DALTON

Reactions of $[Mn(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)Mn(CO)_3]\}]$ and $[WMe(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)Mn(CO)_3]\}]$ with aryllithium reagents

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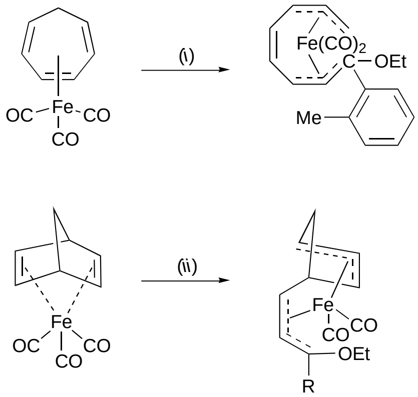
The reactions of $[Mn(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)Mn(CO)_3]\}]$ **1** and $[WMe(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)Mn(CO)_3]\}]$ **2** with aryllithium reagents, LiR (R = *o*-, *m*-, *p*-MeC_6H_4, Ph, *p*-$MeOC_6H_4$ or *p*-$CF_3C_6H_4$), in diethyl ether at low temperature afforded acylmetalate intermediates, which on alkylation with Et_3OBF_4 in aqueous solution at 0 °C gave alkoxycarbene complexes $[Mn(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)R]\}]$ and $[WMe(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)R]\}]$. The structure of $[Mn(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)C_6H_4\text{-}Me\text{-}o]\}]$, established by X-ray diffraction, shows that the carbene ligand is attached to the manganese atom co-ordinated to the η^5-cyclohexadienyl moiety.

Olefin-co-ordinated transition-metal carbene complexes and/or their isomerized products have been examined extensively in our laboratory.[1–17] Earlier we demonstrated[1–12] several novel isomerizations of olefin ligands, and a series of isomerized carbene complexes with novel structure were isolated by the reactions of olefin-ligated metal carbonyl compounds with nucleophiles. The isomerizations and reaction products depend not only on the olefin ligands but also on the central metals.[3–5,8,12–15] For instance, tricarbonyl(cycloheptatriene)iron and tricarbonyl(norbornadiene)iron reacted with aryllithium reagents, and subsequent alkylation with Et_3OBF_4 gave novel ring-opened isomerized complexes (Scheme 1).[3,4] However, the reactions of tricarbonyl(cycloheptatriene)-molybdenum and -chromium[14] and tetracarbonyl(norbornadiene)-chromium, -molybdenum and -tungsten[13,14] with aryllithium reagents under the same conditions gave normal olefin-co-ordinated carbene complexes in which the diene ligand and carbene ligand coexist stably (Scheme 2).

In our previous research the central metals were usually the Group VIIIB metals (d^8) and Group VIB metals (d^6). Continuing our interest in olefin-co-ordinated metal carbene and carbyne complexes, we turned our attention to olefin-ligated carbonyl compounds of Group VIIB metal (d^7), such as tricarbonyl(*exo*-cyclopentadienyl-η^5-cyclohexadienyl)manganese,[18] which gave a series of normal olefin-co-ordinated manganese carbene complexes in this reaction (Scheme 3).[17]

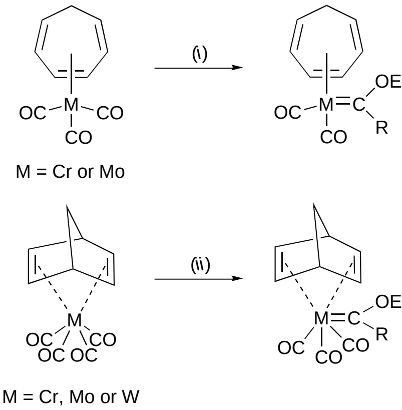
In order further to investigate the effect of different metal centre, on the isomerization of the olefin ligand and the reaction products, we chose $[Mn(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)Mn(CO)_3]\}]$ **1** and $[WMe(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)Mn(CO)_3]\}]$ **2**, in which the two metal centres are not directly bonded to each other, as starting materials in reactions with aryllithium reagents. This paper describes a detailed study of these reactions and the structural characterization of the resulting products.



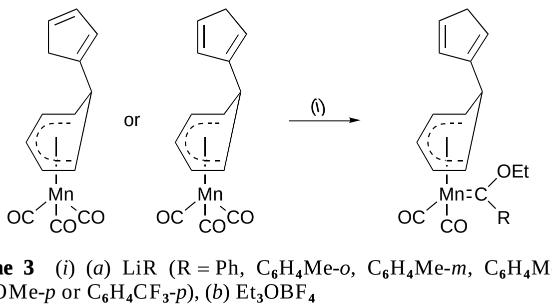
Scheme 1 (*i*) (*a*) LiC_6H_4Me-*o*, (*b*) Et_3OBF_4; (*ii*) (*a*) LiR (R = C_6H_4Me-*o*, C_6H_4Me-*p* or $C_6H_4CF_3$-*p*), (*b*) Et_3OBF_4

Experimental

All the procedures were performed under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques. The solvents were reagent grade, dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under a nitrogen atmosphere. Tetrahydrofuran (thf) and diethyl ether were distilled from sodium–benzophenone, light petroleum (b.p. 30–60 °C) from CaH_2, and CH_2Cl_2 from P_2O_5. The neutral



Scheme 2 (*i*) (*a*) LiR (R = Ph, C_6H_4Me-*o*, C_6H_4Me-*p* or $C_6H_4CF_3$-*p*), (*b*) Et_3OBF_4: (*ii*) (*a*) LiR (R = Ph, C_6H_4Me-*o*, C_6H_4Me-*m*, C_6H_4Me-*p*, C_6H_4OMe-*p* or $C_6H_4CF_3$-*p*), (*b*) Et_3OBF_4



Scheme 3 (*i*) (*a*) LiR (R = Ph, C_6H_4Me-*o*, C_6H_4Me-*m*, C_6H_4Me-*p*, C_6H_4OMe-*p* or $C_6H_4CF_3$-*p*), (*b*) Et_3OBF_4

alumina used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water, and stored under N_2. Compounds **1**,[18] **2**,[18] and **15**,[18] Et_3OBF_4,[19] and aryllithium reagents[20–24] were prepared by literature methods.

The IR spectra were measured on a Shimadzu IR-440 spectrophotometer, ^1H NMR spectra on a Bruker AM-300 spectrometer at ambient temperature in $(CD_3)_2CO$ solution with $SiMe_4$ as the internal reference and electron ionization (EI) mass spectra on a Hewlett-Packard 5989A spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

Preparation

$[Mn(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)C_6H_4Me\text{-}o]\}]$ 3. To a solution of compound **1** (70 mg, 0.16 mmol) in diethyl ether (30 cm^3) at −78 °C was added dropwise $LiC_6H_4Me\text{-}o$[20] (0.38 mmol) in diethyl ether (10 cm^3) with stirring. The light yellow solution was stirred initially at −78 to −65 °C for 0.5 h and then at −60 to −45 °C for 4 h, during which time it turned yellow to orange-red. The resulting solution was evaporated to dryness under vacuum at −50 to −40 °C. To the orange solid residue obtained was added Et_3OBF_4 (*ca.* 3 g). This solid mixture was dissolved in N_2-saturated water (20 cm^3) at 0 °C with vigorous stirring and the mixture covered with light petroleum. Immediately afterward, Et_3OBF_4 (*ca.* 8 g) was added portionwise with vigorous stirring to the aqueous solution until it became acidic. The aqueous solution was extracted with light petroleum. The combined extract was evaporated *in vacuo*, and the residue chromatographed on an alumina column (neutral, 100–200 mesh, 1.6 × 10–15 cm) at −20 °C with light petroleum followed by light petroleum–Et_2O (10 : 1) as the eluent. The orange-yellow band was eluted and collected. Removal of the solvent under vacuum and recrystallization of the crude product from light petroleum–CH_2Cl_2 solution at −80 °C gave 64 mg (71%, based on **1**) of orange-red crystals of compound **3**, m.p. 118–119 °C (decomp.). Mass spectrum: m/z 540 (M^+), 484 ($M^+ - 2CO$), 440 ($M^+ - 2CO - OC_2H_4$), 412 ($M^+ - 3CO - OC_2H_4$), 400 ($M^+ - 5CO$), 384 ($M^+ - 4CO - OC_2H_4$), 356 ($M^+ - 5CO - OC_2H_4$), 344 $[M^+ - Mn(CO)_3 - 2CO]$, 300 $(C_5H_4C_6H_5MnCHC_6H_4CH_3)^+$, 251 $(MnC_5H_4C_6H_6Mn)^+$, 204 $[MnCH(OC_2H_5)C_6H_4CH_3]^+$ and 149 $[(CH_3C_6H_4)CH(OC_2H_5)]^+$ (Found: C, 57.9; H, 4.2. Calc. for $C_{26}H_{22}Mn_2O_6$: C, 57.8; H, 4.1%).

$[Mn(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)C_6H_4Me\text{-}m]\}]$ 4. Similarly, compound **1** (200 mg, 0.48 mmol) dissolved in ether (50 cm^3) was reacted with $LiC_6H_4Me\text{-}m$[20] (1.06 mmol) at −65 to −45 °C for 4 h. Subsequent alkylation and further treatment as describved above gave 165 mg (64%, based on **1**) of orange-red crystals of **4**, m.p. 90–92 °C (decomp). Mass spectrum: m/z 540 (M^+), 484 ($M^+ - 2CO$), 440 ($M^+ - 2CO - OC_2H_4$), 412 ($M^+ - 3CO - OC_2H_4$), 400 ($M^+ - 5CO$), 384 ($M^+ - 4CO - OC_2H_4$), 356 ($M^+ - 5CO - OC_2H_4$), 344 $[M^+ - Mn(CO)_3 - 2CO]$, 300 $(C_5H_4C_6H_5MnCHC_6H_4CH_3)^+$, 251 $(MnC_5H_4C_6H_6Mn)^+$, 204 $[MnCH(OC_2H_5)C_6H_4CH_3]^+$ and 149 $[(CH_3C_6H_4)CH(OC_2H_5)]^+$ (Found: C, 57.7; H, 3.9. Calc. for $C_{26}H_{22}Mn_2O_6$: C, 57.8; H, 4.1%).

$[Mn(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)C_6H_4Me\text{-}p]\}]$ 5. Similarly, compound **1** (150 mg, 0.36 mmol) was allowed to react with $LiC_6H_4Me\text{-}p$[20] (0.80 mmol) at −65 to −45 °C for 4 h. Subsequent alkylation and further treatment as described above afforded 134 mg (70%, based on **1**) of **5** as orange-red crystals, m.p. 58–60 °C (decomp.). Mass spectrum: m/z 540 (M^+), 484 ($M^+ - 2CO$), 440 ($M^+ - 2CO - OC_2H_4$), 412 ($M^+ - 3CO - OC_2H_4$), 400 ($M^+ - 5CO$), 384 ($M^+ - 4CO - OC_2H_4$), 356 ($M^+ - 5CO - OC_2H_4$), 344 $[M^+ - Mn(CO)_3 - 2CO]$, 300 $(C_5H_4C_6H_5MnCHC_6H_4CH_3)^+$, 251 $(MnC_5H_4C_6H_6Mn)^+$, 204 $[MnCH(OC_2H_5)C_6H_4CH_3]^+$ and 149 $[(CH_3C_6H_4)CH(OC_2H_5)]^+$ (Found: C, 57.9; H, 3.55. Calc. for $C_{26}H_{22}Mn_2O_6$: C, 57.8; H, 4.1%).

$[Mn(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)Ph]\}]$ 6. The reaction of compound **1** (200 mg, 0.48 mmol) with LiPh[21] (1.10 mmol) was carried out at −60 to −40 °C for 4 h. Subsequent alkylation and further treatment as described above yielded 150 mg (60%, based on **1**) of **6** as orange-red crystals, m.p. 100–102 °C (decomp.). Mas spectrum: m/z 526 (M^+), 502 ($M^+ - CO$), 470 ($M^+ - 2CO$), 426 ($M^+ - 2CO - OC_2H_4$), 398 ($M^+ - 3CO - OC_2H_4$), 386 ($M^+ - 5CO$), 370 ($M^+ - 4CO - OC_2H_5$), 342 ($M^+ - 5CO - OC_2H_4$), 330 $[M^+ - Mn(CO)_3 - 2CO]$, 251 $(MnC_5H_4C_6H_6Mn)^+$, 190 $[MnCH(OC_2H_5)C_6H_5]^+$ and 135 $[(C_6H_5)CH(OC_2H_5)]^+$ (Found: C, 56.95; H, 3.8. Calc. for $C_{25}H_{20}Mn_2O_6$: C, 57.05; H, 3.85%).

$[Mn(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)C_6H_4OMe\text{-}p]\}]$ 7. A solution of $p\text{-}MeOC_6H_4Br$ (80 mg, 0.34 mmol) in ether (20 cm^3) was mixed with $LiBu^n$[22] (0.34 mmol). After 30 min of stirring at room temperature, the resulting ether solution of $LiC_6H_4OMe\text{-}p$[23] was allowed to react, as described above, with compound **1** (70 mg, 0.17 mmol) at −60 to −40 °C for 4 h, followed by alkylation; further treatment gave 65 mg (70%, based on **1**) of orange-red crystalline **7** which is a viscous oil at room temperature. Mass spectrum: m/z 556 (M^+), 500 ($M^+ - 2CO$), 456 ($M^+ - 2CO - OC_2H_4$), 428 ($M^+ - 3CO - OC_2H_4$), 416 ($M^+ - 5CO$), 400 ($M^+ - 4CO - OC_2H_4$), 372 ($M^+ - 5CO - OC_2H_5$), 360 $[M^+ - Mn(CO)_3 - 2CO]$, 251 $(MnC_5H_4C_6H_6Mn)^+$, 220 $[MnCH(OC_2H_5)C_6H_4OCH_3]^+$ and 165 $[(CH_3OC_6H_4)CH(OC_2H_5)]^+$ (Found: C, 53.2; H, 3.6. Calc. for $C_{26}H_{22}Mn_2O_7{\cdot}0.5CH_2Cl_2$: C, 53.15; H, 3.85%).

$[Mn(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)C_6H_4CF_3\text{-}p]\}]$ 8. A solution of $LiBu^n$ (0.38 mmol) in ether (10 cm^3) was added dropwise to a solution of $p\text{-}CF_3C_6H_4Br$ (86 mg, 0.38 mmol) in ether (20 cm^3). After 30 min of stirring at room temperature the resulting ether solution of $LiC_6H_4CF_3\text{-}p$[24] was treated with compound **1** (80 mg, 0.19 mmol) in ether (40 cm^3) at −60 to −40 °C for 4 h. Subsequent alkylation as above afforded 60 mg (53%, based on **1**) of orange-red crystalline **8** which is a viscous oil at room temperature. Mass spectrum: m/z 594 (M^+), 538 ($M^+ - 2CO$), 494 ($M^+ - 2CO - OC_2H_4$), 466 ($M^+ - 3CO - OC_2H_4$), 454 ($M^+ - 5CO$), 438 ($M^+ - 4CO - OC_2H_4$), 410 ($M^+ - 5CO - OC_2H_5$), 398 $[M^+ - Mn(CO)_3 - 2CO]$, 258 $[MnCH(OC_2H_5)C_6H_4CF_3]^+$, 251 $(MnC_5H_4C_6H_6Mn)^+$ and 203 $[(CF_3C_6H_4)CH(OC_2H_5)]^+$ (Found: C, 52.8; H, 2.65. Calc. for $C_{26}H_{19}F_3Mn_2O_6$: C, 52.55; H, 3.2%).

$[WMe(CO)_3[\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)C_6H_4Me\text{-}o]\}]$ 9. To a solution of compound **2** (200 mg, 0.36 mmol) in ether (50 cm^3) at −70 °C was added dropwise $LiC_6H_4Me\text{-}o$ (0.78 mmol) in ether (10 cm^3) with stirring. The orange-yellow solution was stirred initially at −70 to −65 °C for 0.5 h and then at −65 to −50 °C for 4 h, during which time it turned orange-red to red. The resulting solution was evaporated under vacuum at −50 to −40 °C to dryness. Subsequent alkylation of the residue obtained with Et_3OBF_4 and further treatment as described above gave 65 mg (26%, based on **2**) of orange-yellow crystals of **9** which is a viscous oil at room temperature. Mass spectrum: m/z 628 ($M^+ - 2CO$), 584 ($M^+ - 3CO - CH_3 - H$), 556 ($M^+ - 4CO - CH_3 - H$), 528 ($M^+ - 5CO - CH_3 - H$), 480 $[CH_3(OC)_3WC_5H_4C_6H_6Mn]^+$, 464 $[(OC)_3WC_5H_4C_6H_5Mn]^+$, 380 $(WC_5H_4C_6H_5Mn)^+$, 204 $[MnCH(OC_2H_5)C_6H_4CH_3]^+$, 196 $(C_5H_4C_6H_5Mn)^+$ and $[(CH_3C_6H_4)CH(OC_2H_5)]^+$ (Found: C, 43.7; H, 3.33. Calc. for $C_{27}H_{25}MnO_6W{\cdot}CH_2Cl_2$: C, 43.7; H, 3.55%).

$[WMe(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)C_6H_4Me\text{-}m]\}]$ 10. Similarly, compound **2** (100 mg, 0.18 mmol) was allowed to react with LiC_6H_4Me-*m* (0.39 mmol) at −65 to −50 °C for 4 h. Subsequent alkylation and further treatment as above afforded 35 mg (29%, based on **2**) of **10** as orange-red crystals, m.p. 127–128 °C (decomp.). Mass spectrum: *m/z* 656 $(M^+ - CO)$, 600 $(M^+ - 3CO)$, 480 $[CH_3(OC)_3WC_5H_4C_6H_6Mn]^+$, 464 $[(OC)_3WC_5H_4C_6H_5Mn]^+$, 380 $(WC_5H_4C_6H_5Mn)^+$, 204 $[MnCH(OC_2H_5)C_6H_4CH_3]^+$, 196 $(C_5H_4C_6H_5Mn)^+$ and 149 $[(CH_3C_6H_4)CH(OC_2H_5)]^+$.

$[WMe(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)C_6H_4Me\text{-}p]\}]$ 11. Similarly, compound **2** (200 mg, 0.36 mmol) dissolved in ether (50 cm^3) was treated with LiC_6H_4Me-*p* (0.76 mmol) at −65 to −50 °C for 4 h, followed by alkylation; further treatment as described above yielded 70 mg (29%, based on **2**) of orange-red crystalline **11** which is a red viscous oil at room temperature. Mass spectrum: *m/z* 628 $(M^+ - 2CO)$, 584 $(M^+ - 3CO - CH_3 - H)$, 556 $(M^+ - 4CO - CH_3 - H)$, 528 $(M^+ - 5CO - CH_3 - H)$, 480 $[CH_3(OC)_3WC_5H_4C_6H_6Mn]^+$, 464 $[(OC)_3WC_5H_4C_6H_5Mn]^+$, 380 $(WC_5H_4C_6H_5Mn)^+$, 204 $[MnCH(OC_2H_5)C_6H_4CH_3]^+$, 196 $(C_5H_4C_6H_5Mn)^+$, 149 $[(CH_3C_6H_4)CH(OC_2H_5)]^+$ (Found: C, 45.6; H, 3.15. Calc. for $C_{27}H_{25}MnO_6W{\cdot}0.5CH_2Cl_2$: C, 45.45; H, 3.15%).

$[WMe(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)Ph]\}]$ 12. The reaction of compound **2** (100 mg, 0.18 mmol) with LiPh (0.39 mmol) was carried out as described above at −65 to −50 °C for 4 h. After evaporation of the solvent *in vacuo*, further treatment of the resulting residue as described above gave 48 mg (40%, based on **2**) of orange-red crystals of **12**, m.p. 81–83 °C (decomp.). Mass spectrum: *m/z* 614 $(M^+ - 2CO)$, 570 $(M^+ - 3CO - CH_3 - H)$, 480 $[CH_3(OC)_3WC_5H_4C_6H_6Mn]^+$, 464 $[(OC)_3WC_5H_4C_6H_5Mn]^+$, 380 $(WC_5H_4C_6H_5Mn)^+$, 196 $(C_5H_4C_6H_5Mn)^+$, 190 $[MnCH(OC_2H_5)C_6H_5]^+$ and 135 $[(C_6H_5)CH(OC_2H_5)]^+$ (Found: C, 46.25; H, 3.6. Calc. for $C_{26}H_{23}MnO_6W$: C, 46.6; H, 3.45%).

$[WMe(CO)_3\{\eta^5\text{-}C_5H_4[\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)C_6H_4OMe\text{-}p]\}]$ 13. Compound **2** (120 mg, 0.22 mmol) was treated as described above, with fresh LiC_6H_4OMe-*p* prepared by the reaction of *p*-$MeOC_6H_4Br$ (90 mg, 0.48 mmol) with $LiBu^n$ (0.48 mmol), in ether solution (50 cm^3) at −65 to −50 °C for 4 h. Subsequent alkylation and further treatment yielded 44 mg (30%, based on **2**) of orange-red crystals of **13** which is a viscous oil at room temperature. Mass spectrum: *m/z* 644 $(M^+ - 2CO)$, 602 $(M^+ - 3CO - CH_3 - H)$, 572 $(M^+ - 4CO - CH_3 - H)$, 544 $(M^+ - 5CO - CH_3 - H)$, 480 $[CH_3(OC)_3WC_5H_4C_6H_6Mn]^+$, 464 $[(OC)_3WC_5H_4C_6H_5Mn]^+$, 380 $(WC_5H_4C_6H_5Mn)^+$, 220 $[MnCH(OC_2H_5)C_6H_4OCH_3]^+$, 196 $(C_5H_4C_6H_5Mn)^+$ and $[(CH_3OC_6H_4)CH(OC_2H_5)]^+$ (Found: C, 46.8; H, 3.4. Calc. for $C_{27}H_{25}MnO_7W$: C, 46.3; H, 3.6%).

$[WMe(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)C_6H_4CF_3\text{-}p]\}]$ 14. Similarly compound **2** (100 mg, 0.18 mmol) was treated with fresh $LiC_6H_4CF_3$-*p* prepared by the reaction of *p*-$CF_3C_6H_4Br$ (90 mg, 0.40 mmol) with $LiBu^n$ (0.40 mmol) in ether solution (50 cm^3) at −65 to −50 °C for 4 h. Subsequent alkylation and further treatment as described above yielded 65 mg (45%, based on **2**) of **14** as orange-red crystals, m.p. 70–72 °C (decomp.). Mass spectrum: *m/z* 682 $(M^+ - 2CO)$, 638 $(M^+ - 3CO - CH_3 - H)$, 480 $[CH_3(OC)_3WC_5H_4C_6H_6Mn]^+$, 464 $[(OC)_3WC_5H_4C_6H_5Mn]^+$, 380 $(WC_5H_4C_6H_5Mn)^+$, 258 $[MnCH(OC_2H_5)C_6H_4CF_3]^+$, 203 $[(CF_3C_6H_4)CH(OC_2H_5)]^+$ and 196 $(C_5H_4C_6H_5Mn)^+$ (Found: C, 41.1; H, 2.75. Calc. for $C_{27}H_{22}F_3MnO_6W{\cdot}CH_2Cl_2$: C, 40.85; H, 2.95%).

$[(OC)_3Mn\{(\eta^5\text{-}C_6H_6)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_6H_6)\}Mn(CO)_2\{{=}C(OEt)C_6H_4Me\text{-}o\}]$ 16. The compound $[(OC)_3Mn\{(\eta^5\text{-}C_6H_6)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_6H_6)\}Mn(CO)_3]$ **15**[18] (100 mg, 0.16 mmol) was dissolved in ether (30 cm^3) at −70 °C. To this solution was added dropwise LiC_6H_4Me-*o* (0.33 mmol) with stirring. The light yellow solution was stirred initially at −70 to −55 °C for 0.5 h and then at −55 to −35 °C for 4 h, during which time it turned yellow and a yellow precipitate separated. After evaporation of the solution to dryness *in vacuo*, the residue was subsequently alkylated with Et_3OBF_4 and further treated as described above to give 50 mg (44%, based on **15**) of yellow crystals of **16**, m.p. 42–44 °C (decomp.). Mass spectrum: *m/z* 682 $(M^+ - 2CO)$, 626 $(M^+ - 4CO)$, 618 $(M^+ - C_2H_5 - CH_3C_6H_4)$, 534 $(M^+ - 3CO - C_2H_5 - CH_3C_6H_4)$, 450 $[(MnC_6H_6C_5H_4)_2Fe]^+$, 395 $[Mn(C_6H_6C_5H_4)_2Fe]^+$, 338 $[(C_6H_5C_5H_4)_2Fe]^+$, 196 $(MnC_6H_5C_5H_4)^+$ and 149 $[(CH_3C_6H_4)CH(OC_2H_5)]^+$ (Found: C, 59.75; H, 4.3. Calc. for $C_{37}H_{32}FeMn_2O$: C, 60.2; H, 4.35%).

$[(OC)_3Mn\{(\eta^5\text{-}C_6H_6)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_6H_6)\}Mn(CO)_2\{{=}C(OEt)C_6H_4Me\text{-}p\}]$ 17. Similarly, compound **15** (200 mg, 0.32 mmol) dissolved in ether (40 cm^3) was treated with LiC_6H_4Me-*p* (0.65 mmol) at −55 to −35 °C for 4 h. Subsequent alkylation and further treatment as described above afforded 70 mg (31%, based on **15**) of orange crystalline **17**, m.p. 68–70 °C (decomp.). Mass spectrum: *m/z* 682 $(M^+ - 2CO)$, 638 $(M^+ - 2CO - OC_2H_4)$, 626 $(M^+ - 4CO)$, 618 $(M^+ - C_2H_5 - CH_3C_6H_4)$, 588 $(M^+ - COC_2H_5 - CH_3C_6H_4 - 2H)$, 534 $(M^+ - 3CO - C_2H_5 - CH_3C_6H_4)$, 450 $[(MnC_6H_6C_5H_4)_2Fe]^+$, 395 $[Mn(C_6H_6C_5H_4)_2Fe]^+$, 338 $[(C_6H_5C_5H_4)_2Fe]^+$, 252 $[MnC_6H_5C_5H_4Fe]^+$, 196 $(MnC_6H_5C_5H_4)^+$ and 149 $[(CH_3C_6H_4)CH(OC_2H_5)]^+$ (Found: C, 60.35; H, 4.25. Calc. for $C_{37}H_{32}FeMn_2O_6$: C, 60.2; H, 4.35%).

Crystallography

Single crystals of complex **3** suitable for X-ray diffraction study were obtained by recrystallization from light petroleum–CH_2Cl_2 solution at −80 °C. A crystal of approximate dimensions 0.20 × 0.20 × 0.40 mm was sealed in a capillary under a nitrogen atmosphere. Intensity data for 4152 independent reflections, of which 2516 had $I > 3\sigma(I)$, were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo-Kα radiation (λ 0.710 69 Å) with ω–2θ scan mode in the range $5 \leqslant 2\theta \leqslant 50°$. The intensity data were corrected for Lorentz-polarization effects and an empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.636 to 1.000.

The structure was solved and expanded by Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2516 observed reflections and 308 variable parameters and converged (largest parameter was 0.06 times its e.s.d.).

The standard deviation of an observation of unit weight was 1.74. The weighting scheme was based on counting statistics and included a factor ($p = 0.030$) to downweight the intense reflections. The maximum and minimum peaks on the final Fourier-difference map corresponded to 0.45 and −0.53 e $Å^{-3}$, respectively. All calculations were performed using the TEXSAN crystallographic software package.[25] Details of the crystallographic data and the procedures used for data collection and reduction are given in Table 3.

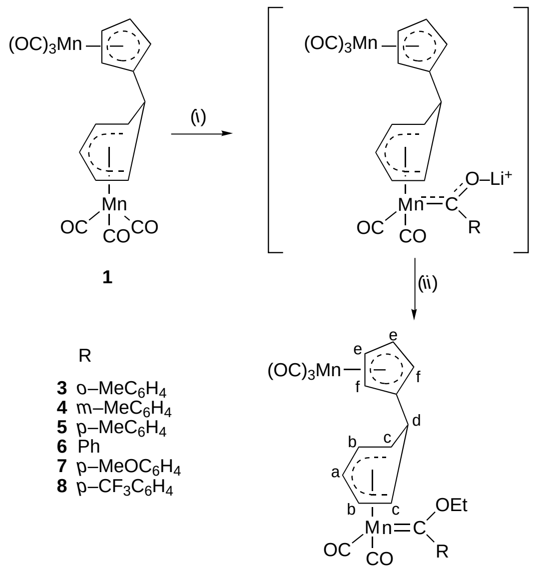
Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/288.

Results and Discussion

Compound **1** was treated with 2 molar equivalents of aryllithium reagents LiR (R = *o*-, *m*-, *p*-MeC_6H_4, Ph, *p*-$MeOC_6H_4$ or *p*-$CF_3C_6H_4$) in ether at −65 to −45 °C for 4 h. The acylmetalate intermediates formed were subsequently alkylated

Table 1 Infrared specta of complexes **1**–**17** in hexane in the ν(CO) region

Complex	$\tilde{\nu}$(CO)/cm^{-1}
1[18]	2020s, 1960s, 1954s
2[18]	2020s, 1994w, 1966s, 1958s, 1940w, 1935s
3	2000s, 1961s, 1947s, 1908m
4	2000s, 1957s, 1943s, 1900m
5	2002s, 1960s, 1948s, 1900m
6	2001s. 1958s, 1950s, 1902m
7	2002s, 1961s, 1952s, 1900m
8	2000s, 1960s, 1945s, 1910m
9	2010s, 1964s, 1953m, 1932vs, 1910w
10	2000s, 1960s, 1953s, 1931vs, 1900w
11	2000s, 1960s, 1953s, 1932vs, 1900w
12	2000s, 1960s, 1956m, 1934vs, 1905s
13	2000s, 1960s, 1955s, 1932vs, 1900m
14	2000s, 1962s, 1954s, 1933vs, 1911w
15[18]	2000s, 1950vs
16	2025s, 1959vs, 1950s, 1905m
17	2020s, 1957vs, 1950s, 1898m



Scheme 4 (*i*) 2LiR, Et_2O, −65 to −45 °C; (*ii*) Et_3OBF_4, water, 0 °C

with Et_3OBF_4 in aqueous solution at 0 °C. After removal of the solvent under high vacuum at low temperature, chromatography of the solid residue on an alumina column at −20 °C, and recrystallization from light petroleum–CH_2Cl_2 solution at −80 °C, orange-red crystalline complexes **3**–**8** were obtained with the composition $[(OC)_3Mn\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2\text{-}Mn{=}C(OEt)R]\}]$ (Scheme 4) in 53–71% yields. The complexes are soluble in polar organic solvents but only slightly soluble in non-polar solvents. They are sensitive to air and temperature in solution but fairly stable in the crystalline state. They are formulated as cyclohexadienyl-co-ordinated manganese carbene complexes on the basis of their elemental analyses and spectroscopic studies and a single-crystal X-ray diffraction study of **3**.

There are two olefin-co-ordinated $Mn(CO)_3$ units in complex **1**. However, neither dicarbene complexes nor cyclopentadienyl-co-ordinated carbene complexes were obtained in the reactions, only products **3**–**8**, even though more than 2 molar equivalents of aryllithium reagents were used. This might be ascribed to the different carbonyls of the two kinds of $Mn(CO)_3$ in **1**. To compare the reactivity, we treated $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$[26] with aryllithium reagents at 0–5 °C to afford the same manganese carbene complexes as reported.[27] It was also reported by Sheridan *et al.*[28] that tricarbonyl(η^5-cyclohexadienyl)manganese reacted with aryllithium at −50 °C to produce the manganese carbene complex. The difference between the temperatures at which tricarbonyl(η^5-cyclopentadienyl)- and tricarbonyl(η^5-cyclohexadienyl)-manganese react with the aryllithiums shows that the reactivities of the two kinds of olefin-co-ordinated $Mn(CO)_3$ in **1** are different. However, when **1** was treated with aryllithium reagents either at 0–5 °C or while the temperature was allowed to rise slowly from −65 to 0–5 °C only cyclohexadienyl-co-ordinated products **3**–**8** were obtained, not the expected cyclopentadienyl-co-ordinated manganese carbene complexes. The carbene formation at the less-electron-rich centre is predictable because cyclopentadienyl is a better donor than cyclohexadienyl.

The IR spectra (Table 1) and the solution ^1H NMR spectra (Table 2), as well as the mass spectra, of complexes **3**–**8** are consistent with the proposed structure. In the ^1H NMR spectra resonances at δ 5.20–3.30 and 1.60–1.40 are attributed to the ethoxy group and at δ 7.80–6.80 to the aryl group, in addition to the expected proton signals of the cyclopentadienyl and cyclohexadienyl groups. As compared with the starting material **1**, the chemical shift of H_a moved upfield and that of H_d changed a little, while use of H_b and H_c remained almost constant in **3**–**8**, indicating that the extent of back donation of d electrons from Mn to the π* orbital of the co-ordinated cyclohexadienyl increased only a little, upon formation of the carbene ligand. The difference between the chemical shifts of the cyclohexadienyl protons might be ascribed to the different distant shielding from the π electrons of the H_a, H_b, H_c and H_d protons, as shown for tricarbonyl(η^5-cyclohexadienyl)-manganese by Winkhaus *et al.*[29] The structural data for **3** show that H_a lies in the shielding area of the aryl ring. So we prefer to consider that the greatest influence on $\delta(H_a)$ comes from the shielding of the aryl ring.

In contrast to the singlet signal of complex **1**, all of the signals of the cyclopentadienyl protons in **3**–**8** split into doublet and triplet or multiplet peaks, indicating that the carbene ligand not only influences the extent of donation of d electrons from Mn to the cyclohexadienyl moiety but also changes the chemical environment of the C_5H_4 ring.

The mass spectra of complexes **3**–**8** (Experimental section) showed, besides their molecular ions, the principal fragments produced by successive loss of CO ligands and peaks generated by further cleavage of these principal fragments. The most important is $[C_5H_4C_6H_5Mn{=}CHR]^+$, which is characteristic of the combination of carbene ligands with manganese.

The molecular structure of complex **3** is shown in Fig. 1. The X-ray study confirmed the assigned structure and has many common features with previously determined carbene complex structures.[17,30] The Mn(1)–C(12) distance is 1.885(6) Å, which signifies a high double-bond character, and is the same within experimental error as that in the analogous carbene complexes $[Mn(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_6)(CO)_2\{{=}C(OEt)Ph\}]$ [1.89(1) Å][17] and $[Mn(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_6)(CO)_2\{{=}C(OEt)C_6H_4Me\text{-}o\}]$ [1.881(4) Å],[17] but slightly longer than that in $[Mn(\eta^5\text{-}C_5H_5)(CO)_2\text{-}\{C(OEt)Ph\}]$ [1.865(4) Å].[30] The C(12)–O(1) bond length of 1.354(7) Å is the same within experimental error as that of the corresponding C–O bond in $[Mn(\eta^5\text{-}C_5H_5)(CO)_2\{C(OEt)Ph\}]$ [1.356(17) Å][30] and comparable with that in $[Mn(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_6)(CO)_2\{{=}C(OEt)Ph\}]$ [1.34(1) Å][17] and $[Mn(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_6)(CO)_2\{{=}C(OEt)C_6H_4Me\text{-}o\}]$ [1.337(4) Å].[17] Unusual features are the O(1)–C(20) [1.484(9) Å] and the C(20)–C(21) [1.44(1) Å] bond lengths of the OEt group; the former is much longer than that of a normal C–O distance and the latter is between normal C–C and C=C distances, both of them being obviously different from that of OEt in analogous carbene complexes. For example, the corresponding O–C and C–C distances are 1.46(1) and 1.54(2) Å in $[Mn(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_6)\text{-}(CO)_2\{{=}C(OEt)Ph\}]$, and 1.471(17) and 1.507(21) Å in $[Mn(\eta^5\text{-}C_5H_5)(CO)_2\{C(OEt)Ph\}]$. It is proposed that the fairly strong electron donation from O(1) to the carbene carbon weakens the bonding between O(1) and C(20), leading to a lengthening of the bond distance and a lowering of the electron density around C(20). To compensate, part of the electron cloud around C(21)

Table 2 Proton NMR spectra of complexes **1**–**17** in $(CD_3)_2CO$ at 20 °C *

Complex	$\delta(C_5H_4C_6H_6)$	δ(aryl)	δ(OEt)	δ(Me)
1[18]	6.07 (t, 1 H), 5.20 (t, 2 H), 4.75 (s, 4 H), 3.51 (t, 2 H), 3.38 (t, 1 H)			
2[18]	6.07 (t, 1 H), 5.45 (t, 2 H), 5.30 (t, 2 H), 5.21 (t, 2 H), 3.45 (m, 3 H)			0.36 (s, 3 H)
3	5.68 (t, 1 H), 5.20 (t, 2 H), 4.68 (m, 4 H), 3.21 (m, 3 H)	7.18 (m, 3 H), 6.84 (m, 1 H), 3.30 (s, 3 H)	4.53 (q, 2 H), 1.43 (t, 3 H)	
4	5.65 (t, 1 H), 5.19 (t, 2 H), 4.75 (t, 2 H), 4.69 (d, 2 H), 3.50 (t, 2 H), 3.30 (t, 1 H)	7.36–7.09 (m, 4 H), 2.34 (s, 3 H)	5.03 (q, 2 H), 1.53 (t, 3 H)	
5	5.65 (t, 1 H), 5.20 (t, 2 H), 4.76 (t, 2 H), 4.70 (d, 2 H), 3.52 (t, 2 H), 3.34 (m, 1 H)	7.36 (m, 2 H), 7.16 (m, 2 H), 2.33 (s, 3 H)	5.13 (q, 2 H), 1.56 (t, 3 H)	
6	5.68 (t, 1 H), 5.20 (t, 2 H), 4.76 (t, 2 H), 4.69 (q, 2 H), 3.51 (t, 2 H), 3.33 (t, 1 H)	7.36 (m, 5 H)	5.08 (q, 2 H), 1.57 (t, 3 H)	
7	5.67 (t, 1 H), 5.20 (t, 2 H), 4.76 (t, 2 H), 4.70 (d, 2 H), 3.53 (t, 2 H), 3.12 (t, 1 H)	7.70 (d, 2 H), 6.93 (d, 2 H), 3.84 (s, 3 H)	3.37 (q, 3 H), 1.60 (t, 3 H)	
8	5.74 (t, 1 H), 5.19 (t, 2 H), 4.83 (t, 2 H), 4.74 (d, 2 H), 3.51 (t, 2 H), 3.25 (t, 1 H)	7.71 (d, 2 H), 7.40 (d, 2 H)	5.08 (q, 2 H), 1.57 (t, 3 H)	
9	5.68 (t, 1 H), 5.45 (d, 1 H), 5.40 (d, 1 H), 5.30 (d, 2 H), 5.24 (d, 2 H), 3.45 (m, 3 H)	7.25–7.13 (m, 3 H), 6.84 (m, 1 H), 3.28 (s, 3 H)	4.52 (q, 2 H), 1.43 (t, 3 H)	0.33 (s, 3 H)
10	5.67–5.61 (m, 1 H), 5.45 (t, 1 H), 5.40 (t, 1 H), 5.30 (t, 2 H), 5.21 (m, 2 H), 3.45 (t, 2 H), 3.37 (t, 1 H)	7.26–7.09 (m, 4 H), 2.36 (s, 3 H)	5.04 (q, 2 H), 1.55 (t, 3 H)	0.36 (s, 3 H)
11	5.67 (t, 1 H), 5.45 (t, 1 H), 5.40 (t, 1 H), 5.30 (t, 1 H), 5.24 (t, 1 H), 5.20 (d, 2 H), 3.46 (t, 2 H), 3.39 (t, 1 H)	7.36 (m, 2 H), 7.19 (m, 2 H), 2.35 (s, 3 H)	5.12 (q, 2 H), 1.58 (t, 3 H)	0.34 (d, 3 H)
12	5.68 (t, 1 H), 5.45 (d, 1 H), 5.39 (d, 1 H), 5.30 (t, 1 H), 5.23 (d, 1 H), 5.21 (d, 2 H), 3.45 (t, 2 H), 3.38 (t, 1 H)	7.34 (m, 5 H)	5.07 (q, 2 H), 1.57 (t, 3 H)	0.34 (d, 3 H)
13	5.69 (t, 1 H), 5.46 (t, 1 H), 5.40 (t, 1 H), 5.30 (t, 2 H), 5.22 (m, 2 H), 3.46 (m, 2 H), 3.08 (t, 1 H)	7.69 (d, 2 H), 6.92 (d, 2 H), 3.86 (s, 3 H)	4.78 (q, 2 H), 1.60 (t, 3 H)	0.35 (d, 3 H)
14	5.72 (t, 1 H), 5.43 (t, 1 H), 5.39 (t, 1 H), 5.28 (t, 1 H), 5.23 (t, 1 H), 5.18 (d, 2 H), 3.43 (t, 2 H), 3.36 (t, 1 H)	7.69 (d, 2 H), 7.38 (d, 2 H)	5.05 (q, 2 H), 1.55 (t, 3 H)	0.33 (d, 3 H)
15[18]	5.74 (t, 2 H), 4.85 (t, 4 H), 3.94 (t, 4 H), 3.75 (t, 4 H), 3.33 (m, 6 H)			
16	5.99 (m, 1 H), 5.60 (t, 1 H), 5.08 (m, 2 H), 4.56 (m, 2 H), 4.02 (t, 2 H), 3.95 (t, 2 H), 3.89 (t, 2 H), 3.83 (t, 2 H), 3.40 (q, 3 H), 3.19 (t, 3 H)	7.36–7.12 (m, 3 H), 6.86 (m, 1 H), 2.32 (s, 3 H)	3.60 (q, 2 H), 1.44 (t, 3 H)	
17	5.97 (t, 1 H), 5.57 (t, 1 H), 5.09 (m, 2 H), 4.65 (t, 2 H), 4.02 (t, 2 H), 3.95 (t, 2 H), 3.89 (t, 2 H), 3.83 (q, 2 H), 3.41 (t, 3 H), 3.23 (t, 3 H)	7.36 (m, 2 H), 7.19 (m, 2 H), 2.36 (s, 3 H)	3.60 (q, 2 H), 1.58 (t, 3 H)	

* Internal reference $SiMe_4$.

Table 3 Crystal data and experimental details for complex **3**

Empirical formula	$C_{26}H_{22}Mn_2O_6$
M	540.33
Crystal symmetry	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	12.018(4)
b/Å	12.415(3)
c/Å	8.758(2)
α/°	106.71(2)
β/°	102.15(2)
γ/°	71.56(2)
U/Å^3	1177.0(6)
Z	2
D/g cm^{-3}	1.525
μ(Mo-Kα)/cm^{-1}	11.12
Orientation reflections, 2θ range/°	14, 23.5–26.4
Data collection range, 2θ/°	2–50.0
No. unique data, total	4152
with $I > 3.00\sigma(I)$, N_o	2516
No. of parameters refined, N_p	308
R[a]	0.047
R'[b]	0.054
Goodness of fit[c]	1.74
Maximum shift/error in final cycle	0.06

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 1/\sigma^2(|F_o|)$. [c] $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$.

moves toward C(20) to form a partial double bond, C(20)–C(21).

The carbene carbon C(12) lies essentially in the benzene ring plane (±0.0068 Å). The C_5H_4 ring plane is oriented at an angle of 84.87° with respect to the η^5-dienyl plane, thus the C_5H_4 ring and η^5-dienyl ring planes are almost perpendicular to each other. The angle between the benzene ring and the C_5H_4 ring planes is 80.09°, thus these planes are also nearly perpendicular to each other. The angle between the benzene ring and the η^5-dienyl C(7)–C(11) plane of 10.54° shows that the benzene ring plane is nearly parallel to the η^5-dienyl ring plane.

The preparation of complexes **9**–**14** is similar to that of **3**–**8**. Compound **2** was treated with 2 molar equivalents of aryllithium reagents. LiR (R = *o*-, *m*-, *p*-MeC_6H_4, Ph, *p*-$MeOC_6H_4$ or *p*-$CF_3C_6H_4$) in ether at −65 to −50 °C for 4 h. After work-up the orange-red crystalline complexes **9**–**14** with compositions $[WMe(CO)_3\{\eta^5\text{-}C_5H_4[(\eta^5\text{-}C_6H_6)(OC)_2Mn{=}C(OEt)R\}]$ (Scheme 5) were isolated in 26–45% yields. The complexes have similar properties to those of **3**–**8**. They are formulated as cyclohexadienyl-co-ordinated manganese carbene complexes on the basis of their elemental analyses and spectroscopic studies. There are two different $M(CO)_3$ units in **2**, however no manganese–tungsten dicarbene complexes or cyclopentadienyl-co-ordinated tungsten carbene complexes were obtained even though more than 2 molar equivalents of aryllithiums were used.

The complexes **9**–**14** showed ^1H NMR spectral data consistent with the assigned structures (see Table 2). Compared with **2**, the cyclohexadienyl signals had greatly changed. The chemical shift of H_a moved upfield and the signal of H_b split into two triplet bands. Whereas a multiplet occurred for **2**, the signals of H_c and H_d were two triplets for **9**–**14**. As for the C_5H_4 ring, there is not much difference in the signals from **2** and **9**–**14**. In

Table 4 Bond distances (Å) and angles (°) for complex **3***

Mn(1)–C(7)	2.231(6)	Mn(1)–C(8)	2.158(6)	O(6)–C(26)	1.145(7)	C(1)–C(2)	1.418(9)
Mn(1)–C(9)	2.152(6)	Mn(1)–C(10)	2.147(6)	C(1)–C(5)	1.411(8)	C(2)–C(3)	1.409(9)
Mn(1)–C(11)	2.244(5)	Mn(1)–C(12)	1.885(6)	C(3)–C(4)	1.407(7)	C(4)–C(5)	1.417(8)
Mn(1)–C(22)	1.792(7)	Mn(1)–C(23)	1.803(7)	C(4)–C(6)	1.522(7)	C(6)–C(7)	1.517(7)
Mn(2)–C(1)	2.142(6)	Mn(2)–C(2)	2.139(6)	C(6)–C(11)	1.520(8)	C(7)–C(8)	1.409(8)
Mn(2)–C(3)	2.134(6)	Mn(2)–C(4)	2.153(5)	C(8)–C(9)	1.399(9)	C(9)–C(10)	1.412(9)
Mn(2)–C(5)	2.147(5)	Mn(2)–C(24)	1.779(9)	C(10)–C(11)	1.380(8)	C(12)–C(13)	1.501(8)
Mn(2)–C(25)	1.803(7)	Mn(2)–C(26)	1.798(7)	C(13)–C(14)	1.401(8)	C(13)–C(18)	1.392(8)
O(1)–C(12)	1.354(7)	O(1)–C(20)	1.484(9)	C(14)–C(15)	1.387(9)	C(15)–C(16)	1.395(10)
O(2)–C(22)	1.152(7)	O(3)–C(23)	1.140(7)	C(16)–C(17)	1.358(10)	C(17)–C(18)	1.392(9)
O(4)–C(24)	1.148(8)	O(5)–C(25)	1.134(7)	C(18)–C(19)	1.494(9)	C(20)–C(21)	1.44(1)
C(4)–Mn(2)–C(25)	152.1(3)	C(4)–Mn(2)–C(26)	95.8(2)	C(10)–Mn(1)–C(22)	90.1(2)	C(10)–Mn(1)–C(12)	135.3(2)
C(5)–Mn(2)–C(24)	153.0(3)	C(5)–Mn(2)–C(25)	113.9(3)	C(11)–Mn(1)–C(12)	169.0(2)	C(10)–Mn(1)–C(23)	122.3(3)
C(5)–Mn(2)–C(26)	97.1(3)	C(24)–Mn(2)–C(25)	91.5(3)	C(11)–Mn(1)–C(23)	86.7(2)	C(11)–Mn(1)–C(22)	102.3(2)
C(24)–Mn(2)–C(26)	90.2(3)	C(25)–Mn(2)–C(26)	92.1(3)	C(12)–Mn(1)–C(23)	102.4(3)	C(12)–Mn(1)–C(22)	83.4(3)
C(12)–O(1)–C(20)	122.8(5)	C(2)–C(1)–C(5)	108.4(6)	C(1)–Mn(2)–C(24)	139.7(3)	C(22)–Mn(1)–C(23)	95.3(3)
C(1)–C(2)–C(3)	107.2(5)	C(2)–C(3)–C(4)	108.9(6)	C(1)–Mn(2)–C(26)	129.9(3)	C(1)–Mn(2)–C(25)	90.3(3)
C(3)–C(4)–C(6)	124.2(5)	C(3)–C(4)–C(5)	107.7(5)	C(2)–Mn(2)–C(24)	102.3(3)	C(2)–Mn(2)–C(25)	103.3(3)
C(1)–C(5)–C(4)	107.8(5)	C(5)–C(4)–C(6)	128.0(5)	C(2)–Mn(2)–C(26)	159.8(3)	C(3)–Mn(2)–C(4)	38.3(2)
C(4)–C(6)–C(11)	111.3(5)	C(4)–C(6)–C(7)	117.0(5)	C(3)–Mn(2)–C(25)	140.9(3)	C(3)–Mn(2)–C(24)	90.5(3)
C(6)–C(7)–C(8)	120.0(5)	C(7)–C(6)–C(11)	102.7(4)	C(3)–Mn(2)–C(26)	127.0(3)	C(4)–Mn(2)–C(24)	115.1(3)
C(8)–C(9)–C(10)	116.8(5)	C(7)–C(8)–C(9)	120.3(5)	C(12)–C(13)–C(14)	118.4(5)	C(12)–C(13)–C(18)	121.0(5)
C(6)–C(11)–C(10)	119.7(5)	C(9)–C(10)–C(11)	121.9(6)	C(14)–C(13)–C(18)	120.4(5)	C(13)–C(14)–C(15)	120.2(6)
Mn(1)–C(12)–C(13)	123.8(4)	Mn(1)–C(12)–O(1)	132.5(4)	C(14)–C(15)–C(16)	119.0(6)	C(15)–C(16)–C(17)	120.3(6)
C(7)–Mn(1)–C(12)	109.8(2)	O(1)–C(12)–C(13)	103.2(5)	C(16)–C(17)–C(18)	122.1(7)	C(13)–C(18)–C(17)	117.9(6)
C(7)–Mn(1)–C(23)	86.0(3)	C(7)–Mn(1)–C(22)	166.2(2)	C(13)–C(18)–C(19)	121.3(6)	C(17)–C(18)–C(19)	120.7(6)
C(8)–Mn(1)–C(12)	91.6(2)	C(8)–Mn(1)–C(22)	142.1(3)	O(1)–C(20)–C(21)	107.8(8)	Mn(1)–C(22)–O(2)	178.1(6)
C(8)–Mn(1)–C(23)	122.3(3)	C(9)–Mn(1)–C(12)	102.0(2)	Mn(1)–C(23)–O(3)	173.8(6)	Mn(2)–C(24)–O(4)	178.1(7)
C(9)–Mn(1)–C(22)	106.6(3)	C(9)–Mn(1)–C(23)	148.8(3)	Mn(2)–C(25)–O(5)	179.2(6)	Mn(2)–C(26)–O(6)	179.8(6)

* Estimated standard deviations in the least significant figure are given in parentheses.

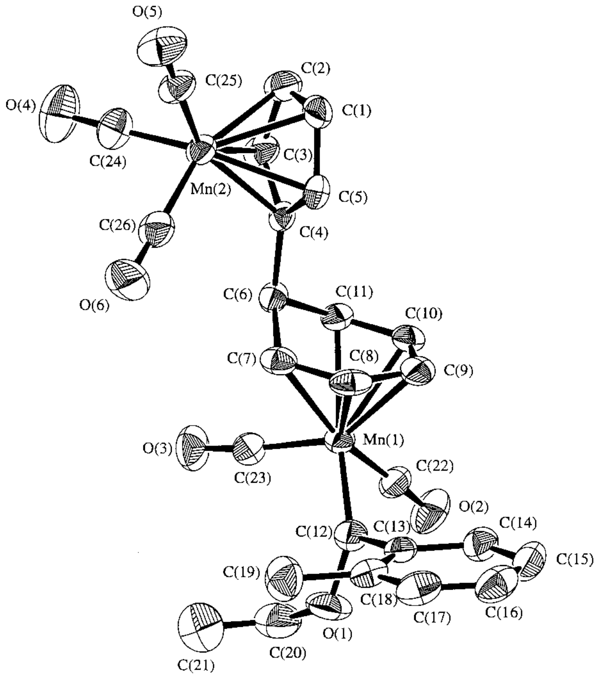
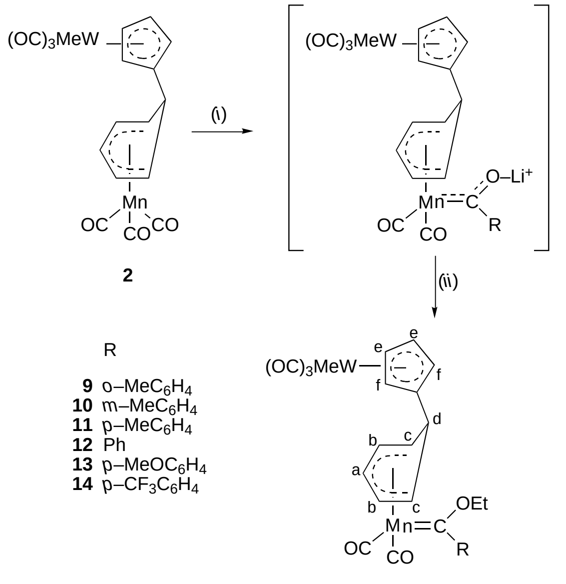


Fig. 1 Molecular structure of complex **3** showing the atom-labelling scheme and probability ellipsoids

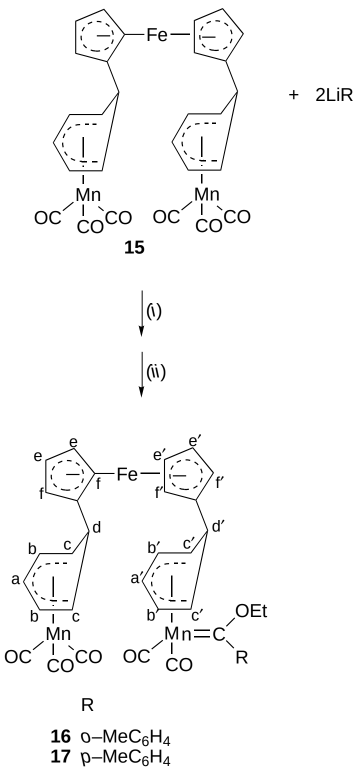
addition, the chemical shift of the methyl protons attached to the W(CO)$_3$ moiety is almost unchanged. It seems that the carbene ligand has much more influence on the chemical environment of the cyclohexadienyl than that of the cyclopentadienyl moiety, which suggests that the carbene ligand is attached to Mn instead of W.

The mass spectra of complexes **9–14** showed no molecular ion peaks due to the difficulty of vaporization, but showed principal fragments produced by loss of CO and carbene ligands and peaks such as [MnCH(OEt)R]$^+$ and [CH(OEt)R]$^+$, which are characteristic of the carbene ligands.



Scheme 5 (*i*) 2LiR, Et$_2$O, −65 to −50 °C; (*ii*) Et$_3$OBF$_4$, water, 0 °C

As mentioned above, the starting materials, **1** and **2**, both have two different M(CO)$_3$ (M = Mn or W) units co-ordinated to the different olefin ligands. Owing to the different reactivities of the carbonyls, only one kind of manganese carbene complex was obtained when treating **1** and **2** with aryllithium reagents. Thus, we chose [(OC)$_3$Mn{(η^5-C$_6$H$_6$)(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_4$)(η^5-C$_6$H$_6$)}Mn(CO)$_3$] **15**, in which the two Mn(CO)$_3$ units have the same chemical environment, as starting material for the reaction under the same conditions. However, we did still not obtain the expected dicarbene complex. When compound **15** was treated with 2 molar equivalents of LiR (R = *o*- or *p*-MeC$_6$H$_4$) in ether at −55 to −35 °C for 4 h, followed by alkylation with Et$_3$OBF$_4$ in aqueous solution at 0 °C, work-up afforded orange-red crystalline complexes **16** and **17** (Scheme 6) in 44 and 31% yields. These complexes have properties similar



Scheme 6 (*i*) Et_2O, −55 to −35 °C; (*ii*) Et_3OBF_4, water, 0 °C

to those of **3**–**8**. They are formulated as cyclohexadienyl-co-ordinated manganese carbene complexes with only one carbene on the basis of their elemental analyses and spectroscopic studies. Similarly, even increasing the amount of the aryllithium reagents used gave no dicarbene manganese complexes.

In the ^1H NMR spectra of complexes **16** and **17**, resonances at δ 3.60 and 1.58–1.44 attributed to the ethoxy group and at δ 7.36–6.86 assigned to the aryl group, in addition to the expected proton signals of the cyclopentadienyl and cyclohexadienyl groups, were observed. As compared with **15**, the proton signals of the cyclohexadienyl ring of **16** and **17** changed greatly. In **15**, H_a and $H_{a'}$ and H_b and $H_{b'}$ shared the same triplet signals, and the signals of H_c, $H_{c'}$ and H_d, $H_{d'}$ appeared as a multiplet. On the other hand, for **16** and **17**, the signals of H_a, $H_{a'}$ and H_b, $H_{b'}$ all split into two multiplet or triplet bands, and the signals of H_c, $H_{c'}$ and H_d, $H_{d'}$ also appeared as a triplet or a quartet. As for the C_5H_4 rings, the proton signals appeared as two triplet bands for **15** but as four triplets for **16** and **17**. The ^1H NMR spectra showed that the chemical environments of the two cyclohexadienyl ligands in both complexes **16** and **17** are very different from that of **15**, being characteristic of a complex with only one carbene ligand.

The mass spectra of complexes **16** and **17** showed no molecular ions but the principal fragments produced by successive loss of CO ligands and peaks such as $[Mn(C_6H_6C_5H_4)_2Fe]^+$, $[C_6H_5C_5H_4Fe]^+$, $[MnC_6H_5C_5H_4]^+$ and $[RCH(OC_2H_5)]^+$, all of which provided useful structure information.

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