mixture was concentrated in vacuo and was purified by flash chromatography using hexanes–diethyl ether as eluent to give 29 (1.52 g, 99%) as a crimson solid which was recrystallised from diethyl ether–dichloromethane–hexanes as red rods, m.p. 169–171°C. (Found: C, 59.0; H, 3.5. $C_{33}H_{24}CrMnO_7P$. Calc.: C, 59.1; H, 3.6%). (Found: $M^{+ \cdot}$, 670.0045. $C_{33}H_{24}CrMnO_7P$. Calc.: M, 670.0056). ν_{max} (KBr) 2014 (sharp), 1957 (broad), and 1892 (broad), (Cr–C≡O and Mn–C≡O), 1582 (C=C), 1496 cm^{-1} ($R_2C=O$). δ_H 1.24, t, J 7.2 Hz, 3H, 2-COCH$_2$CH_3; 2.13, dqd, J 18.2, 7.2, 2.3 Hz, 1H, 2-COCH_2CH$_3$; 2.62, dqd, J 18.3, 7.2, 2.3 Hz, 1H, 2-COCH_2CH$_3$; 5.11, dd, J 6.5, 1.0 Hz, 1H, H3; 5.14, td, J 6.5, 1.0 Hz, 1H, H4; 5.27, td, J 6.1, 1.1 Hz, 1H, H5; 6.18, bd, J 6.2 Hz, 1H, H6. δ_c 7.85, 2-COCH$_2$CH_3, 30.13, 2-COCH_2CH$_3$; 91.00, C4; 91.75,

C3; 92.75, C5; 104.58, C6; 105.99, C2; 128.43, d, J 9.0 Hz, 6C, PPh$_3$ C$_{meta}$; 130.15, 3C, PPh$_3$ C$_{para}$; 131.15, d, J 35.0 Hz, 3C, PPh$_3$ C$_{ipso}$; 133.80, d, J 10 Hz, 6C, PPh$_3$ C$_{ortho}$; 169.60, d, J 16.4 Hz, Cl; 214.85 (d, J 23.0 Hz), 216.07 (d, J 22.2 Hz), 226.73 (d, J 20.0 Hz), Mn(CO)$_3$; 218.72, 2-COCH$_2$CH$_3$; 234.09 (3C), Cr(CO)3. m/z DEI 670($M^{+\cdot}$, 0), 586(M–3CO, 2), 502(3), 447(2), 380(2), 262(M–Mn(CO)$_3$(PPh$_3$) + H, 100), 183(55), 108(30), 52(Cr$^+$, 15). m/z FAB 670($M^{+\cdot}$, 4), 586(M–3CO, 16), 534(4), 502(2), 273(2).

3.19. Coupling reactions of [(((1,2,3,4,5,6-η)-2-acetylphenyl)-C,O)tetracarbonylmanganese]tricarbonyl-chromium (26)

3.19.1. Thermally-promoted insertion of diphenylacetylene

A solution of **26** (0.15 g, 0.36 mmol) and diphenylacetylene (0.25 g, 1.42 mmol) in benzene (20 ml) was heated to reflux under positive nitrogen pressure for 24 h. The reaction mixture was diluted with diethyl ether, filtered and concentrated in vacuo to give a deep red oil which was redissolved in diethyl ether and exposed to bright sunlight for 24 h. Filtration and purification by PLC using diethyl ether–hexanes as eluent afforded in order of increasing polarity: (i) 1,3-diphenylbut-2-en-1-one (**31**) (8 mg, 5%); (ii) 1-methyl-2,3-diphenyl-1H-inden-1-ol (**52**) (25 mg, 24%) as a clear oil. (Found: $M^{+\cdot}$, 298.1365. C$_{22}$H$_{18}$O. Calc.: M, 298.1358). ν_{max} (KBr) 3357 (OH), 1602, 1487 and 1456 cm^{-1} (C=C). δ_H 1.95, s, 1-OH; 2.06, s, 3H, 1-CH$_3$; 7.20–7.44, m, 14 H, aromatic H. δ_c 24.00, 1-CH$_3$; 83.31, Cl; 120.78, 121.84, 126.61, 127.28, 127.54, 127.94 (2C), 128.44, 128.49 (2C), 129.25 (2C), and 129.42 (2C), aromatic C–H; 134.67 and 134.72, [2-Ph and 3-Ph] C$_{ipso}$; 138.69, 142.15, 146.95 and 149.50, C2, C3, C3a and C7a. m/z 298($M^{+\cdot}$, 100), 283(M–CH$_3$, 69), 281(M–OH, 17), 265(18), 252(18), 220(32).

3.19.2. Thermally-promoted insertion of methyl propenoate

3.19.2.1. Without decomplexation.
A nitrogen-degassed solution of **26** (0.79 g, 1.87 mmol) and methyl propenoate (1.50 ml, 0.017 mmol) in benzene (80 ml) was heated to reflux under positive nitrogen pressure for 23 h. The reaction mixture was diluted with diethyl ether, filtered and purified by flash chromatography on silica gel using hexanes–diethyl ether as eluent to give in order of increasing polarity: (i) (η^6-benzene)tricarbonylchromium (**17**) (19 mg, 5%); (ii) tricarbonyl [(3a,3,4,5,6,7,7a-η)-3-methyl-2-methoxycarbonyl-1H-indene] chromium (**48**) (97 mg, 16%) which was recrystallised from diethyl ether as orange micro rods, m.p. 142–145°C. (Found: C, 55.6; H, 3.6. C$_{15}$H$_{12}$CrO$_5$. Calc.: C, 55.6; H, 3.7%). (Found: $M^{+\cdot}$, 324.0085.

C$_{15}$H$_{12}$CrO$_5$. Calc.: M, 324.0090). ν_{max} (KBr) 1961 and 1866 (Cr–C≡O), 1698 cm^{-1} (CO$_2$CH$_3$). δ_H 2.43, t, J 2.3 Hz, 3H, 3-CH$_3$; 3.71, q, J 2.3 Hz, 2H, (H1)$_2$; 3.82, s, 3H, 2-CO$_2$CH$_3$; 5.22, td, J 6.4, 0.9 Hz, 1H, H5; 5.44, td, J 6.4, 0.8 Hz, 1H, H6; 5.75, bd, J 6.3 Hz, 1H, H4; 5.81, bd, J 6.4 Hz, 1H, H7. δ_c 11.97, 3-CH$_3$; 38.72, Cl; 51.50, 2-CO$_2$CH$_3$; 88.44, 88.67, 89.36 and 92.61, C4, C5, C6 and C7; 112.03 and 113.29, C3a and C7a; 130.55, C2; 150.04, C3; 164.52, 2-CO$_2$CH$_3$; 232.59 (3C), Cr(CO)$_3$. m/z 324($M^{+\cdot}$, 30), 293(M–OCH$_3$, 5), 268(324–CO, 17), 240(268–CO, 93), 212 (20), 182(32), 157(50), 128(20), 52(Cr$^+$, 100); (iii) a mixture (2:2:1) (0.15 g) consisting of **48, 14**, and an unidentified compound; (iv) a mixture (4:1) (0.36 g, 56%) of two tricarbonylchromium indenol complexes. The major isomer was obtained pure after repetitive recrystallisation from diethyl ether and assigned as the α diastereoisomer of tricarbonyl[(1β,2β)-(3a,4,5,6,7, 7a,-η)-2,3-dihydro-1-methyl-2-methoxycarbonyl-1H-inden-1-ol]chromium (**36**) yellow rods, m.p. 154–156 °C. (Found: C, 52.6; H, 3.9. C$_{15}$H$_{14}$CrO$_6$. Calc.: C, 52.7; H, 4.1%). (Found: $M^{+\cdot}$, 342.0200. C$_{15}$H$_{14}$CrO$_6$. Calc.: M, 342.0196). ν_{max} (KBr) 3402 (OH), 1960 and 1874 (Cr–C≡O), 1709 cm^{-1} (CO$_2$CH$_3$). δ_H 1.80, s, 3H, 1-CH$_3$; 2.95, dd, J 15.4, 7.6 Hz, 1H, H3β; 3.24, dd, J 10.1, 7.6 Hz, 1H, H2α; 3.25, dd, J 15.4, 10.2 Hz, 1H, H3α; 3.26, s, 1H, 1-OH; 3.81, s, 3H, 2-CO$_2$CH$_3$; 5.13, td, J 6.3, 0.9 Hz, 1H, H5; 5.27, bd, J 6.3 Hz, 1H, H4; 5.49, td, J 6.2, 0.8 Hz, 1H, H6; 5.69, bd, J 6.4 Hz, 1H, H7. δ_c 25.25, 1-CH$_3$; 31.91, C3; 52.24, C2 and 2-CO$_2$CH$_3$; 79.85, Cl; 86.56, 88.38, 90.68 and 95.39, C4, C5, C6 and C7; 113.48 and 113.96, C3a and C7a; 172.42, 2-CO$_2$CH$_3$; 232.38 (3C), Cr(CO)$_3$. m/z 342($M^{+\cdot}$, 50), 324(M–H$_2$O, 3), 310(M–CH$_3$OH, 1), 286(M–2CO, 10), 258(286–CO, 80), 240(258–H$_2$O, 90), 227(10), 212(40), 198(50), 129(40), 52(Cr$^+$, 100). The minor diastereoisomer could not be isolated pure.

3.19.2.2. With decomplexation.
Treatment of **26** (0.10 g, 0.24 mmol) with methyl propenoate (0.15 ml, 0.17 mmol) in refluxing benzene for 11.5 h afforded a red oil which was redissolved in diethyl ether and exposed to bright sunlight for 3 h. Filtration through Celite followed by purification by PLC (silica gel, hexanes–diethyl ether, multiple elution) afforded in order of increasing polarity: (i) 2-methoxycarbonyl-3-methyl-1H-indene (**53**) (3 mg, 6%) as a white solid which was recrystallised from hexanes–chloroform to give white needles, m.p. 65–68°C. (Found: $M^{+\cdot}$, 188.0836. C$_{12}$H$_{12}$O$_2$. Calc.: M, 188.0837). ν_{max} (KBr) 1705 (CO$_2$CH$_3$), 1608, 1574 and 1434 cm^{-1} (C=C). δ_H 2.55, t, J 2.4 Hz, 3H, 3-CH$_3$; 3.65, q, J 2.3 Hz, 2H, (H1)$_2$, 3.83, s, 3H, 2-CO$_2$CH$_3$; 7.30–7.55, m, 4H, H4, H5, H6 and H7. δ_c 12.38, 3-CH$_3$; 38.71, Cl; 51.16, 2-CO$_2$CH$_3$; 121.12, 123.96, 126.57 and 127.68, C4, C5, C6, and C7; 129.43, C2; 143.48 and 145.20; C3a

and C7a; 151.69, C3; 166.36, 2-CO_2CH_3. m/z 188(M^+, 69), 173(M–CH_3, 5), 157(M–OCH_3, 21), 129(100);   (ii)   (1β,2β)-2,3-dihydro-2-methoxycarbonyl-1-methyl-1H-inden-1-ol (**40**) (33 mg, 68%) as a white solid which was recrystallised from hexanes–diethyl ether as white rods, m.p. 53–55°C. (Found: M^+·, 206.0939. $C_{12}H_{14}O_3$. Calc.: M, 206.0943). ν_{max} (KBr) 3458 (OH), 1732 (CO_2CH_3), 1520, 1480 and 1437 cm^{-1} (C=C). δ_H 1.76, s, 3H, 1-CH_3; 2.84, s, 1H, 1-OH; 3.10, dd, J 13.8, 8.0 Hz, 1H, H3β; 3.21, dd, J 8.0, 6.2 Hz, 1H, H2α; 3.43, dd, J 13.8, 6.2 Hz, 1H, H3α; 3.78, s, 3H, 2-CO_2CH_3; 7.21–7.42, m, 4H, H4, H5, H6 and H7. δ_c 25.56, 1-CH_3; 32.75, C3; 51.83, 2-CO_2CH_3; 54.55, C2; 81.02, C1; 122.69, 124.75, 127.17 and 128.74, C4, C5, C6 and C7; 140.71 and 145.91, C3a and C7a; 173.40, 2-CO_2CH_3. m/z 206(M^+·, 2), 191(M–CH_3, 21), 188(M–H_2O, 100), 175(M–OCH_3, 20), 159(191–CH_3OH, 60), 146(47), 131(80), 129(60), 103(30), 77(20), 43(33);   (iii) (1β,2α)-2,3-dihydro-2-methoxy-carbonyl-1-methyl-1H-inden-1-ol (**41**) (10 mg, 21%) as a clear oil. (Found: M^+·, 206.0941. $C_{12}H_{14}O_3$. Calc.: M, 206.0943). ν_{max} (KBr) 3444 (OH), 1732 (CO_2CH_3), 1518, 1480 and 1437 cm^{-1} (C=C). δ_H 1.38, s, 3H, 1-CH_3; 2.49, s, 1H, 1-OH; 3.08, dd, J 15.1, 7.8 Hz, 1H, H3α; 3.21, dd, J 15.1, 9.8 Hz, 1H, H3β; 3.36, dd, J 9.8, 7.8 Hz, 1H, H2β; 3.81, s, 3H, 2-CO_2CH_3; 7.19–7.39, m, 4H, H4, H5, H6 and H7. δ_c 25.14, 1-CH_3; 31.87, C3; 51.87, 2-CO_2CH_3; 58.37, C2; 82.68, C1; 122.37, 124.75, 127.34 and 128.40, C4, C5, C6 and C7; 138.68 and 147.00, C3a and C7a; 172.99, 2-CO_2CH_3. m/z 206(M^+·, 5), 191(M–CH_3, 72), 188(M–H_2O, 61), 175(M–OCH_3, 17), 159(191–CH_3OH, 92), 146(52), 131(100), 103(35, 77(32), 43(38).

3.19.3. Thermally-promoted insertion of tert-butyl propenoate

Treatment of **26** (0.21 g, 0.49 mmol) with tert-butyl propenoate (0.20 ml, 0.15 mmol) in refluxing benzene for 22.5 h afforded a red oil which was redissolved in diethyl ether and exposed to bright sunlight for 3 h. Filtration and purification by PLC (silica gel, hexanes–diethyl ether, multiple elution) afforded in order of increasing polarity: (i) 3-methyl-2-(1,1-dimethyl-ethoxycarbonyl)-1H-indene (**54**) (16 mg, 14%) as a clear oil. (Found: M^+·, 230.1304. $C_{15}H_{18}O_2$. Calc.: M, 230.1307). ν_{max} (KBr) 1688 ($CO_2C(CH_3)_3$), 1456 cm^{-1} (C=C). δ_H 1.57, s, 9H, 2-$CO_2C(CH_3)_3$; 2.51, t, J 2.4 Hz, 3H, 3-CH_3; 3.61, q, J 2.3 Hz, 2H, (H1)$_2$; 7.25–7.51, m, 4H, H4, H5, H6 and H7. δ_c 12.33, 3-CH_3; 28.40 (3C), 2-$CO_2C(CH_3)_3$; 38.98, C1; 80.17, 2-$CO_2C(CH_3)_3$; 120.93, 123.83, 126.44 and 127.32, C4, C5, C6 and C7; 131.59, C2; 143.35 and 145.53, C3a and C7a; 149.89, C3; 165.49, 2-$CO_2C(CH_3)_3$. m/z 230(M^+, 35), 174(M–CH_2=$C(CH_3)_2$, 100), 157(M–$OC(CH_3)_3$, 38), 130(70); 115(20), 57(37);   (ii)

(1β,2β)-2,3-dihydro-2-(1,1-dimethylethoxycarbonyl)-1-methyl-1H-inden-1-ol (**44**) (53 mg, 47%) as a white solid which was recrystallised from hexanes–diethyl ether as white needles, m.p. 111–114°C. (Found: C, 72.3; H, 7.9. $C_{15}H_{20}O_3$. Calc.: C, 72.6; H, 8.1%). (Found: M^+·–H_2O, 230.1309. $C_{15}H_{18}O_2$. Calc.: M–H_2O, 230.1307). ν_{max} (KBr) 3418 (OH), 1716 ($CO_2C(CH_3)_3$), 1455 cm^{-1} (C=C). δ_H 1.51, s, 9H, 2-$CO_2C(CH_3)_3$; 1.73, s, 3H, 1-CH_3; 3.06, dd, J 19.1, 8.1 Hz, 1H, H3α; 3.06, s, 1-OH; 3.08, dd, J 11.7, 8.2 Hz, 1H, H2α; 3.36, dd, J 19.1, 11.7 Hz, 1H, H3β; 7.21–7.39, m, H4, H5, H6 and H7. δ_c 26.64, 1-CH_3; 28.18 (3C), 2-$CO_2C(CH_3)_3$; 32.96, C3; 55.17, C2; 80.92 and 81.36, C1 and 2-$CO_2C(CH_3)_3$; 122.69, 124.79, 127.13 and 128.64, C4, C5, C6 and C7; 140.90 and 146.32, C3a and C7a; 172.53, 2-$CO_2C(CH_3)_3$. m/z 248(M^+·, < 1), 230(M–H_2O, 12), 192(10), 177(18), 174(32), 159(33), 146(33), 130(32), 57(100);   (iii) (1β,2α)-2,3-dihydro-2-methoxycarbonyl-1-methyl-1H-inden-1-ol (**45**) (24 mg, 21%) as a white solid which was recrystallised from diethyl ether as white needles, m.p. 59–62°C. (Found: M^+·, 248.1416. $C_{15}H_{20}O_3$. Calc.: M, 248.1412). ν_{max} (KBr) 3432 (OH), 1722 ($CO_2C(CH_3)_3$), 1479 and 1456 cm^{-1} (C=C). δ_H 1.41, s, 3H, 1-CH_3; 1.53, s, 9H, 2-$CO_2C(CH_3)_3$; 2.58, s, 1H, 1-OH; 3.02, dd, J 14.3, 7.4 Hz, 1H, H3β; 3.12, dd, J 14.3, 9.0 Hz, 1H, H3α; 3.24, dd, J 9.0, 7.4 Hz, 1H, H2β; 7.15–7.39, m, H4, H5, H6 and H7. δ_c 25.03, 1-CH_3, 28.22, 3C, 2-$CO_2C(CH_3)_3$; 31.79, C3; 59.08, C2; 81.30, 2-$CO_2C(CH_3)_3$; 82.40, C1; 122.30, 124.69, 127.17 and 128.17, C4, C5, C6 and C7; 138.83 and 147.25, C3a and C7a; 171.76, 2-$CO_2C(CH_3)_3$. m/z 248(M^+·, 1), 230(M–H_2O, 10), 192(M–CH_2=$C(CH_3)_3$, 11), 177(70), 174(82), 159(90), 146(57), 131(50), 57(100), 43(32).

3.19.4. Thermally-promoted insertion of triethoxyvinyl-silane

Treatment of **26** (0.10 g, 0.24 mmol) with tri-ethoxyvinylsilane (0.40 ml, 1.75 mmol) in refluxing benzene for 8 h afforded a red oil which was redissolved in diethyl ether and exposed to bright sunlight for 3 h. Filtration and attempted purification by PLC (silica gel, hexanes–diethyl ether, multiple elution) afforded ten bands of similar intensity, none of which were investigated further.

3.19.5. Chemically-promoted coupling with Me_3NO and methyl propenoate

A nitrogen-degassed solution of **26** (0.10 g, 0.23 mmol) in acetonitrile (5 ml) was treated with trimethylamine N-oxide (27 mg, 0.36 mmol) at room temperature under a nitrogen atmosphere. The red solution slowly deepened in colour. The reaction mixture was stirred at ambient temperature for 10 min and was then treated with methyl propenoate (0.10 ml, 0.95 mmol).

After 100 h at room temperature the reaction mixture was diluted with diethyl ether and filtered. It was then redissolved in diethyl ether and exposed to bright sunlight for 3 h. Work-up and purification (PLC, diethyl ether–hexanes, multiple elution) afforded only acetophenone (2) (21 mg, 74%).

3.20. Tricarbonyl[(((1,2,3,4,5,6-η)-2-(1-oxopropyl)-phenyl)C,O)tetracarbonylmanganese]chromium (27)

3.20.1. Thermally-promoted insertion of diphenylacetylene

A solution of 27 (0.15 g, 0.34 mmol) and diphenylacetylene (0.25 g, 1.38 mmol) in benzene (20 ml) was heated to reflux under positive nitrogen pressure for 23 h. The reaction mixture was diluted with diethyl ether, filtered and concentrated in vacuo to give a deep red oil which was redissolved in diethyl ether and exposed to bright sunlight for 24 h. Filtration and purification by PLC using diethyl ether–hexanes as eluent gave in order of increasing polarity: (i) 3 (22 mg, 48%); (ii) 1-ethyl-2,3-diphenyl-1H-inden-1-ol (55) (27 mg, 25%) as a white solid which was recrystallised from diethyl ether–hexanes as crystalline rods, m.p. 154–157°C. (Found: C, 88.2; H, 6.5. $C_{23}H_{20}O$. Calc.: C, 88.4; H, 6.5%). (Found: $M^{+\cdot}$, 312.1506. $C_{23}H_{20}O$. Calc.: M, 312.1514). ν_{max} (KBr) 3352 (OH), 1602, 1484 and 1444 cm^{-1} (C=C). δ_H 1.19, t, J 7.5 Hz, 3H, 1-CH_2CH_3; 1.97, dq, J 13.1, 7.4 Hz, 1H, 1-CH_2CH$_3$; 2.15, s, 1-OH; 2.16, dq, J 13.1, 7.4 Hz, 1H, 1-CH_2CH$_3$; 7.20–7.52, m, 14 H, aromatic H. δ_c 7.91, 1-CH$_2$CH_3; 29.80, 1-CH_2CH$_3$; 86.98, C1; 120.60, 122.02, 126.52, 127.27, 127.54, 127.97 (2C), 128.40, 128.50 (2C), 129.29 (2C) and 129.32 (2C), aromatic C–H; 134.74 and 134.85, [2-Ph and 3-Ph] C_{ipso}; 140.39, 143.26, 145.18 and 147.75, C2, C3, C3a and C7a. m/z 312($M^{+\cdot}$, 39), 283(M–CH$_2$CH$_3$, 100), 265(14), 252(15), 252(15), 105(10), 77(10).

3.20.2. Thermally-promoted insertion of phenylacetylene

A solution of 27 (0.22 g, 0.67 mmol) and phenylacetylene (0.28 g, 2.67 mmol) in benzene (20 ml) was heated to reflux under positive nitrogen pressure for 11 h. The reaction mixture was concentrated to give a red oil (0.15 g) which was redissolved in diethyl ether and exposed to bright sunlight for 3 h. Attempted purification by PLC afforded 17 bands of similar intensities, none of which were investigated further.

3.20.3. Thermally-promoted insertion of 3-hexyne

Treatment of 27 (0.22 g, 0.51 mmol) with 3-hexyne (0.26 g, 1.84 mmol) in refluxing benzene for 24 h afforded a red oil which was purified by flash chromatography to give in order of increasing polarity: (i) a mixture (1:1) (46 mg) of 1,2,3-triethyl-1H-inden-1-ol (61) and a single diastereoisomer of tricarbonyl-

[(3a,4,5,6,7,7a-η)-1,2,3-triethyl-1H-inden-1-ol]chromium (50) as a yellow oil. For 50 (Found: $M^{+\cdot}$, 352.0768. $C_{18}H_{20}CrO_4$. Calc.: M, 352.0767). ν_{max} (KBr) 3417 (OH), 1962 and 1886 (Cr–C≡O), 1456 cm^{-1} (C=C). δ_H 0.56, t, J 7.5 Hz, 3H, 1-CH$_2$CH_3; 1.16 and 1.17, t, J 7.5 Hz, 3H each, 2-CH$_2$CH_3 and 3-CH$_2$CH_3; 1.52, s, 1H, 1-OH; 1.85–2.51, m, 6H, 1-CH_2CH$_3$, 2-CH_2CH$_3$ and 3-CH_2CH$_3$; 5.05, bt, J 6.1 Hz, 1H, H5; 5.36, bd, J 6.2 Hz, 1H, H4; 5.46, bt, J 6.2 Hz, 1H, H6; 5.82, bd, J 6.1 Hz, 1H, H7. δ_c 7.98, 1-CH$_2$CH_3; 13.47 and 14.23, 2-CH$_2$CH_3 and 3-CH$_2$CH_3; 17.96 and 18.18, 2-CH_2CH$_3$ and 3-CH_2CH$_3$; 29.55, 1-CH_2CH$_3$; 84.90, C1; 83.62, 86.55, 90.13 and 94.06, C4, C5, C6 and C7; 116.47 and 118.69, C3a and C7a, 136.74 and 152.36, C2 and C3; 233.38 (3C), Cr(CO)$_3$. m/z 352(M^+, 18), 296(M–2CO, 12), 268(296–CO, 100), 253(268–CH$_3$, 20), 52(Cr$^+$, 32); (ii) 15 (94 mg, 70%).

A solution of a mixture (1:1) (40 mg) of 50 and 61 in diethyl ether (20 ml) was exposed to bright sunlight for 4 h. Work-up in the usual manner and purification (PLC, diethyl ether–hexanes) afforded 61 (27 mg, 25%) as a white solid which was recrystallised from diethyl ether as white needles, m.p. 54–56°C (distilled at 100–105 °C, 0.03 mm Hg). (Found: C, 83.1; H, 9.3. $C_{15}H_{20}O$. Calc.: C, 83.3; H, 9.3%). (Found: $M^{+\cdot}$, 216.1516. $C_{15}H_{20}O$. Calc.: M, 216.1514). ν_{max} (KBr) 3348 (OH), 1456 cm^{-1} (C=C). δ_H 0.48, t, J 7.5 Hz, 3H, 1-CH$_2$CH_3; 1.16 and 1.18, t, J 7.5 Hz, 3H each, 2-CH$_2$CH_3 and 3-CH$_2$CH_3; 1.61, s, 1H, 1-OH; 1.93 and 2.07, dq, J 13.1, 7.4 Hz, 1H each, 1-CH_2CH$_3$; 2.24 and 2.39, dq, J 14.0, 7.6 Hz, 1H each, 2-CH_2CH$_3$; 2.46(9) and 2.47(3), q, J 7.7 Hz, 1H each, 3-CH_2CH$_3$; 7.12(9), td, J 7.7, 1.0 Hz, 1H, H6; 7.12(8), dd, J 7.1, 1.2 Hz, 1H; H7; 7.23, td, J 7.2, 1.2 Hz, 1H, H5; 7.31, dd, J 7.7, 1.0 Hz, 1H, H4. δ_c 7.99, 1-CH$_2$CH_3; 13.50 and 14.24, 2-CH$_2$CH_3 and 3-CH$_2$CH_3; 17.67 and 18.44, 2-CH_2CH$_3$ and 3-CH_2CH$_3$; 29.17, 1-CH_2CH$_3$; 86.28, C1; 118.42, 121.40, 125.09 and 128.11, C4, C5, C6 and C7; 139.47, 143.78, 146.60 and 147.74, C2, C3, C3a and C7a. m/z 216(M^+, 33), 187(M–CH$_2$CH$_3$, 100), 159(20), 141(10), 128(12), 115(11).

3.20.4. Thermally-promoted insertion of dimethyl acetylenedicarboxylate

Treatment of 27 (0.20 g, 0.46 mmol) with dimethyl acetylenedicarboxylate (0.26 g, 1.84 mmol) in refluxing benzene for 12 h afforded a red oil which was redissolved in diethyl ether and exposed to bright sunlight for 3 h. Filtration and purification by PLC (hexanes–diethyl ether, multiple sweeps) afforded in order of increasing polarity: (i) 3-ethyl-1,2-bismethoxycarbonyl-1H-indene (59) (25 mg, 21%) as a white solid which was recrystallised from diethyl ether–hexanes as microneedles, m.p. 85–87°C. (Found: $M^{+\cdot}$, 260.1054. $C_{15}H_{16}O_4$. Calc.: M, 260.1049). ν_{max} (KBr) 1741 (non-conjugated CO$_2$CH$_3$), 1712 (conjugated CO$_2$CH$_3$),

1609 and 1434 cm^{-1} (C=C). δ_H 1.27, t, J 7.5 Hz, 3H, 3-CH$_2$CH_3; 2.93–3.22, m, 2H, 3-CH_2CH$_3$; 3.69, s, 3H, 1-CO$_2$CH$_3$; 3.83, s, 3H, 2-CO$_2$CH$_3$; 4.65, s, 1H, H1; 7.32–7.61, m, 4H, H4, H5, H6 and H7. δ_c 13.30, 3-CH$_2$CH_3; 19.85, 3-CH_2CH$_3$; 51.43, 1-CO$_2$CH$_3$; 52.44, 2-CO$_2$CH$_3$; 55.25, C1; 121.65, 123.67, 128.08 and 128.56, C4, C5, C6 and C7; 141.33 (2C) and 143.56, C2, C3a and C7a; 160.04, C3; 165.01, 2-CO$_2$CH$_3$; 170.77, 1-CO$_2$CH$_3$. m/z 260(M^+, 37), 228(M–CH$_3$OH, 39), 213(228–CH$_3$, 9), 200(M–HCO$_2$CH$_3$, 100), 169(47), 142(63), 115(20), 59(20); (ii) 1-ethyl-1-hydroxy-2,3-bismethoxycarbonyl-1H-indene (60) (22 mg, 17%) as a clear oil. (Found: M^+, 276.1002. C$_{15}$H$_{16}$O$_5$. Calc.: M, 276.0998). ν_{max} (KBr) 3479 (OH), 1724 (CO$_2$CH$_3$), 1614, 1461 and 1436 cm^{-1} (C=C). δ_H 0.60, t, J 7.4 Hz, 3H, 3-CH$_2$CH_3; 2.20, q, J 7.5 Hz, 2H, 3-CH_2CH$_3$; 3.01, s, 1H, 1-OH; 3.87, s, 3H, 1-CO$_2$CH$_3$; 3.95, s, 3H, 2-CO$_2$CH$_3$; 7.31–7.47, m, 4H, H4, H5, H6 and H7. δ_c 7.94, 3-CH$_2$CH_3; 31.19, 3-CH_2CH$_3$; 52.21 and 52.43, 1-CO$_2$CH_3 and 2-CO$_2$CH_3; 85.67, C1; 122.78, 123.01, 129.05 and 129.36; C4, C5, C6 and C7; 137.33, 140.53, 141.14 and 147.44, C2, C3, C3a and C7a; 164.31 and 164.77, 1-CO$_2$CH$_3$ and 2-CO$_2$CH$_3$. m/z 276(M^+, 10), 247(M–CH$_2$CH$_3$, 18), 215(100), 187(20).

3.20.5. Thermally-promoted insertion of methyl propenoate

3.20.5.1. Without decomplexation. A nitrogen-degassed solution of 27 (1.30 g, 2.98 mmol) and methyl propenoate (2.00 ml, 23.26 mmol) in benzene (80 ml) was heated to reflux under positive nitrogen pressure for 23 h. The reaction mixture was diluted with diethyl ether and filtered through Celite. Concentration in vacuo afforded a deep red oil which was purified by flash chromatography on silica gel using hexanes–diethyl ether as eluent to give in order of increasing polarity: (i) 13 (19 mg, 3%); (ii) tricarbonyl-[(3a,4,5,6,7,7a-η)-3-ethyl-1H-indene]chromium (49) (0.10 g, 12%) as a yellow oil. (Found: M^+, 280.0193. C$_{14}$H$_{12}$CrO$_3$. Calc.: M, 280.0193). ν_{max} (KBr) 1954 and 1867 (Cr–C≡O), 1666 and 1614 cm^{-1} (C=C). δ_H 1.26, t, J 7.4 Hz, 3H, 3-CH$_2$CH_3; 2.40, qdt, J 7.4, 1.9, 1.8 Hz, 2H, 3-CH_2CH$_3$; 3.40, t, J 1.7 Hz, 2H, (H1)$_2$; 5.24, td, J 6.2, 1.3 Hz, 1H, H5; 5.28, td, J 6.3, 1.3 Hz, 1H, H6; 5.68, dd, J 5.8, 1.9 Hz, 1H, H4; 5.82, dd, J 5.5, 1.8 Hz, 1H, H7; 6.16, dt, J 3.9, 1.8H, 1H, H2. δ_c 11.84, 3-CH$_2$CH_3, 20.27, 3-CH_2CH$_3$; 37.86, C1; 86.81, 90.39, 90.51 and 90.75, C4, C5, C6 and C7; 114.33 and 116.06, C3a and C7a; 129.30, C2; 144.10, C3; 233.82 (3C), Cr(CO)$_3$. m/z 280(M^+, 20), 252(M–CO, 3), 224(252–CO, 13), 196(224–CO, 91), 52(Cr$^+$, 100). A solution of complex 49 (90 mg, 0.32 mmol) in diethyl ether (30 ml) was exposed to bright sunlight for 3 h. Concentration and purification by PLC afforded 3-ethyl-1H-indene (56)

(22 mg, 48%) as a clear oil. (Found: M^+, 144.0933. C$_{11}$H$_{12}$. Calc.: M, 144.0939). ν_{max} (KBr) 3066, 3018, 2966 and 2935 (C–H), 1461 and 1398 cm^{-1} (C=C). δ_H 1.26, t, J 7.4 Hz, 3H, 3-CH$_2$CH_3; 2.49–2.63, m, 2H, 3-CH_2CH$_3$; 3.31, td, J 1.7, 1.7 Hz, 2H, (H1)$_2$; 6.20, tt, J 1.8, 1.7 Hz, H2; 7.19, td, J 7.1, 1.6 Hz, 1H, H5; 7.29, btd, J 7.2, 1.1 Hz, 1H, H6; 7.36, bdd, J 7.0, 1.4 Hz, 1H, H4; 7.49, bdd, J 7.3, 0.8 Hz, 1H, H7. δ_c 12.36, 3-CH$_2$CH_3; 20.77, 3-CH_2CH$_3$; 37.60, C1; 118.83, C2; 123.68, 124.42, 125.92 and 126.69, C4, C5, C6 and C7; 144.55, 145.51 and 146.20, C3, C3a and C7a. m/z 144(M^+, 45), 129(M–CH$_3$, 100), 115(M–CH$_2$CH$_3$, 30); (iii) tricarbonyl[(3a,4,5,6,7,7a-η)-3-ethyl-2-methoxycarbonyl-1H-indene]chromium (51) (0.16 g, 16%) which was recrystallised from diethyl ether as orange globular crystals, m.p. 139–141°C. (Found: C, 56.8; H, 3.9. C$_{16}$H$_{14}$CrO$_5$. Calc.: C, 55.8; H, 4.2%). (Found: M^+, 338.0243. C$_{16}$H$_{14}$CrO$_5$. Calc.: M, 338.0246). ν_{max} (KBr) 1966 and 1888 (Cr–C≡O), 1715 cm^{-1} (CO$_2$CH$_3$). δ_H 1.27, t, J 7.6 Hz, 3H, 3-CH$_2$CH_3; 2.80–2.95, m, 2H, 3-CH_2CH$_3$; 3.71–3.74, m, 2H, (H1)$_2$; 3.82, s, 3H, 2-CO$_2$CH$_3$; 5.19, bt, J 6.2 Hz, 1H, H5; 5.46, bt, J 6.1 Hz, 1H, H6; 5.73, bd, J 6.2 Hz, 1H, H4; 5.86, bd, J 6.4 Hz, 1H, H7. δ_c 13.24, 3-CH$_2$CH_3; 19.58, 3-CH_2CH$_3$; 38.72, C1; 51.50, 2-CO$_2$CH_3; 88.32, 88.94 (2C) and 92.96, C4, C5, C6 and C7; 112.25 and 113.97, C3a and C7a; 130.03, C2; 150.88, C3; 164.23, 2-CO$_2$CH$_3$; 232.67 (3C), Cr(CO)$_3$. m/z 338(M^+, 34), 307(M–OCH$_3$, 4), 282(M–2CO, 18), 254(282–CO, 100), 226 (28), 196(38), 171(52), 128(20), 52(Cr$^+$, 87); (iv) a mixture (0.20 g) of two diastereoisomers of tricarbonyl[(3a,4,5,6,7,7a-η)-3-ethyl-2,3-dihydro-2-methoxymethyl-1H-inden-1-ol]chromium, 15, and tricarbonyl[methyl (1,2,3,4,5,6-η)-4-methyl-5-oxo-5-phenylpentanoate]chromium (35). A solution of this mixture (0.20 g) in diethyl ether (50 ml) was exposed to bright sunlight for 3 h. The reaction mixture was filtered, concentrated in vacuo and purified by PLC to give in order of increasing polarity: (a) 3 (9 mg, 2%); (b) methyl 4-methyl-5-oxo-5-phenylpentanoate (32) (8 mg, 1%) as a clear oil. (Found: M^+, 220.1101. C$_{13}$H$_{16}$O$_3$. Calc.: M, 220.1099). ν_{max} (KBr) 1736 (CO$_2$CH$_3$), 1682 (R$_2$CO), 1597, 1579 and 1448 cm^{-1} (C=C). δ_H 1.21, d, J 6.5 Hz, 3H, 4-CH$_3$; 1.70–1.90, 2.05–2.50 and 3.48–3.65, m, 5H, (H2)$_2$, (H3)$_2$ and H4; 3.65, s, 3H, CO$_2$CH$_3$; 7.41–7.61, m, 3H, (H$_{meta}$)$_2$ and H$_{para}$; 7.97, bd, J 7.5 Hz, 2H, (H$_{ortho}$)$_2$. δ_c 17.36, 4-CH$_3$; 28.27, C2; 31.48, C2; 39.55, C4; 51.55, CO$_2$CH_3; 128.31 (2C), C$_{ortho}$; 128.67 (2C), C$_{meta}$; 133.04, C$_{para}$; 136.34, C$_{ipso}$; 173.74, CO$_2$CH$_3$; 203.52, C5. m/z 220(M^+, 10), 205 (M–CH$_3$, 3), 189(M–OCH$_3$, 10), 105(100), 77(30); (c) (1β,2β)-1-ethyl-2,3-dihydro-2-methoxycarbonyl-1H-inden-1-ol (42) (30 mg, 5%) as a clear oil. (Found: C, 70.8; H, 7.3. C$_{13}$H$_{16}$O$_3$. Calc.: C, 70.9; H, 7.3%). (Found: M^+–H$_2$O, 202.0993. C$_{13}$H$_{14}$O$_2$. Calc.: M–H$_2$O, 202.0994).

(Found: $M^{+\cdot}$–CH$_2$CH$_3$, 191.0708. C$_{11}$H$_{11}$O$_3$. Calc.: M–CH$_2$CH$_3$, 191.0708). ν_{max} (KBr) 3480 (OH), 1735 (CO$_2$CH$_3$), 1459 and 1438 cm^{-1} (C=C). δ_H 0.89, t, J 7.4 Hz, 3H, 1-CH$_2$CH_3; 1.91–2.20, m, 2H, 1-CH_2CH$_3$; 3.00–3.20, m, 1H, H3β; 3.13, s, 1H, 1-OH; 3.25–3.45, m, H2α and H3α; 3.75, s, 3H, 2-CO$_2$CH$_3$; 7.20–7.35, m, 4H, H4, H5, H6 and H7. δ_c 8.99, 1-CH$_2$CH_3; 31.98, 1-CH_2CH$_3$; 33.37, C3; 50.70, 2-CO$_2$CH$_3$; 51.89, C2; 84.72, C1; 123.21, 124.76, 127.12 and 128.69, C4, C5, C6 and C7; 141.16 and 144.75, C3a and C7a; 174.19, 2-CO$_2$CH$_3$. m/z 202(M–H$_2$O, 5), 191(M–CH$_2$CH$_3$, 73), 159(191–CH$_3$OH, 100), 143(60), 131(53), 103(25), 77(15); (d) (1β,2α)-1-ethyl-2,3-di-hydro-2-methoxycarbonyl-1H-inden-1-ol (43) (15 mg, 3%) as a clear oil. (Found: $M^{+\cdot}$–H$_2$O, 202.0991. C$_{13}$H$_{14}$O$_2$. Calc.: M–H$_2$O, 202.0994). (Found: $M^{+\cdot}$–CH$_2$CH$_3$, 191.0708. C$_{11}$H$_{11}$O$_3$. Calc.: M–CH$_2$CH$_3$, 191.0707). ν_{max} (KBr) 3484 (OH), 1736 (CO$_2$CH$_3$), 1464 and 1438 cm^{-1} (C=C). δ_H 0.86, t, J 7.4 Hz, 3H, 1-CH$_2$CH_3; 1.68, q, J 7.4 Hz, 2H, 1-CH_2CH$_3$; 2.38, bs, 1H, 1-OH; 3.04, dd, J 15.4, 7.9 Hz, 1H, H3α; 3.26, dd, J 15.4, 10.4 Hz, 1H, H3β; 3.40, dd, J 10.2, 7.9 Hz, 1H, H2β; 3.81, s, 3H, 2-CO$_2$CH$_3$; 7.22–7.35, m, 4H, H4, H5, H6 and H7. δ_c 7.61, 1-CH$_2$CH_3; 30.19, 1-CH_2CH$_3$; 51.83, 2-CO$_2$CH$_3$; 58.76, C2; 84.90, C1; 123.95, 124.74, 126.62 and 128.22; C4, C5, C6 and C7; 139.28 and 144.82, C3a and C7a; 172.87, 2-CO$_2$CH$_3$. m/z 202(M–H$_2$O, 3), 191(M–CH$_2$CH$_3$, 69), 159(191–CH$_3$OH, 100), 143(10), 103(22), 77(20); (v) the α diastereoisomer of tricarbonyl-[(1β,2β)-(3a,4,5,6,7,7a,-η)-1-ethyl-2,3-dihydro-2-methoxycarbo-nyl-1H-inden-1-ol]chromium (37) (0.57 g, 54%) as an orange solid which was recrystallised from diethyl ether as orange micro prisms, m.p. 158–164°C. (Found: C, 53.8; H, 4.3. C$_{16}$H$_{16}$CrO$_6$. Calc.: C, 53.9; H, 4.5%). (Found: $M^{+\cdot}$, 356.0348. C$_{16}$H$_{16}$CrO$_6$. Calc.: M, 356.0352). ν_{max} (KBr) 3456 (OH), 1967, 1898 and 1888 (Cr–C≡O), 1716 (CO$_2$CH$_3$), and 1438 cm^{-1} (C=C). δ_H 1.10, t, J 7.5 Hz, 3H, 1-CH$_2$CH_3; 1.98, dq, J 15.0, 7.5 Hz, 1H, 1-CH_2CH$_3$; 2.13, dq, J 15.0, 7.5 Hz, 1H, 1-CH_2CH$_3$; 3.00, dd, J 14.2, 6.7 Hz, 1H, H3β; 3.19, dd, J 10.0, 6.7 Hz, 1H, H2α; 3.25, dd, J 14.2, 9.9 Hz, 1H, H3α; 3.80, s, 3H, 2-CO$_2$CH$_3$; 4.41, s, 1H, 1-OH; 5.09, td, J 6.3, 0.8 Hz, 1H, H5; 5.23, bd, J 6.3 Hz, 1H, H4; 5.52, td, J 6.3, 0.7 Hz, 1H, H6; 5.73, bd, J 6.4 Hz, 1H, H7. δ_c 8.40, 1-CH$_2$CH_3; 32.15, C3; 33.48, 1-CH_2CH$_3$; 49.01, C2; 52.44, 2-CO$_2$CH$_3$; 82.31, C1; 86.05, 87.98, 91.52 and 95.64, C4, C5, C6 and C7; 114.24 (2C), C3a and C7a; 174.65, 2-CO$_2$C$_H$3; 232.53 (3C), Cr(CO)$_3$. m/z 356($M^{+\cdot}$, 33), 338(M–H$_2$O, 3), 324(M–CH$_3$OH, 2), 300(M–2CO, 8), 272(300–CO, 73), 257(100), 239(14), 226(15), 212(14), 196(20), 129(20), 52(Cr$^+$, 79).

3.20.5.2. With decomplexation.

Treatment of 27 (0.10 g, 0.23 mmol) with methyl propenoate (0.15 ml, 0.17

mmol) in refluxing benzene for 10.5 h afforded a red oil which was redissolved in diethyl ether and exposed to bright sunlight for 2 h. Filtration and purification by PLC (silica gel, hexanes–diethyl ether, multiple sweeps) afforded in order of increasing polarity: (i) 3-ethyl-2-methoxycarbonyl-1H-indene (57) (1 mg, 3%) as a clear oil. (Found: C, 77.1; H, 6.9. C$_{13}$H$_{14}$O$_2$. Calc.: C, 77.2; H, 7.0%). (Found: $M^{+\cdot}$, 202.0993. C$_{13}$H$_{14}$O$_2$. Calc.: M, 202.0994). ν_{max} (KBr) 1707 (CO$_2$CH$_3$), 1600, 1576 and 1435 cm^{-1} (C=C). δ_H 1.24, t, J 7.5 Hz, 3H, 3-CH$_2$CH_3; 3.07, bq, J 7.5 Hz, 2H, 3-CH_2CH$_3$; 3.66, bs, 2H, (H1)$_2$; 3.83, s, 3H, 2-CO$_2$CH$_3$; 7.30–7.58, m, 4H, H4, H5, H6 and H7. δ_c 13.46, 3-CH$_2$CH_3; 19.80, 3-CH_2CH$_3$; 38.76, C1; 51.12, 2-CO$_2$CH$_3$; 121.16, 124.10, 127.49 and 128.54, C4, C5, C6, and C7; 128.57, C2; 143.84 and 144.15, C3a and C7a; 157.71, C3; 165.99, 2-CO$_2$CH$_3$. m/z 202(M^+, 67), 171(M^+–OCH$_3$, 28), 143(100), 128(74), 115(35); (ii) 42 (36 mg, 71%); (iii) 43 (13 mg, 25%).

3.20.6. Thermally-promoted insertion of tert-butyl propenoate

Treatment of 27 (0.20 g, 0.46 mmol) with tert-butyl propenoate (0.20 ml, 0.15 mmol) in refluxing benzene for 11.5 h afforded a red oil which was redissolved in diethyl ether and exposed to bright sunlight for 3 h. Filtration and purification by PLC (hexanes–diethyl ether, multiple sweeps) afforded in order of increasing polarity: (i) 3-ethyl-2-(1,1-dimethylethoxycarbonyl)-1H-indene (58) (12 mg, 11%) as a clear oil (distilled at 100–105°C, 0.04 mm Hg). (Found: C, 78.4; H, 8.0. C$_{16}$H$_{20}$O$_2$. Calc.: C, 78.7; H, 8.3%). (Found: $M^{+\cdot}$, 244.1466. C$_{16}$H$_{20}$O$_2$. Calc.: M, 244.1463). ν_{max} (KBr) 1698 (CO$_2$C(CH$_3$)$_3$), 1600, 1574 and 1456 cm^{-1} (C=C). δ_H 1.24, t, J 7.5 Hz, 3H, 3-CH$_2$CH_3; 1.57, s, 9H, 2-CO$_2$C(CH$_3$)$_3$; 3.02, bq, J 7.5 Hz, 2H, 3-CH_2CH$_3$; 3.61, bs, 2H, (H1)$_2$; 7.26–7.52, m, 4H, H4, H5, H6 and H7. δ_c 13.55, 3-CH$_2$CH_3; 19.83, 3-CH$_2$CH$_3$; 28.40 (3C), 2-CO$_2$C(CH$_3$)$_3$; 39.04, C1; 80.18, 2-CO$_2$C(CH$_3$)$_3$; 120.96, 124.04, 126.41 and 127.22, C4, C5, C6, and C7; 130.97, C2; 143.79 and 144.54, C3a and C7a; 155.70, C3; 165.23, 2-CO$_2$C(CH$_3$)$_3$. m/z 244(M^+, 28), 188(M–CH$_2$=C(CH$_3$)$_2$, 100), 171(38), 143(94), 129(55), 115(22), 57(C(CH$_3$)$_3^+$, 47); (ii) 1,1-dimethylthyl 4-methyl-5-oxo-5-phenylpentanoate (33) (18 mg, 15%) as a clear oil (distilled at 105–110°C, 0.05 mm Hg). (Found: C, 72.9; H, 8.2. C$_{16}$H$_{22}$O$_3$. Calc.: C, 73.3; H, 8.5%). (Found: $M^{+\cdot}$, 262.1586. C$_{16}$H$_{22}$O$_3$. Calc.: M, 262.1569). ν_{max} (KBr) 1728 (CO$_2$Me), 1683 (R$_2$CO), 1597, 1580 and 1448 cm^{-1} (C=C). δ_H 1.21, d, J 6.5 Hz, 3H, 4-CH$_3$; 1.42, s, 9H, CO$_2$C(CH$_3$)$_3$; 1.65–1.83 and 2.02–2.35, m, 4H, (H2)$_2$, and (H3)$_2$; 3.57, sextet, J 6.8 Hz, H4; 7.46, bt, J 7.1 Hz, 2H, (H$_{meta}$)$_2$; 7.56, bt, J 7.2 Hz, 1H, H$_{para}$; 7.96, bd, J 7.3 Hz, 2H, (H$_{ortho}$)$_2$. δ_c 17.31, 4-CH$_3$; 28.04 (3C), CO$_2$C(CH$_3$)$_3$; 28.53, C3;

32.98, C2; 39.54, C4; 80.28, $CO_2C(CH_3)_3$; 128.29 (2C), C_{ortho}; 128.64 (2C), C_{meta}; 132.97, C_{para}; 136.45, C_{ipso}; 172.67, $CO_2C(CH_3)_3$; 203.77, C5. m/z 262($M^{+\cdot}$, 1), 206 (M–CH_2=$C(CH_3)_2$, 3), 189(27), 105(100), 77(30), 57($C(CH_3)_3^+$, 32); (iii) $(1\beta,2\beta)$-1-ethyl-2,3-dihydro-2-(1,1-dimethylethoxycarbonyl)-1H-inden-1-ol (46) (48 mg, 40%) as a white solid which was recrystallised from hexanes–dichloromethane as white needles, m.p. 86–88°C. (Found: C, 73.3; H, 8.5. $C_{16}H_{22}O_3$. Calc.: C, 73.3; H, 8.3%). (Found: $M^{+\cdot}$, 262.1800. $C_{16}H_{22}O_3$. Calc.: M, 262.1807). ν_{max} (KBr) 3427 (OH), 1716 ($CO_2C(CH_3)_3$), 1460 and 1368 cm^{-1} (C=C). δ_H 0.90, t, J 7.4 Hz, 3H, 1-CH_2CH_3; 1.49, s, 9H, 2-$CO_2C(CH_3)_3$; 1.96, dq, J 13.9, 7.4 Hz, 1H, 1-CH_2CH_3; 2.08, dq, J 13.8, 7.4 Hz, 1H, 1-CH_2CH_3; 3.08, dd, J 13.0, 7.4 Hz, 1H, H3β; 3.20, dd, J 7.3, 5.2 Hz, 1H, H2α; 3.31, dd, J 12.9, 5.2 Hz, 1H, H3α; 3.41, s, 1H, 1-OH; 7.20–7.32, m, H4, H5, H6 and H7. δ_c 8.97, 1-CH_2CH_3; 28.12 (3C), 2-$CO_2C(CH_3)_3$; 32.07, 1-CH_2CH_3; 32.07, C3; 51.31, C2; 81.37, 2-$CO_2C(CH_3)_3$; 84.44, C1; 123.13, 124.70, 127.03 and 128.51, C4, C5, C6 and C7; 141.29 and 145.28, C3a and C7a; 172.40, 2-$CO_2C(CH_3)_3$. m/z(NH$_3$) 278(M^+–H + NH$_3^+$, 4), 262(M, 8), 245(M–OH, 47), 233(M–CH_2CH_3, 8), 194(37), 189(80), 177(100), 159(82), 145(78), 131(25), 115(12), 103(11), 77(10); (iv) $(1\beta,2\alpha)$-1-ethyl-2,3-dihydro-2-methoxycarbonyl-1H-inden-1-ol (47) (17 mg, 14%) as a clear oil. (Found: $M^{+\cdot}$–CH_2CH_3, 233.1177. $C_{14}H_{17}O_3$. Calc.: M–CH_2CH_3, 233.1178). ν_{max} (KBr) 3444 (OH), 1722 ($CO_2C(CH_3)_3$), 1456 cm^{-1} (C=C). δ_H 0.85, t, J 7.4 Hz, 3H, 1-CH_2CH_3; 1.54, s, 9H, 2-$CO_2C(CH_3)_3$; 2.42, s, 1H, 1-OH; 1.74, q, J 7.4 Hz, 2H, 1-CH_2CH_3; 2.99, dd, J 15.4, 8.1 Hz, 1H, H3β; 3.16, dd, J 15.4, 10.0 Hz, 1H, H3α; 3.30, dd, J 10.0, 8.1 Hz, 1H, H2β; 7.20–7.38, m, H4, H5, H6 and H7. δ_c 7.75, 1-CH_2CH_3; 28.23 (3C), 2-$CO_2C(CH_3)_3$, 30.26, C3; 31.97, 1-CH_2CH_3; 59.42, C2; 81.31, 2-$CO_2C(CH_3)_3$; 84.70, C1; 123.92, 124.69, 126.49 and 128.05, C4, C5, C6 and C7; 139.49 and 144.93, C3a and C7a; 171.68, 2-$CO_2C(CH_3)_3$. m/z(NH$_3$) 278(M^+–H + NH$_3^+$, 18), 262(M, 11), 245(M–OH, 40), 233(M–CH_2CH_3, 7), 206(10), 194(40), 189(73), 177(100), 159(86), 145(82), 131(22).

Attempted thermally-promoted insertion reactions between 27 and vinyl acetate or ethoxyvinyl ether afforded after decomplexation and purification 3 (70–85%) as the only isolable product.

3.20.7. Chemically-promoted coupling with Me_3NO and methyl propenoate

A nitrogen-degassed solution of 27 (0.20 g, 0.23 mmol) in acetonitrile (5 ml) was treated with trimethylamine N-oxide (52 mg, 0.36 mmol) at room temperature under a nitrogen atmosphere. The red solution slowly deepened in colour. The reaction mixture was

stirred at ambient temperature for 5 min and was then treated with methyl propenoate (0.15 ml, 1.7 mmol). After 180 h at room temperature the reaction mixture was diluted with diethyl ether, filtered and concentrated. It was then redissolved in diethyl ether and exposed to bright sunlight for 3 h. Work-up and purification (PLC, diethyl ether–hexanes, multiple sweeps) afforded 3 (40 mg, 74%).

3.21. Coupling reactions of tricarbonyl[(((1,2,3,4,5,6-η)-2-(1-oxopropyl)phenyl)-C,O)tricarbonylmanganese-(triphenylphosphine)]chromium (29)

3.21.1. Thermally-promoted insertion of methyl propenoate

A solution of 29 (0.20 g, 0.30 mmol) and methyl propenoate (0.15 ml, 0.17 mmol) in benzene (20 ml) was heated to reflux under positive nitrogen pressure for 23 h. The reaction mixture was diluted with diethyl ether and filtered to give 29 as a red oil (0.19 g, 96%).

3.21.2. Thermally-promoted coupling with tert-butyl propenoate in toluene

A solution of 29 (0.20 g, 0.30 mmol) and tert-butyl propenoate (0.15 ml, 0.17 mmol) in toluene (20 ml) was heated to reflux under positive nitrogen pressure for 24 h. The reaction mixture was diluted with diethyl ether, filtered and purified (PLC, diethyl ether–hexanes, multiple sweeps) to give: (i) triphenylphosphine (43 mg); (ii) 57 (6 mg, 8%); (iii) 3 (17 mg, 41%); (iv) 33 (30 mg, 37%).

3.21.3. Chemically-promoted coupling with Me_3NO and methyl propenoate

A nitrogen-degassed solution of 29 (0.20 g, 0.30 mmol) in acetonitrile (5 ml) was treated with trimethylamine N-oxide (35 mg, 0.46 mmol) at room temperature under a nitrogen atmosphere. No apparent colour change was observed. The reaction mixture was stirred at ambient temperature for 5 min and was then treated with methyl propenoate (0.15 ml, 0.17 mmol). After 200 h at room temperature the reaction mixture was diluted with diethyl ether filtered and purified (PLC, diethyl ether, multiple sweeps) to give: (i) triphenylphosphine (42 mg); (ii) 3 (33 mg, 80%); (iii) 32 (7 mg, 10%).

3.22. Coupling reactions of tetracarbonyl[(2-(1-oxopropyl)phenyl)-C,O]manganese (24)

3.22.1. Thermally-promoted insertion of phenylacetylene

A solution of 24 (0.20 g, 0.67 mmol) and phenylacetylene (0.28 g, 2.67 mmol) in benzene (20 ml) was heated to reflux under positive nitrogen pressure for 11 h. The reaction mixture was concentrated to give a red

oil (0.15 g). Attempted purification by PLC afforded 15 bands of similar intensities, none of which were investigated further.

3.22.2. Thermally-promoted insertion of diphenylacetylene

A solution of **24** (0.20 g, 0.67 mmol) and diphenylacetylene (0.48 g, 2.67 mmol) in benzene (20 ml) was heated to reflux under positive nitrogen pressure for 11 h. The reaction mixture was concentrated and purified (PLC, diethyl ether–hexanes) to give **55** (0.19 g, 92%).

3.22.3. Thermally-promoted insertion of 3-hexyne

A solution of **24** (0.20 g, 0.67 mmol) and 3-hexyne (0.22 g, 2.67 mmol) in benzene (20 ml) was heated to reflux under positive nitrogen pressure for 12.5 h. The reaction mixture was concentrated and purified (PLC, diethyl ether–hexanes) to give **61** (0.13 g, 92%).

3.22.4. Thermally-promoted insertion of methyl propenoate

A solution of **24** (0.20 g, 0.67 mmol) and methyl propenoate (0.15 ml, 1.75 mmol) in benzene (20 ml) was heated to reflux under positive nitrogen pressure for 11.5 h. The reaction mixture was concentrated and purified (PLC, diethyl ether–hexanes) to give in order of increasing polarity: (i) **57** (40 mg, 30%); (ii) an unidentified compound (19 mg); (iii) **42** (3 mg, 2%); (iv) **43** (48 mg, 33%).

3.22.5. Thermally-promoted insertion of tert-butyl propenoate

A solution of **24** (0.20 g, 0.67 mmol) and *tert*-butyl propenoate (0.15 ml, 1.75 mmol) in benzene (20 ml) was heated to reflux under positive nitrogen pressure for 11 h. The reaction mixture was concentrated and purified (PLC, diethyl ether–hexanes) to give in order of increasing polarity: (i) **58** (60 mg, 37%); (ii) **46** (58 mg, 33%); (iii) **47** (21 mg, 12%).

3.22.6. Chemically-promoted coupling with Me_3NO and methyl propenoate

A nitrogen-degassed solution of **24** (0.20 g, 0.67 mmol) in acetonitrile (5 ml) was treated with trimethylamine N-oxide (75 mg, 1.00 mmol) at room temperature under a nitrogen atmosphere. A deep red solution formed immediately. The reaction mixture was stirred at ambient temperature for 5 min and was then treated with methyl propenoate (0.15 ml, 0.17 mmol). After 24 h at room temperature the reaction mixture was diluted with diethyl ether, filtered, and purified (PLC, diethyl ether, multiple elution) to give in order of increasing polarity: (i) methyl 3-[2-((1-oxopropyl)phenyl)]propanoate (**34**) (22 mg, 15%) as a clear oil (distilled at 100–105°C, 0.05 mm Hg). (Found: C, 70.5; H, 7.1. $C_{13}H_{16}O_3$. Calc.: C, 70.9; H, 7.3%). (Found: M^+,

220.1100. $C_{13}H_{16}O_3$. Calc.: M^+, 220.1099). ν_{max}(KBr) 1739 (RCO_2CH_3), 1689 (R_2CO), 1600, 1573 and 1437 cm^{-1} (C=C). δ_H 1.20, t, J 7.3 Hz, 3H, $COCH_2CH_3$; 2.66, bt, J 7.9 Hz, 2H, $CH_2CH_2CO_2CH_3$; 2.93, q, J 7.2 Hz, 2H, $COCH_2CH_3$; 3.65, s, 3H, $CH_2CH_2CO_2CH_3$; 7.24–7.46, m, 3H and 7.61–7.67, m, 1H, aromatic H. δ_c 8.36, $COCH_2CH_3$; 29.47, $CH_2CH_2CO_2CH_3$; 34.72, $COCH_2CH_3$; 35.77, $CH_2CH_2CO_2CH_3$; 51.49, $CH_2CH_2CO_2CH_3$; 126.33, 128.53, 131.28 and 131.32, aromatic CH; 137.95 and 140.41, C_{ipso}; 173.47, $CH_2CH_2CO_2CH_3$; 204.87, $COCH_2CH_3$. m/z 220(M^+, 20), 202($M-H_2O$, 3), 191($M-CH_2CH_3$, 45), 189($M-OCH_3$, 13), 163(23), 159(50), 145(10), 143(20), 131(100), 103(30), 91(22), 77(24); (ii) **42** (66 mg, 45%); (iii) **43** (34 mg, 23%).

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