Manganese-mediated synthesis of *cis*-disubstituted cyclohexadienes via double nucleophilic addition to coordinated arenes

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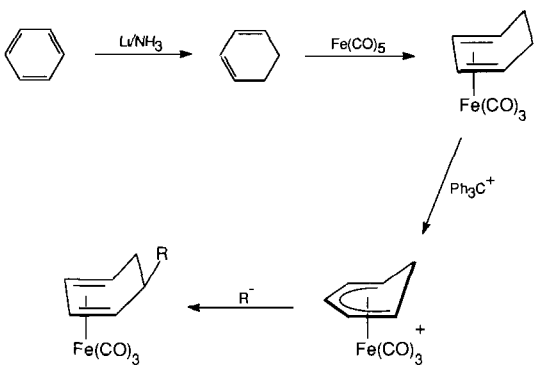
Abstract

The addition of carbon donor nucleophiles to (arene)$Mn(CO)_2L^+$ (L = CO, $P(OPh)_3$, PMe_3), followed by replacement of a CO with NO^+, affords monofunctionalized (cyclohexadienyl)Mn(CO)(NO)L^+ complexes (**12**). A study has been made of nucleophilic addition to **12** to yield cyclohexadiene complexes (**13**). The yield of the reaction of **12** with soft stabilized carbon donors (e.g. $NaCH(CO_2Et)CN$) improves substantially when the ligand L = CO is replaced by L = $P(OPh)_3$ or PMe_3. Hydride donors give good yields of monofunctionalized cyclohexadiene complexes regardless of the nature of L. When L ≠ CO, significant chiral discrimination takes place and the product is obtained as a mixture of diastereomers. Oxidation of the (cyclohexadiene)Mn(CO)(NO)L complexes with $FeCl_3$ or Me_3NO generates the free hydrocarbon ligand as *cis*-disubstituted cyclohexa-1,3-dienes or cyclohexen-1-ones, the latter resulting from hydrolysis of a methoxy substituent Hard carbon donors such as LiPh and LiMe attack a CO in **12**, ultimately converting to *trans*-disubstituted cyclohexadienes. This work shows that the manganese-mediated double nucleophilic addition to arenes can be an efficient route to functionalized cyclohexadienes.

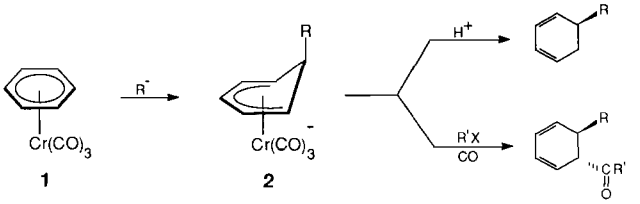
Introduction

The conversion of arenes to functionalized cyclohexadienes is an important reaction that can be facilitated by coordination to transition metals. The procedures that offer the most promise of being general in nature are based on iron, chromium and manganese. These are outlined in Schemes 1–3 with benzene as the generic arene, although in many cases of synthetic interest the arene starting material would bear a variety of substituents. Several more specialized reactions that generate cyclohexadienes from arenes have also been reported [1].

Provided the appropriate diene can be obtained from the arene starting material, the chemistry in Scheme 1 provides good yields of monosubstituted products [2]; in certain specific cases disubstitution can be realized [3]. Strong nucleophiles add to (arene)$Cr(CO)_3$ (**1**) according to Scheme 2. Treatment of the anionic cyclohexadienyl intermediate (**2**) with acid leads to monosubstituted dienes [4]. Recent elegant work by Kündig *et al.* [5] has shown that the sequence of nucleophilic



Scheme 1



Scheme 2

addition to **1** followed by attack on **2** by a variety of electrophiles generates *trans*-disubstituted cyclohexadienes. The cationic manganese complexes (arene)-

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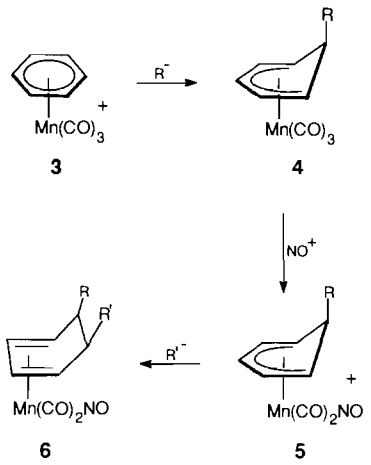
$Mn(CO)_3^+$ (**3**) are much more electrophilic than the neutral chromium analogues and a very wide range of nucleophiles has been found to react rapidly to give cyclohexadienyl complexes **4** in good yield (see Scheme 3) [6, 7]. The addition of a second nucleophile to **4** would constitute a direct route to disubstituted cyclohexadienes. This approach is limited by the weak electrophilicity of **4**, with the result that many convenient nucleophiles (stabilized enolates, ketone enolates, Grignard reagents, most hydride donors, etc.) do not react. Very recent reports have shown that strong nucleophiles can react with **4** in two ways. The hard bases LiMe and LiPh attack a CO ligand in **4** to give isolable acylmetalates (**7**). These react with acid to afford mixtures of isomeric cyclohexenyl complexes, from which cyclohexadienes can be obtained after decomplexation from the metal [8]. McDaniel and co-workers [9] found that strong ester, nitrile and sulfur-stabilized lithium carbanions add directly to the ring in **4** to give transient anionic (cyclohexadiene)$Mn(CO)_3^-$ species that decompose to afford good yields of *cis*-disubstituted cyclohexadienes.

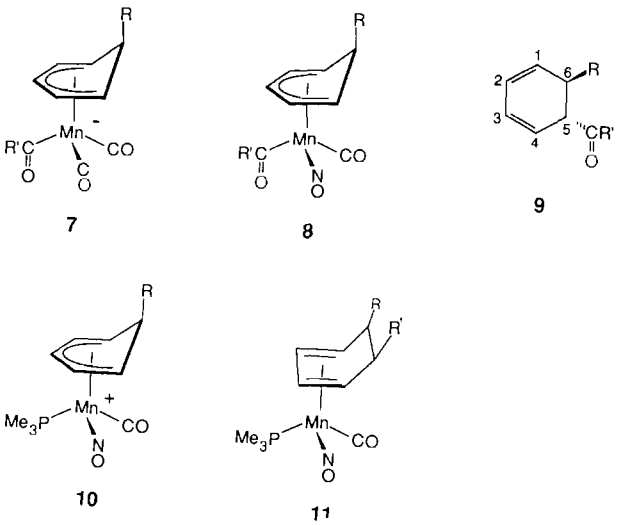
In order to render the complexed dienyl ring in **4** receptive to nucleophiles of varying strengths, we 'reactivated' **4** by treatment with $NOPF_6$ to afford the cationic nitrosyl analogue **5**, which was determined to be more electrophilic than even (arene)$Mn(CO)_3^+$ [10–12]. The overall procedure in Scheme 3 amounts to double nucleophilic addition to an arene. When the second nucleophile is a hydride donor, high yields of monosubstituted diene complexes **6** (R′ = H) are obtained. The hydride addition was found to be highly regioselective as well as stereospecific*. Decomplexation of the diene from **6** can be accomplished with a variety of oxidizing agents (*vide infra*) [13, 14]. The procedure in Scheme 3 (R′ = H) has recently been used by Miles and Brinkman [14] to synthesize the sesquiterpene (+)-juvabione. In comparison to the iron-based chemistry in Scheme 1, the synthesis of monosubstituted cyclohexadienes based on manganese offers the advantage of facile complexation of the arene starting material to $Mn(CO)_3^+$ without the initial Birch reduction and subsequent hydride abstraction required with iron.

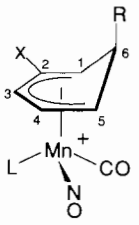
When the nucleophile R'^- in Scheme 3 is a carbon donor, the yields of **6** are generally low [10]. With certain donors (LiMe, LiPh, etc.) attack occurs at a CO ligand in **5** to give the acyl species **8**, which is thermally unstable and spontaneously decomposes to generate the *trans*-disubstituted diene **9** in moderate yield (*vide infra*) [8, 11, 13]. Apparently, the acyl group in **8** readily migrates to the cyclohexadienyl ring, which is followed by decomplexation of diene **9**. In general, however, the reaction of **5** with carbon donors leads predominantly to decomposition. We reasoned that this disappointing result could be due to interference by redox pathways and that substitution of a CO in **5** by a more electron-donating phosphine ligand may diminish the role of single electron transfer steps while maintaining sufficiently high electrophilicity so that weak carbon donors could add to the ring. In a preliminary communication [15] we showed that the addition of $NaCH(CO_2Me)_2$ to **10** (R = Me, Ph) results in good yields of the *cis*-disubstituted diene complex **11**. The chiral metal center in **10** leads to significant diastereoselectivity in the reaction to give **11**. Diastereomeric forms of **11** for R = Ph, R′ = $CH(CO_2Me)_2$ and for R = Ph, R′ = H were separated and individually characterized by NMR and X-ray crystallography.



Scheme 3.

*As detailed in ref. 11, hydride attacks **5** to give a formyl intermediate that transforms to **6**, with the incoming H atom situated *endo* to the metal, not *exo* as normally found in nucleophilic addition reactions Note that R′ in structure **6** is drawn in the exo position.





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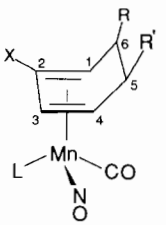


13

Herein we present a study of the nucleophilic addition of a series of stabilized carbon donors and several other types of donors to complex **12** having L=CO, PMe_3 and $P(OPh)_3$, and X=H and OMe. It is shown that good yields of **13** can be obtained when L is a phosphorus ligand and that significant chiral discrimination takes place. Decomplexation and, in some cases, hydrolysis of the diene ligand is discussed. The propensity for a nucleophile to attack a CO ligand in **12** in preference to the dienyl ring is explored as a function of the nature of L and the nucleophile.

Results and discussion

The cyclohexadienyl complexes [(RCH)Mn(CO)(NO)L]X (**12**; X=PF_6^- or BF_4^-) were readily synthesized by nucleophilic addition of R'^- to [(arene)$Mn(CO)_2$L]X, followed by reaction with $NOPF_6$ or $NOBF_4$. The yield of each step in this two-reaction sequence was generally moderate to high (see 'Experimental').

The addition of carbon donor and sulfur donor nucleophiles (R'^-) to **12** gave yields of the diene complex **13** that depended markedly on the nature of the nucleophile and of the ligand L. In contrast, hydride donors were found to react with **12** to produce **13** in high yield regardless of the identity of L. Table 1 lists some results with 'soft' stabilized carbon donors and with hydride and sulfur donors. The reactions were conveniently followed by monitoring the ν(CO) and ν(NO) bands in the IR. Conventional methodology was used to isolate the cyclohexadiene complexes (**13**), which were sufficiently stable thermally to allow facile characterization by IR, NMR and MS (see 'Experimental').

It is apparent from Table 1 that replacement of a CO ligand in **12** with $P(OPh)_3$ or PMe_3 leads to improved yields of **13** with stabilized carbon donor nucleophiles. This is especially evident with additions to **12-3** compared to **12-4** as well as with the addition of $NaCH(CN)_2$ and NaCp to **12-5** compared to **12-6**. It is possible that the better yields obtained when the ligand L is $P(OPh)_3$ or PMe_3, rather than CO, stems from a decreased probability of single electron transfer with the former, more electron-rich, complexes. In most of the addition reactions in Table 1, chiral discrimination is possible, and this led to the formation of diastereomeric product mixtures that were easily discernible by NMR. The C donor nucleophiles produced only modest diastereoselectivity, with the ratio of diastereomers being variable from experiment to experiment but always in the range 1.4–2.0. The addition of the H donor $NaBH_4$ to **12-6** gave a 2:1 ratio of diastereomers, but certain other H donors, such as $LiBEt_3H$ and R-Alpine Hydride, gave ratios >10:1 [16]. In spite of the generally modest diastereoselectivity observed for nucleophilic additions to **12**, the fact [15] that the diastereomers can be separated via chromatography means that optically pure cyclohexadiene complexes **13** can be obtained provided the cyclohexadienyl complexes **12** that are chiral (**12-2, 12-3, 12-4, 12-6**) can be resolved; this is currently under investigation.

The potential synthetic utility of nucleophilic additions to manganese complexes such as **12** depends on the ease with which the cyclohexadiene ligand can be removed from **13**. This was accomplished by treatment of **13** with a mild oxidizing agent. Thus, **13-23** liberated 5-phenylcyclohexa-1,3-diene in 90% yield when stirred with $FeCl_3$ in THF. With most cases of **13** having X=H, trimethylamine oxide in benzene was used to generate the free *cis*-disubstituted cyclohexa-1,3-dienes (**14**) in unoptimized yields that averaged 50–60% (pathway (a) in Scheme 4)*. When the diene complexes **13** (X=H) had a chiral center in the R′ substituent, the free dienes **14** were obtained as a mixture of a diastereomers.

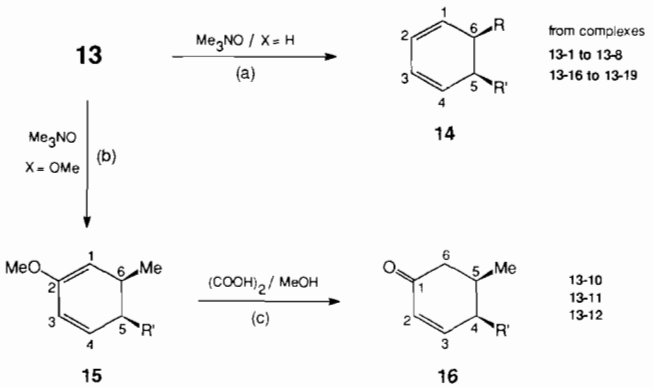
Complexes **13-10** to **13-12**, having X=OMe, were oxidized to **15**, which were readily hydrolyzed with oxalic acid in methanol to *cis*-4,5-disubstituted 2-cyclohexen-1-ones (**16**) by pathways (b) and (c) in Scheme 4. Such structural units are important in natural products chemistry and it is especially noteworthy that the manganese-mediated reactions permit the introduction of a wide variety of substituents in the otherwise-difficult-to-functionalize 5-position in **16**. This is so because (arene)$Mn(CO)_2L^+$ complexes react cleanly with a wide range of nucleophiles and a methoxy substituent on the arene ring is a strong *meta*-director in nucleophilic additions, which leads to **12** (X=OMe) after treatment with NO^+ [17]. The oxidation of **13-9** differed from the other methoxy-substituted complexes in that double bond isomerization occurred to produce diene **17** (51% yield) and, after hydrolysis, the disubstituted 3-cyclohexen-1-one **18** (84% yield) as shown in Scheme 5; this type of isomerization was described by us previously [18].

*Prolonged exposure of **13-16** to **13-19** to Me_3NO/benzene led to rearomatization to disubstituted arenes, limiting the reaction time to 1–2 h produced the diene with minimal rearomatization

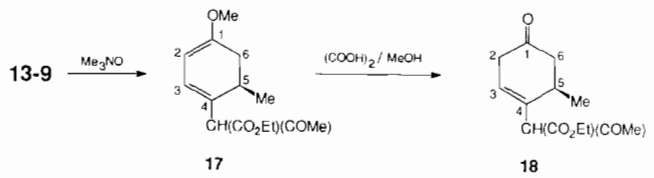
TABLE 1. Results of nucleophilic addition to (cyclohexadienyl)Mn(CO)(NO)L$^+$ complexes (**12**) to yield (cyclohexadiene)Mn(CO)(NO)L complexes (**13**)[a]

Reactant complex	X	R	L	Nucleophile	Yield of **13** (%)[b]	Product complex
12-1	H	Me	CO	$NaCH(CO_2Et)(COMe)$	67	**13-1**
12-1	H	Me	CO	$NaCH(CO_2Et)CN$	59	**13-2**
12-1	H	Me	CO	$NaCH(CO_2Me)(SO_2Ph)$	67	**13-3**
12-1	H	Me	CO	$NaSCH_2CH_2OH$	60	**13-4**
12-2	H	Me	$P(OPh)_3$	$NaCH(CO_2Et)(COMe)$	79	**13-5**
12-2	H	Me	$P(OPh)_3$	$NaCH(CO_2Et)CN$	82	**13-6**
12-2	H	Me	$P(OPh)_3$	$NaCH(CO_2Me)(SO_2Ph)$	83	**13-7**
12-2	H	Me	$P(OPh)_3$	$NaSCH_2CH_2OH$	83	**13-8**
12-3	OMe	Me	CO	$NaCH(CO_2Et)(COMe)$	18	**13-9**
12-3	OMe	Me	CO	$NaCH(CO_2Et)CN$	27	**13-10**
12-3	OMe	Me	CO	$NaCH(CO_2Me)(SO_2Ph)$	28	**13-11**
12-3	OMe	Me	CO	$NaSCH_2CH_2OH$	50	**13-12**
12-4	OMe	Me	$P(OPh)_3$	$NaCH(CO_2Et)(COMe)$	62	**13-13**
12-4	OMe	Me	$P(OPh)_3$	$NaCH(CO_2Et)CN$	80	**13-14**
12-4	OMe	Me	$P(OPh)_3$	$NaCH(CO_2Me)(SO_2Ph)$	82	**13-15**
12-5	H	Ph	CO	$NaCH(CO_2Et)(COMe)$	66	**13-16**
12-5	H	Ph	CO	$NaCH(CO_2Et)CN$	59	**13-17**
12-5	H	Ph	CO	$NaCH(CO_2Me)(SO_2Ph)$	62	**13-18**
12-5	H	Ph	CO	$NaSCH_2CH_2OH$	87	**13-19**
12-5	H	Ph	CO	$NaBH_4$	85	**13-20**
12-5	H	Ph	CO	$NaCH(CN)_2$	[c]	**13-21**
12-5	H	Ph	CO	NaCp	[c]	**13-22**
12-6	H	Ph	PMe_3	$NaBH_4$	85	**13-23**
12-6	H	Ph	PMe_3	$NaCH(CN)_2$	94	**13-24**
12-6	H	Ph	PMe_3	NaCp	62	**13-25**
12-6	H	Ph	PMe_3	$NaCH(CO_2Me)_2$	80	**13-26**

[a]See 'Experimental' for procedural and characterization details [b]Isolated yield. [c]A mixture of products was formed, with the diene complex **13** being a minor component (<10%).



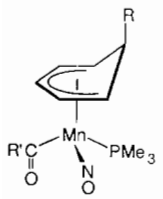
Scheme 4.



Scheme 5.

The reaction of **12** (X = H; L = CO, PMe_3) with the hard nucleophiles LiPh and LiMe was also investigated. Sheridan *et al.* [8] have recently shown that LiPh adds to the neutral tricarbonyl **4** to give the anionic benzoyl complex **7** (R = Me; R′ = Ph), which was converted to the corresponding neutral nitrosyl complex **8** in 46% yield. The free *trans*-disubstituted diene (**9**, R = Me; R′ = Ph) was obtained in 65% yield by prolonged stirring of **8** in solution at room temperature. We found that complexes **8** are also formed when the nucleophilic addition/NO^+ steps are reversed Thus, treatment of **5** (R = Ph) with LiPh or LiMe at −78 °C led to a high *in situ* conversion to **8** (R′ = Ph, Me) as shown by IR spectroscopy. In accordance with the results of Sheridan *et al.* [8], we found that these complexes readily liberate the free diene **9** at room temperature, possibly by a mechanism involving acyl migration to the dienyl ring to give an unstable transient diene complex with an open coordination site. In an attempt to trap the diene complex prior to dissociation of the free diene, PMe_3 was added to a low temperature solution of **8** (R = Ph; R′ = Me). Upon warming, only decomposition occurred. The low temperature addition of LiPh and LiMe to

10 (R = Ph, Me) also occurred at the carbonyl to give acyl complexes (**19**). Similarly to the behavior of **8**, complexes **19** were found to be thermally unstable at room temperature with respect to liberation of free diene **9**, even in the presence of excess PMe_3 or CO.



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Conclusions

In this work we have shown that the manganese-mediated double nucleophilic addition to arenes to afford *cis*-disubstituted cyclohexa-1,3-dienes and cyclohexen-1-ones is an efficient process when the L ligand in **12** is $P(OPh)_3$ or PMe_3 and when the nucleophile R'^- is a soft stabilized carbon donor. High yields of monofunctionalized cyclohexadienes result from the addition of hydride donors to **12** (L = PR_3 or CO). Particularly attractive features of this chemistry include the use of arenes as starting materials, the ease of complexation of the arenes to the $Mn(CO)_2L^+$ moiety, and the wide range of chemical groups that can be introduced in the first nucleophilic addition step (R in **12**). Also of importance is the fact that the chiral metal center in **12** ($L \neq CO$) provides a potential route to optically pure cyclohexadienes.

Hard carbon donors such as LiPh and LiMe attack the CO in **12**, ultimately affording *trans*-disubstituted cyclohexadienes; how useful or general this reaction sequence will prove to be is yet to be determined.

Experimental

The details of the synthesis of $[(arene)Mn(CO)_2L]PF_6$ (L = CO, PMe_3) and of $[(cyclohexadienyl)Mn(CO)(NO)L]PF_6$ (**12**; L = CO, PMe_3; R = Ph, Me) have been reported previously [10, 11, 16]. The analogous complexes with L = $P(OPh)_3$ were synthesized similarly in yields that averaged *c.* 70%. The addition of hydride donors to **12** (L = CO, PMe_3) and of $NaCH(CO_2Me)_2$ to **12** (L = PMe_3) to generate **13** followed our published procedures [10, 15]. Details of the syntheses of new compounds are summarized below and IR, NMR and MS analytical data are provided in Table 2.

Nucleophilic addition to [(cyclohexadienyl)Mn(CO)(NO)L]BF_4 (or -PF_6) (12; L = CO, $P(OPh)_3$, PMe_3; R = Ph, Me; X = H, OMe)

A typical synthesis is as follows. To a THF solution of NaH (82 mg, 3.4 mmol) at 0 °C under nitrogen, $CH_2(CO_2Et)(COMe)$(0.43 ml) was added with stirring. After 10 min the solution became clear and the carbanion solution was then added via syringe to a suspension of the tetrafluoroborate salt of **12-1** (0.77 g, 2.0 mmol) in 30 ml of THF. After stirring at 0 °C for 10 min, the reaction mixture was warmed to room temperature, poured into 50 ml of saturated NH_4Cl, and extracted three times with 30 ml portions of diethyl ether. The combined ether extracts were washed with water (30 ml × 3), dried ($MgSO_4$), and stripped *in vacuo* to yield crude **13-1**. Analytically pure **13-1** (0.49 g, 67%) was obtained after column chromatography on silica gel using cyclohexane/diethyl ether (4:1) as elutant. The compounds **13-2** to **13-19** were synthesized by the same procedure used to prepare **13-1**.

The addition of NaCp (0.10 ml of 2 M THF solution) to a 30 ml CH_2Cl_2 solution of **12-5** (39 mg. 0.090 mmol) at −78 °C led to a rapid color change. An IR taken after warming to room temperature suggested attack had occurred predominantly at a CO ligand; however, decomposition accompanied solvent removal and filtration through alumina left (6-*exo*-PhC_6H_6)$Mn(CO)_3$ as the only CO-containing species. The addition of NaCp to **12-6** by the same procedure produced the diene complex **13-25** in 62% yield.

The anion of malononitrile was prepared by adding NaH (20 mg, 0.83 mmol) to $CH_2(CN)_2$ (54 mg, 0.81 mmol) in 10 ml THF at room temperature. This solution was cooled to −78 °C and 1.2 ml added to a THF solution of **12-5** at −78 °C (36 mg, 0.081 mmol, 10 ml). As with NaCp, IR spectra implied carbonyl attack, but workup again led to (6-*exo*-PhC_6H_6)$Mn(CO)_3$ as the principal organometallic species. In contrast, the addition of $NaCH(CN)_2$ to **12-6** by the same procedure produced **13-24** in 94% yield.

Decomplexation of cyclohexadienes from complexes 13

Two methods of freeing the diene from the metal in **13** were tried. The first is based on the method of Nesmeyanov *et al.* [19]: diene complex **13-23** (13 mg, 0.038 mmol) was dissolved in THF and treated with excess $FeCl_3$. After stirring for 1 h, the brown reaction mixture was evaporated and the residue dissolved in 2 M HCl and extracted twice with CH_2Cl_2. The CH_2Cl_2 solution was washed with saturated aqueous $NaHSO_3$, then with saturated aqueous NaCl, and dried over $MgSO_4$. Evaporation left 5.4 mg (90%) of a colorless oil, which gave a ^1H NMR spectrum identical to the literature report [20] for 5-phenylcyclohexa-1,3-diene.

TABLE 2 Characterization of new compounds

Compound	
9 (R = R′ = Ph)	^{1}H NMR (C_6D_6) δ 7.4 (m, Ph), 5 81 (m, $H^{2,3}$), 5 75 (m, H^1), 5 38 (m, H^4), 4 59 (d, J = 10 2, H^6), 4.27 (ddd, J = 10.2, 4.4, 2.3, H^5), MS m/z 260 (M^+), 258 ($M^+ - 2H$), 181 ($M^+ - Ph$), 155 ($M^+ - COPh$), 105 ($COPh^+$), 77 (Ph^+)
9 (R = Me, R′ = Ph)	^{1}H NMR ($CDCl_3$) δ 7.5 (m, Ph), 5.99 (m, H^3), 5 87 (m, H^2), 5.76 (dd, J = 9.5, 3.3, H^1), 5.58 (dd, J = 9 4, 3 7, H^4), 3.97 (dt, J = 11.9, 3.2, H^5), 3.08 (m, H^6), 1 08 (d, J = 7 1, CH_3), MS m/z 198 (M^+), 196 ($M^+ - 2H$), 183 ($M^+ - Me$), 105 ($PhCO^+$), 93 ($C_6H_6Me^+$)
9 (R = Ph, R′ = Me)	^{1}H NMR ($CDCl_3$) 7.4 (m, Ph), 6 07 (m, $H^{2,3}$), 5 82 (ddt, J = 9 3, 4 6, 1 1, H^1), 5 73 (ddt, J = 9 4, 5 0, 1 1, H^4), 4.15 (ddd, J = 7 3, 4 6, 1 9, H^6), 3 41 (ddd, J = 7 5, 5.1, 2 0, H^5), 2.15 (s, CH_3)
13-1	IR (NaCl) 2030, 1975, 1732, 1720 cm^{-1}; ^{13}C NMR (C_6D_6) (major diastereomer) δ 200 0 (C=O), 168 2 (CO_2), 89.4, 86.3, 73.5, 65 8, 32.8, 28.2 (cyclohexadiene), 61 0 (OCH_2CH_3), 39.2 (CH), 29.9 ($COCH_3$), 21.9 (CH_3), 13.7 (OCH_2CH_3), (minor diastereomer) 200.0 (C=O), 168.4 (CO_2), 89 4, 86.3, 73.5, 66.8, 33.5, 29.0 (cyclohexadiene), 61 0 (OCH_2CH_3), 39.8 (CH), 29.90 ($COCH_3$), 21.9 (CH_3), 13 7 (OCH_2CH_3); MS m/z 307 ($M^+ - 2CO$), 277 ($M^+ - 2CO - NO$), 262 ($M^+ - 2CO - NO - Me$), 234 ($M^+ - 2CO - NO - Me - COMe$)
13-2	IR (NaCl) 2240, 2030, 1970, 1735, 1727 cm^{-1}; ^{13}C NMR (C_6D_6) (major diastereomer) δ 165 9 (CO_2), 116 8 (CN), 89 7, 87 6, 73 4, 62.6, 40.8, 34.1 (cyclohexadiene), 64.5 (OCH_2CH_3), 40.8 (CH), 21.2 (CH_3), 13 8 (OCH_2CH_3); (minor diastereomer) 165.4 (CO_2), 116 8 (CN), 89 4, 87 3, 73 0, 62 4, 41 4, 33 3 (cyclohexadiene), 64 5 (OCH_2CH_3), 41.1 (CH), 21.2 (CH_3), 13 8 (OCH_2CH_3); MS m/z 290 ($M^+ - 2CO$), 260 ($M^+ - 2CO - NO$), 245 ($M^+ - 2CO - NO - CH_3$), 234 ($M^+ - 2CO - NO - CH_3 - CN$)
13-3	IR (KBr) 2038, 1974, 1737, 1322, 1142 cm^{-1}; ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 222 3 (CO), 166.5 (CO_2), 137 7, 134 3, 129 4, 129.1 (Ph), 89.5, 86 8, 72.4, 65.9, 33.8, 26.9 (cyclohexadiene), 52.5 (OCH_3), 39.4 (CH), 22 0 (CH_3), (minor diastereomer) 222.3 (CO), 165 9 (CO_2), 137 7, 134 3, 129 4, 129 1 (Ph), 89 4, 86 7, 73 3, 65 4, 33 6, 26 9 (cyclohexadiene), 52.5 (OCH_3), 39.5 (CH), 23 2 (CH_3); MS m/z 391 ($M^+ - 2CO$), 360 ($M^+ - 2CO - NO - H$), 346 ($M^+ - 2CO - NO - CH_3$)
13-4	IR (Et_2O) 3370, 2038, 1973, 1737 cm^{-1}; ^{13}C NMR (CCl_4 + d_6-acetone) δ 221 7 (CO), 86.4, 86.3, 71 6, 60 0, 46 8, 34 3 (cyclohexadiene), 68.0 (OCH_2), 33 7 (SCH_2), 22 7 (CH_3), MS m/z 255 ($M^+ - 2CO$), 225 ($M^+ - 2CO - NO$), 210 ($M^+ - 2CO - NO - CH_3$), 148 ($M^+ - 2CO - NO - SCH_2CH_2OH$)
13-5	IR (NaCl) 1968, 1736, 1719, 1708 cm^{-1}; ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 192.8 (CO), 159 8 (CO_2), 142 0, 120 6, 115.9, 112 1 (Ph), 79 7, 75 3, 64 6, 57.3, 55 2, 52.3 (cyclohexadiene), 64.4 (OCH_2), 30 1 (CH), 23 7 ($COCH_3$), 20 1 (CH_3), 13 3 (OCH_2CH_3), (minor diastereomer) 192 8 (CO), 159 6 (CO_2), 142 0, 120.6, 115.9, 112 1 (Ph), 79.6, 75.4, 64.8, 57 3, 55.1, 52 1 (cyclohexadiene), 64.4 (OCH_2), 30 1 (CH), 23 7 ($COCH_3$), 20 1 (CH_3), 13 3 (OCH_2CH_3), MS m/z 516 ($M^+ - CH(CO_2Et)COMe$), 488 ($M^+ - CH(CO_2Et)COMe - CO$)
13-6	IR (NaCl) 2243, 1967, 1735, 1720 cm^{-1}, ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 229.3 (CO), 165 1 (CO_2), 150 1, 128.8, 124.1, 120 1 (Ph), 116 4 (CN), 88.2, 84.4, 71.9, 60 2, 40 2, 32.9 (cyclohexadiene), 61.7 (OCH_2), 42.5 (CH), 20 5 (CH_3), 12 9 (OCH_2CH_3); (minor diastereomer) 229.3 (CO), 164.6 (CO_2), 150.1, 128.8, 124 1, 120.1 (Ph), 116 4 (CN), 88 0, 84.0, 71 7, 60.4, 40.6, 32.9 (cyclohexadiene), 61.7 (OCH_2), 42 1 (CH), 20.5 (CH_3), 12.9 (OCH_2CH_3), MS m/z 600 ($M^+ - CO$), 516 ($M^+ - CH(CN)CO_2Et$), 488 ($M^+ - CH(CN)CO_2Et - CO$)
13-7	IR (NaCl) 1970, 1738, 1720 cm^{-1}; ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 230 0 (CO), 166.5 (CO_2), 151 1, 129.7, 125 0, 121 1 (POPh), 138 1, 137.4, 133.9, 128.8 (SO_2Ph), 89.3, 85.6, 84.2, 72.7, 33.9, 26 8 (cyclohexadiene), 52.4 (OCH_3), 39 8 (CH), 23 3 (CH_3); (minor diastereomer) 230 0 (CO), 166.0 (CO_2), 151.1, 129.7, 125.0, 121.1 (POPh), 138.1, 137.4, 133 9, 128 8 (SO_2Ph), 89.3, 87 0, 84.2, 72.5, 33.7, 26 8 (cyclohexadiene), 52.4 (OCH_3), 39.5 (CH), 21 9 (CH_3), MS m/z 488 ($M^+ - CH(CO_2Me)SO_2Ph - CO$). *Anal* Calc. for $C_{35}H_{33}MnO_9NPS$ C, 57 61, H, 4.53, N, 1.72. Found C, 57.92; H, 4 98; N, 1 54%
13-8	IR (NaCl) 1965, 1720 cm^{-1}, ^{13}C NMR ($CDCl_3$) δ 230.6 (CO), 151.2, 129 7, 125 0, 121.1 (Ph), 87 9, 85.2, 84 3, 48 1, 35 2, 34 5 (cyclohexadiene), 60.6 (OCH_2), 26.8 (SCH_2), 23.5 (CH_3), MS m/z 488 ($M^+ - SCH_2CH_2OH - CO$)

(*continued*)

TABLE 2. (*continued*)

Compound	
13-9	IR (NaCl) 2030, 1968, 1735, 1727 cm^{-1}, ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 223.8, 220.5 (CO), 201.5 (C=O), 168 4 (CO_2), 141 3, 67.9, 65.5, 64.4, 57.3, 34.5 (cyclohexadiene), 61.5 (OCH_2), 54.6 (OCH_3), 38 9 (CH), 29.8 ($COCH_3$), 22 0 (CH_3), 14.0 (OCH_2CH_3), (minor diastereomer) 223.8, 220 5 (CO), 203.3 (C=O), 168.7 (CO_2), 141.4, 67.4, 65.4, 64.3, 56.6, 35.0 (cyclohexadiene), 61.4 (OCH_2), 54.6 (OCH_3), 39 5 (CH), 29.3 ($COCH_3$), 21.6 (CH_3), 13.9 (OCH_2CH_3); MS *m/z* 337 ($M^+ - 2CO$), 307 ($M^+ - 2CO - NO$), 292 ($M^+ - 2CO - NO - CH_3$), 264 ($M^+ - 2CO - NO - COMe$), 233 ($M^+ - 2CO - NO - CO_2Et - H$)
13-10	IR (NaCl) 2035, 1975, 1750–1715(br) cm^{-1}; ^{13}C NMR ($CCl_4 + d_6$-acetone)(major diastereomer) δ 224 0, 220.8 (CO), 165.3 (CO_2), 115.9 (CN), 142.0, 67.7, 64.8, 62.4, 42.6, 36.0 (cyclohexadiene), 63.5 (OCH_2CH_3), 54.4 (OCH_3), 40.5 (CH), 21 2 (CH_3), 14.1 (OCH_2CH_3), (minor diastereomer) 224.0, 220.8 (CO), 164 7 (CO_2), 115.9 (CN), 141.7, 76.5, 64.8, 62.2, 42 7, 35.1 (cyclohexadiene), 73.5 (OCH_2CH_3), 54.6 (OCH_3), 40.9 (CH), 20.9 (CH_3), 14.1 (OCH_2CH_3); MS *m/z* 320 ($M^+ - 2CO$), 264 ($M^+ - 2CO - NO - CN$), 235 ($M^+ - 2CO - NO - CN - Et$), 219 ($M^+ - 2CO - NO - OEt$), 123 ($M^+ - Mn(CO)_2NO - CHCO_2Et(CN)$)
13-11	IR (NaCl) 2035, 1973, 1743, 1736 cm^{-1}; ^{13}C NMR ($CCl_4 + d_6$-acetone)(major diastereomer) δ 162.3 (CO_2), 139.5, 133.6, 128.8, 128.7 (Ph), 141.2, 68.3, 63.2, 56 0, 47.8, 35.3 (cyclohexadiene), 60.6 (OCH_3), 52 4 (CO_2CH_3), 39 5 (CH), 24 7 (CH_3); (minor diastereomer) 162.3 (CO_2), 139.5, 133 6, 128.8, 128 7 (Ph), 141.3, 68.0, 63.9, 56.8, 48.4, 35 4 (cyclohexadiene), 60 0 (OCH_3), 52.4 (CO_2CH_3), 39.2 (CH), 24.7 (CH_3); MS *m/z* 421 ($M^+ - 2CO$), 390 ($M^+ - 2CO - NO - H$), 358 ($M^+ - 2CO - NO - OMe - 2H$), 299 ($M^+ - 2CO - NO - OMe - CO_2Me - 2H$)
13-12	IR (NaCl) 3400, 2025, 1970, 1730 cm^{-1}; ^{13}C NMR ($CCl_4 + d_6$-acetone) δ 224.0, 222 0 (CO), 67.1 (OCH_2), 141.8, 66 0, 64 1, 60 1, 40.8, 25.9 (cyclohexadiene), 54.5 (OCH_3), 36.8 (SCH_2); MS *m/z* 237 ($M^+ - 2CO - OCH_3 - OH$), 200 ($M^+ - Mn(CO)_2NO$), 122 ($M^+ - Mn(CO)_2NO - SCH_2CH_2OH - H$)
13-13	IR (NaCl) 1970, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) (assigned peaks only) δ 7.45–7 1 (Ph), 4.09 (q, $J=7$, OCH_2), 3.5 (s, OCH_3), 3.19 (d, $J=9$, CH), 2 12 (s, $COCH_3$), 1.18 (t, $J=7$, OCH_2CH_3), 0 54 (d, $J=7$, CH_3)
13-14	IR (NaCl) 2220, 1975, 1720 cm^{-1}, ^1H NMR ($CDCl_3$)(assigned peaks only) 7.5–6.9 (Ph), 3.88 (q, $J=7$, OCH_2), 3.15 (d, $J=10$, CH), 2.98 (s, OCH_3), 0.95 (CH_3), 0 93 (t, $J=7$, OCH_2CH_3)
13-15	IR (NaCl) 1970, 1740 cm^{-1}; ^1H NMR ($CDCl_3$)(assigned peaks only) δ 8.0–6 9 (Ph), 3.99 (d, $J=11$, CH), 2 95 (s, OCH_3), 2.87 (s, CO_2CH_3), 0 86 (d, $J=7$, CH_3)
13-16	IR (NaCl) 2038, 1978, 1740, 1715 cm^{-1}; ^1H NMR ($CDCl_3$)(assigned peaks only) δ 7.36–7.13 (Ph), 4 22 (q, $J=7$, OCH_2), 3 51 (d, $J=8$, CH), 2.27 (s, $COCH_3$), 1.27 (t, $J=7$, OCH_2CH_3); ^{13}C NMR δ 222.0 (CO), 201 6 (C=O), 168 0 (CO_2), 143.3, 128 5, 127.8, 126.4 (Ph), 89.1, 87 4, 70 0, 65 4, 42 2, 34.7 (cyclohexadiene), 61 4 (OCH_2), 41.0 (CH), 30.2 ($COCH_3$), 14.0 (OCH_2CH_3), MS *m/z* 369 ($M^+ - 2CO$), 338 ($M^+ - 2CO - NO$), 284 ($M^+ - 2CO - NO - Mn$)
13-17	IR (NaCl) 2240, 2040, 1980, 1740 cm^{-1}; ^1H NMR ($CDCl_3$)(assigned peaks only) δ 7.38–7.18 (Ph), 4.31 (q, $J=7$, OCH_2), 3 66 (d, $J=5$, CH), 1 33 (t, $J=7$, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 222.0 (CO), 165.3 (CO_2), 140.8, 128.5, 128.1, 127.5 (Ph), 116.5 (CN), 89.0, 88.8, 69 3, 62.8, 44.1, 27.0 (cyclohexadiene), 64.5 (CH_2), 41 0 (CH), 13.8 (CH_3); MS *m/z* 352 ($M^+ - 2CO$), 322 ($M^+ - 2CO - NO$), 267 ($M^+ - 2CO - NO - Mn$)
13-18	IR (NaCl) 2040, 1980, 1742 cm^{-1}, ^1H NMR ($CDCl_3$)(assigned peaks only) δ 7.97–7.11 (Ph), 4.02 (d, $J=7$, CH), 3.53 (s, CO_2Me), ^{13}C NMR ($CDCl_3$) δ 221 0 (CO), 165.1 (CO_2), 142.6, 137.8, 134 3, 131 4, 131.0, 129.1, 128 5, 127.7, 123.9, 122.5 (Ph), 90.1, 87.4, 72.4, 67.5, 34.2, 29.6 (cyclohexadiene), 52 6 (CH_3), 41 8 (CH); MS *m/z* 453 ($M^+ - 2CO$), 281 ($M^+ - 2CO - NO - SO_2Ph - H$)
13-19	IR (NaCl) 2025, 1970, 1730 cm^{-1}, ^1H NMR ($CDCl_3$) δ 7.35–7.24 (Ph), 3 48 (t, $J=5.9$, OCH_2), 2 50 (t, $J=5.9$, SCH_2), 1.8 (OH), ^{13}C NMR ($CDCl_3$) δ 222.0 (CO), 142 2, 129.3, 127.6, 126.8 (Ph), 88 5, 87.6, 70 1, 48.1, 47 3, 35.3 (cyclohexadiene), 69.0 (OCH_2), 30.1 (SCH_2), MS *m/z* 317 ($M^+ - 2CO$), 287 ($M^+ - 2CO - NO$), 232 ($M^+ - 2CO - NO - Mn$)
13-24	IR (C_5H_{12}) 1963, 1717 cm^{-1}; ^1H NMR ($CDCl_3$)(major diastereomer) δ 7.3 (Ph), 5.44 ($H^{2,3}$), 3 44 (H^4), 3.29 ($H^{5,6}$), 3 11 (d, $J=6$, CH), 2.31 (H^1), 1.40 (d, $J=9$, PMe_3); (minor diastereomer) 7 3 (Ph), 5.44 ($H^{2,3}$), 4 01 (d, $J=11$, H^6), 3 44 (H^1), 3.02 (d, $J=5$, CH), 2.67 (d, $J=11$, H^5), 2 31 (H^4), 1.45 (d, $J=9$, PMe_3)

(*continued*)

TABLE 2 (*continued*)

Compound	
13-25	IR (C_5H_{12}) 1956, 1702 cm^{-1}, ^1H NMR ($CDCl_3$) (major diastereomer) δ 7 2 (Ph), 6 2 (m, Cp), 5.37 ($H^{2,3}$), 3 86 (d, $J=10$, H^5), 3 52 (H^4), 3 32 (t, $J=9$, H^6), 2 30 (H^1), 1.40 (d, $J=9$, PMe_3), (minor diastereomer) 7 2 (Ph), 6 2 (m, Cp), 5 37 ($H^{2,3}$), 3.97 (d, $J=11$, H^6), 3 52 (H^1), 3 29 (d, $J=11$, H^5), 2.30 (H^4), 1.42 (d, $J=9$, PMe_3)
13-20, 13-23, 13-26	See refs. 10 and 15
14 ($R=Me$, $R'=CH(CO_2Et)COMe$)	^1H NMR ($CDCl_3$) (major diastereomer) δ 5 91 (m, H^{1-4}), 4.20 (q, $J=7.1$, OCH_2), 3 72 (d, $J=12$, CH), 3 31 (m, H^5), 2 35 (m, H^6), 2 26 (s, $COCH_3$), 1.27 (t, $J=7.3$, OCH_2CH_3), 0.85 (d, $J=7.1$, CH_3), (minor diastereomer) 5 87 (m, H^{1-4}), 4 19 (q, $J=7$ 1, OCH_2), 3 73 (d, $J=10$ 4, CH), 3 31 (m, H^5), 2.35 (m, H^6), 2.27 (s, $COCH_3$), 1 28 (t, $J=7$ 1, OCH_2CH_3), 0 81 (d, $J=7.1$, CH_3), MS *m/z* 222, (M^+), 207 (M^+-Me), 176 ($M^+-COMe-2H$), 148 ($M^+-COMe-Et-2H$), 105 ($M^+-CO_2Et-COMe-H$)
14 ($R=Me$, $R'=CH(CO_2Et)CN$)	^1H NMR ($CDCl_3$) (major diastereomer) δ 7 27 (m, H^{1-4}), 4.28 (q, $J=7.2$, OCH_2), 3.55 (d, $J=8$ 8, CH), 3.10 (m, H^5), 2 64 (m, H^6), 1.33 (t, $J=7.1$, OCH_2CH_3), 1 04 (d, $J=7.4$, CH_3); (minor diastereomer) 7 27 (m, H^{1-4}), 4.28 (q, $J=7$ 2, OCH_2), 3 59 (d, $J=7$ 0, CH), 3 10 (m, H^5), 2 64 (m, H^6), 1.34 (t, $J=7.2$, OCH_2CH_3), 1 02 (d, $J=7$ 4, CH_3) MS *m/z* 205 (M^+), 190 (M^+-Me), 162 ($M^+-Me-CN-2H$), 149 ($M^+-Et-CN-H$), 135 ($M^+-Et-CN-Me$), 105 ($M^+-CO_2Et-CN-H$)
14 ($R=Me$, $R'=CH(CO_2Me)SO_2Ph$)	^1H NMR ($CDCl_3$) (major diastereomer) δ 7.91 (Ph), 5.83 (m, H^{1-4}), 4 27 (d, $J=12$, CH), 3 60 (s, OCH_3), 3.13 (m, H^5), 2 78 (m, H^6), 0 81 (d, $J=7$ 2, CH_3), (minor diastereomer) 7 91 (Ph), 5 83 (m, H^{1-4}), 4 23 (d, $J=8$ 3, CH), 3 54 (s, OCH_3), 3 13 (m, H^5), 2 78 (m, H^6), 0 96 (d, $J=6.9$, CH_3), MS *m/z* 275 (M^+-OMe), 164 (M^+-SO_2Ph-H), 105 ($M^+-CO_2Me-SO_2Ph-H$)
14 ($R=Me$, $R'=SCH_2CH_2OH$)	^1H NMR ($CDCl_3$) δ 5.95 (m, H^{1-4}), 3 68 (t, OCH_2), 3.43 (dd, $J=7$ 7, 5.3, H^5), 2 86 (m, H^6), 2 68 (dt, $J=5$ 9, 1.4, SCH_2), 2 07 (OH), 1 27 (d, $J=7$ 3, CH_3), MS *m/z* 170 (M^+), 137 (M^+-CH_2OH-2H), 125 ($M^+-CH_2CH_2OH$), 92 ($M^+-SCH_2CH_2OH-2H$)
14 ($R=Ph$, $R'=CH(CO_2Et)COMe$)	^1H NMR ($CDCl_3$) δ 7 26 (Ph), 5 79 (m, H^{1-4}), 4 21 (q, $J=7$ 2, OCH_2), 3 95 (m, H^6), 3 64 (m, H^5), 3.51 (d, $J=8.4$, CH), 2.27 (s, $COCH_3$), 1 27 (t, $J=7$ 2, OCH_2CH_3), MS *m/z* 284 (M^+), 241 (M^+-COMe), 210 (M^+-CO_2Et-H), 167 ($M^+-CO_2Et-COMe-H$)
14 ($R=Ph$, $R'=CH(CO_2Et)CN$)	^1H NMR ($CDCl_3$)(major diastereomer) δ 7 26 (Ph), 6.1 (m, H^{1-4}), 4 14 (q, $J=7$ 2, OCH_2), 4 04 (ddd, $J=10$, 6.2, 2 9, H^6), 3.31 (m, H^5), 3 11 (d, $J=7.8$, CH), 1 25 (t, $J=7.2$, OCH_2CH_3), (minor diastereomer) 7.38 (Ph), 6.05 (m, H^{1-4}), 4 16 (q, $J=7$ 2, OCH_2), 3 60 (m, H^6), 3 12 (d, $J=8$ 8, CH), 1 27 (t, $J=7.2$, OCH_2CH_3), MS *m/z* 265 (M^+-2H), 193 (M^+-CO_2Et-H), 165 ($M^+-CO_2Et-CN-3H$)
14 ($R=Ph$, $R'=CH(CO_2Me)SO_2Ph$)	^1H NMR ($CDCl_3$) δ 7.69 (SO_2Ph), 7 24 (Ph), 6.45–5.76 (m, H^{1-4}), 41 9 (d, $J=10$, CH minor diastereomer), 4.14 (d, $J=9$ 8, CH major diastereomer), 3.55 (s, OCH_3), 3.18 (m, H^5), 2 84 (m, H^6)
14 ($R=Ph$, $R'=SCH_2CH_2OH$)	^1H NMR ($CDCl_3$) δ 7.21 (Ph), 5 98–5.55 (m, H^{1-4}), 3.67 (t, OCH_2), 3.53 (OH), 3 44 (dd, $J=9$ 4, 5 0, H^5), 2.87 (t, $J=5$ 7, SCH_2), 2 72 (m, H^6); MS *m/z* 231 (M^+), 213 ($M^+-OH-2H$), 199 (M^+-CH_2OH-2H), 155 (M^+-Ph)
15 ($R'=CH(CO_2Et)CN$)	IR (NaCl) 2243, 1740 cm^{-1}; ^1H NMR ($CDCl_3$)(major diastereomer) δ 5 96 (m, $H^{1,3}$), 4 65 (m, H^4), 4.28 (q, $J=7$ 1, OCH_2), 3.83 (d, $J=8$ 3, CH), 3.54 (s, OCH_3), 3.0 (m, $H^{5,6}$), 1.31 (t, $J=8.4$, OCH_2CH_3), 1.02 (d, $J=7$ 0, CH_3), (minor diastereomer) 5 96 ($H^{1\,3}$), 4.65 (m, H^4), 4.30 (q, $J=7$ 1, OCH_2), 3 73 (d, $J=8.8$, CH), 3 54 (s, OCH_3), 3 0 (m, $H^{5,6}$), 1.31 (t, $J=8$ 4, OCH_2CH_3), 1.03 (d, $J=7.0$, CH_3), MS *m/z* 235 (M^+), 220 (M^+-Me), 193 ($M^+-Me-CN-H$), 174 ($M^+-Me-OEt-H$), 162 ($M^+-Me-OMe-CN-H$), 149 ($M^+-Me-OEt-CN$)
15 ($R'=SCH_2CH_2OH$)	MS *m/z* 200 (M^+), 168 ($M^+-OMe-H$), 153 ($M^+-OMe-Me-H$), 123 ($M^+-OMe-Me-CH_2CH_2OH$)
16 ($R'=CH(CO_2Et)CN$)	IR (NaCl) 2243, 1738, 1673 cm^{-1}, ^1H NMR ($CDCl_3$) (major diastereomer) δ 6 83 (dd, $J=10$, 3 1, H^3), 6.21 (dd, $J=10$, 2.4, H^2), 4.33 (q, $J=7$, OCH_2), 3.66 (d, $J=6$ 8, CH), 3.38 (m, H^4), 2 54 (m, $H^{5,6}$), 1.36 (t, $J=7$, OCH_2CH_3), 1 07 (d, $J=6$ 8, CH^3), (minor diastereomer) 6 59 (td, $J=10$, 2, H^3), 6.12 (dd, $J=10$, 2, H^2), 4.34 (q, $J=7$, OCH_2), 3.56 (d, $J=10$, CH), 3.38 (m, H^4), 2 54 (m, $H^{5,6}$), 1 36 (t, $J=7$, OCH_2CH_3), 1.10 (d, $J=CH_3$), MS *m/z* 221 (M^+), 176 (M^+-OEt), 148 (M^+-CO_2Et), 109 ($M^+-CH(CN)CO_2Et$)

(*continued*)

TABLE 2. (*continued*)

Compound	
16 ($R' = CH(CO_2Me)SO_2Ph$)	IR (NaCl) 1738, 1675 cm^{-1}; ^1H NMR ($CDCl_3$) (major diastereomer) δ 7.92 (Ph), 6.85 (md, $J = 10.7$, H^3), 6.04 (dd, $J = 10.3$, 2.6, H^2), 4.16 (d, $J = 11.7$, CH), 3.68 (m, H_4), 3.51 (s, OCH_3), 2.74 (m, $H^{5,6}$), 0.99 (d, $J = 6.8$, CH_3); (minor diastereomer) 7.92 (Ph), 6.48 (td, $J = 10.5$, 1.9, H^3), 6.12 (dd, $J = 10.5$, 1.9, H^2), 4.15 (d, $J = 6.1$, CH), 3.68 (m, H^4), 3.51 (s, OCH_3), 2.74 (m, $H^{5,6}$), 0.89 (d, $J = 7.1$, CH_3), MS *m/z* 291 ($M^+ - OMe$)
16 ($R' = SCH_2CH_2OH$)	IR (NaCl) 1667 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.03 (dd, $J = 9.9$, 5.4, H^3), 5.95 (td, $J = 10.0$, 0.8, H^2), 3.80 (t, $J = 6.8$, OCH_2), 3.54 (dd, $J = 5.2$, 4.2, H^4), 2.46 (m, $H^{5,6}$), 2.14 (OH), 1.24 (d, $J = 8.0$, CH_3), MS *m/z* 186 (M^+), 141 ($M^+ - CH_2CH_2OH$), 109 ($M^+ - SCH_2CH_2OH$)
17	IR (NaCl) 1692, 1660, 1638 cm^{-1}, ^1H NMR ($CDCl_3$) (major diastereomer) δ 4.93 (ddd, $J = 8.5$, 4.1, 1.5, H^3), 4.82 (dd, $J = 4.0$, 1.5, H^2), 4.13 (q, $J = 7.2$, OCH_2), 3.56 (s, OCH_3), 3.06 (d, $J = 8.5$, CH), 2.30 (m, $H^{5,6\alpha}$), 2.17 (s, $COCH_3$), 1.89 (dd, $J = 17.8$, 4.0 $H^{6\beta}$), 1.23 (t, $J = 7.2$, OCH_2CH_3), 0.78 (d, $J = 7.1$, CH_3, minor diastereomer) 4.93 (ddd, $J = 8.5$, 4.1, 1.5, H^3), 4.82 (dd, $J = 4.0$, 1.5 H^2), 4.15 (q, $J = 7.2$, OCH_2), 3.56 (s, OCH_3), 3.04 (d, $J = 8.6$, CH), 2.33 (m, $H^{5,6\alpha}$), 2.17 (s, $COCH_3$), 1.89 (dd, $J = 17.8$, 4.0, $H^{6\beta}$), 1.23 (t, $J = 7.2$, OCH_2CH_3), 0.78 (d, $J = 7.1$, CH_3); MS *m/z* 252 (M^+), 206 ($M^+ - OEt - H$), 191 ($M^+ - OEt - Me - H$), 163 ($M^+ - CO_2Et - Me - H$), 122 ($M^+ - CH(CO_2Et)COMe - H$)
18	IR (NaCl) 1719, 1690, 1635 cm^{-1}, ^1H NMR ($CDCl_3$) (major diastereomer) δ 5.05 (t, $J = 3.4$, H^3), 4.19 (q, $J = 7.1$, OCH_2), 3.45 (d, $J = 10.2$, CH), 2.70 (dd, $J = 17.6$, 3.4, H^6), 2.19 (s, $COCH_3$), 2.08 (m, $H^{2,5}$), 1.30 (t, $J = 7.2$, OCH_2CH_3), 0.93 (d, $J = 6.8$, CH_3), (minor isomer) 5.10 (t, $J = 3.4$, H^3), 4.20 (q, $J = 7.2$, OCH_2), 3.49 (d, $J = 8.8$, CH), 2.83 (dd, $J = 17.6$, 3.4, H^6), 2.20 (s, $COCH_3$), 2.08 (m, $H^{2,5}$), 1.30 (t, $J = 7.2$, OCH_2CH_3), 0.93 (d, $J = 6.8$, CH_3), MS *m/z* 238 (M^+), 193 ($M^+ - OEt$)
19 ($R = R' = Ph$)	IR (C_5H_{12}) 1711, 1570 cm^{-1}, ^1H NMR (C_6D_6) δ 7.4 (m, Ph), 5.25 (t, $J = 5.3$, H^3), 4.71 (t, $J = 6.4$, $H^{2\text{ or }4}$), 4.51 (t, $J = 6.5$, $H^{4\text{ or }2}$), 3.38 (q, $J = 5.2$, $H^{5\text{ or }1}$), 3.29 (t, $H^{1\text{ or }5}$), 3.09 (t, $J = 5.9$, H^6), 1.22 (d, $J = 9.3$, PMe_3)

The $FeCl_3$ method of decomplexation was used for complex **13-23** only. In all other cases oxidative decomplexation of **13** to liberate the diene was effected with Me_3NO [21]. (The relative merits of the two methods were not ascertained.) The following procedure is an example. Me_3NO (0.16 g, 2.1 mmol) was added to complex **13-1** (81 mg, 0.22 mmol) in 20 ml of benzene. The mixture was refluxed for 4 h, cooled to room temperature and filtered. The filtrate was diluted with 50 ml of diethyl ether, washed with water (30 ml × 2) and dried ($MgSO_4$). The solution was stripped and the product purified by column chromatography on silica gel with cyclohexane/ether (4:1) elutant to give 46 mg (92%) of a 1.2:1 mixture of diastereomers of **14** (R = Me, R′ = CH(CO_2Et)(COMe)) free from detectable impurities. The same procedure was used to oxidize other complexes **13** (X = H) to give **14** as in Scheme 4. The yields of pure diene **14** obtained from the respective complexes **13** were as follows: **13-1** (92%), **13-2** (52%), **13-3** (45%), **13-4** (58%), **13-5** (51%), **13-6** (50%), **13-7** (54%), **13-8** (62%), **13-16** (50%), **13-18** (49%), **13-19** (52%).

The oxidation of **13-10** with Me_3NO as described above gave the corresponding diene **15** (37%). Hydrolysis to the cyclohexen-1-one **16** was induced by stirring **15** with a *c.* 2:1 excess of oxalic acid in methanol for 1 h. The reaction mixture was poured into saturated aqueous $NaHCO_3$, extracted with diethyl ether, and dried ($MgSO_4$). Solvent evaporation and chromatography on silica gel gave pure **16** in 64% yield. With **13-11** and **13-12**, the oxidation with Me_3NO led directly to a mixture of **15** and **16**, which converted to pure **16** when the respective mixtures were chromatographed. The yields of **16** were 59% from **13-11** and 35% from **13-12**. Complex **13-9** reacted with Me_3NO to give the isomerized diene **17** (51%), which was hydrolyzed by oxalic acid/methanol to **18** (84%), as shown in Scheme 5.

Addition of LiPh and LiMe to [(6-exo-PhC_6H_6)Mn(CO)(NO)L]PF_6 (5, 10; R = Ph)

When LiPh (0.075 ml of a 2 M solution in 70:30 C_6H_{12}:Et_2O) was added to a slurry of **5** (R = Ph) (48 mg, 0.11 mmol) in 20 ml of CH_2Cl_2 at −78 °C, the solution became homogeneous and red–orange in color. After warming to room temperature, the solution was stripped *in vacuo* and the resulting red oil was flashed through a plug of alumina. The IR indicated a 5:3 mixture of **8** (R = R′ = Ph; IR (C_5H_{12}) = 2022, 1752, 1600(w) cm^{-1}) and (PhC_6H_6)$Mn(CO)_3$. The reaction mixture was thermally unstable and liberated free diene **9** (see Table 2). The addition of LiMe to **5** by the

same procedure gave clean conversion to the acetyl product **8** (R = Ph, R′ = Me); IR (CH_2Cl_2) = 2005, 1737 cm^{-1}.

LiPh was added dropwise to **10** (R = Ph) (52 mg, 0.11 mmol) in CH_2Cl_2 at −78 °C until the reactant completely disappeared. An *in situ* IR spectrum at −67 °C confirmed that the reaction was rapid at this temperature. After warming to room temperature, the red–orange solution was filtered through a plug of alumina and evaporated. ^1H NMR of the resultant red oil indicated a 2.8:1 mixture of **19:9**, with a combined yield of 72%. Prolonged stirring at room temperature liberated the diene from **19**. Similar behavior was found with the nucleophile LiMe and with **10** (R = Me), although these reactions were characterized only by IR (see Table 2).

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