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Chemistry of the Metal Carbonyls. Part 74.[1] Reactions of Phenylmanganese Pentacarbonyl with Cycloheptatrienes, and Related Studies

By **Jennifer C. Burt, Selby A. R. Knox, Ronald J. McKinney,** and **F. Gordon A. Stone,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Phenyl-group migration occurs on treatment of [MPh(CO)$_5$] (M = Mn or Re) with cycloheptatriene, yielding substituted cycloheptadienyl complexes [M{1—5-η-C$_7$H$_8$(Ph-6)}(CO)$_3$]. Hydride abstraction with [CPh$_3$][BF$_4$] gives an isomeric mixture of salts [Mn(1—6-η-C$_7$H$_7$Ph)(CO)$_3$][BF$_4$], whose reactions with nucleophiles have been studied. The complex [MnPh(CO)$_5$] also reacts with substituted cycloheptatrienes C$_7$H$_7$(R-7) (R = Me or Ph) to give [Mn{1—5-η-C$_7$H$_7$(R)(Ph)}(CO)$_3$] as an isomeric mixture. No products have been isolated from reactions of cycloheptatriene with [MnR(CO)$_5$] (R = Me or SiMe$_3$), but a low yield of the migration product has been obtained from [Mn(CH$_2$Ph)(CO)$_5$] and the triene.

RECENTLY we found that in reactions of the complexes [Ru(CO)$_4$(MMe$_3$)$_2$] and [{Ru(CO)$_4$(MMe$_3$)}$_2$] (M = Si or Ge) with cycloheptatriene,[2] cyclo-octatetraene,[3] or azulene,[4] labilization of trimethyl-silyl and -germyl groups occurs, the MMe$_3$ groups being transferred to the entering organic ligand. The mechanism of these transfers is not clearly understood although they appear to be intramolecular,[2] a process which is well documented[5] for the migration of alkyl or aryl groups from transition metals to carbonyl ligands. In contrast to the so-called carbonyl-insertion reactions, there have been relatively few reports of alkyl or aryl ligand migration from a metal to a co-ordinated organic group. However, these include ethyl[6] and phenyl[7] migration from molybdenum to a cyclopentadienyl ligand, phenyl migration from vanadium to a cyclopentadienyl group,[8] and, very recently, transfer of a phenyl group from niobium to cyclo-octatetraene.[9]

Initial co-ordination of an unsaturated group followed by transfer of a σ-bonded organic ligand must be important steps in many insertion reactions; for example, in reactions of [MnR(CO)$_5$] (R = Me or Ph) with butadiene,[10] or [MnMe(CO)$_5$] with *o*-styryldiphenylphosphine,[11] where formally acetyl or benzoyl groups are transferred. The present study was undertaken in order to establish whether phenyl groups would transfer to cycloheptatrienes in reactions of the latter with phenylmanganese pentacarbonyl.

RESULTS AND DISCUSSION

Phenylmanganese pentacarbonyl reacted with cycloheptatriene in heptane at reflux to give air-stable white crystalline [Mn{1—5-η-C$_7$H$_8$(Ph-6)}(CO)$_3$] (1a) in good yield, in addition to [Mn$_2$(CO)$_{10}$] and small amounts of the known[12] [Mn(1—5-η-C$_7$H$_9$)(CO)$_3$] (2a). The formulation (1a) is strongly indicated by the mass spectrum, which had intense ions corresponding to the molecular ion $[M]^+$, $[M - n\text{CO}]^+$ (n = 1—3), and to C$_7$H$_8$Ph$^+$, and by the carbonyl i.r. spectrum which is typical of the essentially *fac*-Mn(CO)$_3$ group. The ^{1}H n.m.r. spectrum (Table) is in turn consistent with a cycloheptadienyl

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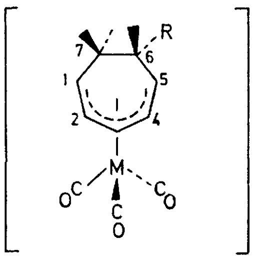
Complex	Colour	M.p. (θ_c/°C)	$\bar{\nu}$(CO) [a]/cm^{-1}	^{1}H N.m.r. (τ) [b]
[Mn{1—5-η-C_7H_8(Ph-6-*endo*)}$(CO)_3$] (1a)	White	112—113	2 021s, 1 952s, 1 942s	2.8 (5 H, m), 4.22 (1 H, t), 4.66 (1 H, dd), 5.20 (1 H, dd), 6.02 (1 H, dd), 6.30 (1 H, dd), 7.0 (1 H, td), 7.45 (1 H, dd), 7.9 (1 H, m)
[Mn{1—5-η-C_7H_8(Ph-6-*exo*)}$(CO)_3$] [c]		74—75	2 010s, 1 935s	2.88 (5 H, s), 4.18 (1 H, t), 4.56 (1 H, dd), 5.00 (1 H, dd), 6.00 (3 H, m), 7.90 (1 H, q), 9.10 (1 H, m)
[Re{1—5-η-C_7H_8(Ph-6-*endo*)}$(CO)_3$] (1b)	White	125--126	2 028s, 1 951s, 1 939s	2.76 (5 H, m), 4.04 (1 H, t), 4.34 (1 H, dd), 4.68 (1 H, dd), 5.48 (1 H, m), 5.94 (1 H, d), 6.80 (1 H, td), 7.4 (2 H, m)
[Re(1—5-η-C_7H_9)$(CO)_3$] (2b)	White	40—41	2 024s, 1 949s, 1 935s	4.14 (1 H, tt), 4.58 (2 H, dd), 5.72 (2 H, m), 7.88 (4 H, m)
[Mn(1—6-η-C_7H_7Ph)$(CO)_3$][BF_4] (3)	Yellow	250 (decomp.)	2 078s, 2 010s [d]	see text
[Mn{1—5-η-C_7H_7(Ph-6-*endo*)(D-7-*exo*)}$(CO)_3$] (4)	Pale yellow	106—108	2 020s, 1 951s, 1 943s	2.81 (5 H, m), 4.19 (1 H, t), 4.62 (1 H, dd), 5.13 (1 H, dd), 5.98 (1 H, dd), 6.29 (1 H, dd), 7.10 (1 H, m), 7.94 (1 H, m)
[Mn{1—5-η-C_7H_7(Me-7-*exo*)(Ph-6-*endo*)}$(CO)_3$] (5)	Pale yellow	108—109	2 020s, 1 949s, 1 941 s	2.79 (5 H, m), 4.16 (1 H, dd), 4.63 (1 H, dd), 5.17 (1 H, dd), 5.98 (1 H, dd), 6.40 (1 H, m), 6.9 (1 H, m), 8.6 (1 H, m), 9.29 (3 H, d)
[Mn{1—5-η-C_7H_7(Me-6-*exo*)(Ph-1)}$(CO)_3$] (6)	Yellow	92—93	2 018s, 1 952s, 1 938s	2.70 (5 H, m), 3.82 (1 H, d), 4.19 (1 H, t), 5.19 (1 H, dd), 6.04 (1 H, m), 6.6 (1 H, m), 8.0 (1 H, m), 9.12 (3 H, d), 9.2 (1 H, m)
[Mn{1—5-η-C_7H_8(Me-6-*exo*)}$(CO)_3$] [c]	Pale yellow	38—39	2 010s, 1 950s	4.20 (1 H, t), 4.68 (1 H, q), 5.22 (1 H, q), 6.14 (1 H, d), 6.45 (1 H, m), 6.80 (1 H, m), 8.02 (1 H, sxt), 9.02 (3 H, d), 9.35 (1 H, spt)
[Mn{1—5-η-C_7H_7(Ph-1)(OMe-6-*exo*)}$(CO)_3$] (7)	Yellow	87—89	2 020s, 1 954s, 1 943s	2.75 (5 H, m), 3.83 (1 H, d), 4.26 (1 H, t), 5.02 (1 H, dd), 5.53 (1 H, m), 5.96 (1 H, m), 6.61 (3 H, s), 7.6 (1 H, m), 9.2 (1 H, m)
[Mn{1—5-η-C_7H_8(OMe-6-*exo*)}$(CO)_3$] [c]	Yellow	60—61	2 010s, 1 950s	4.20 (1 H, t), 4.60 (1 H, q), 5.05 (1 H, q), 5.80 (1 H, sxt), 6.17 (1 H, m), 6.80 (1 H, m), 6.80 (3 H, s), 7.90 (1 H, sxt), 9.38 (1 H, spt)

[a] In hexane solution, unless otherwise indicated. [b] In $CDCl_3$ solution, unless otherwise indicated. [c] From ref. 12, i.r. in CCl_4 solution, ^{1}H n.m.r. in CS_2 solution. [d] In dichloromethane solution.

ligand monosubstituted in the 6 position, showing five inequivalent dienyl protons and three aliphatic protons. Evidence that the phenyl substituent occupies the 6-*endo* position in (1a) is supplied by the work of Haque *et al.*[12] who described a complex of the same formulation, obtained by reaction of phenyl-lithium with the co-ordinated cycloheptatriene complex [Mn(1—6-η-C_7H_8)-$(CO)_3$][BF_4]. For this complex the phenyl substituent was firmly assigned [12] to the *exo*-6 position, as a result of double-resonance studies [13] on related complexes of the same stereochemistry and as expected for an inter-molecular nucleophilic attack on the C_7 ring. The ^{1}H n.m.r. values for both species are given in the Table, revealing their different character, and suggesting *endo*-6-phenyl substitution in (1a). Detailed analysis [13] of the ^{1}H n.m.r. spectra of [Mn{1—5-η-C_7H_8(R-6-*exo*)}-$(CO)_3$] (R = Me or OMe) led to the suggestion that a twist conformation about C^6 and C^7 holds the *exo*-H^7 proton of these species above and within the shielding region of the cycloheptadienyl π system, thus explaining the high-field (τ *ca.* 9) resonance. Extending this notion to (1a) we anticipate the conformation shown below which holds the *endo*-phenyl substituent furthest from the metal, allowing the assignment of the aliphatic proton signals at τ 7.0, 7.5, and 7.9 to *endo*-H^7, *exo*-H^7, and *exo*-H^6 respectively by comparison with the data of the earlier study.[13] The *endo*-phenyl stereochemistry



(1a) M = Mn, R = Ph
(1b) M = Re, R = Ph
(1c) M = Mn, R = $PhCH_2$
(2a) M = Mn, R = H
(2b) M = Re, R = H

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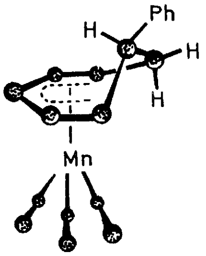
[13] M. I. Foreman and F. Haque, *J. Chem. Soc.* (*B*), 1971, 418.

assigned to (1a) is supported by the observation (discussed below) that the complex undergoes smooth and presumably *exo*-hydride abstraction by $[CPh_3][BF_4]$, in contrast[12] to its *exo*-phenyl isomer. An *endo*-phenyl configuration for (1a) is, of course, to be expected of an intramolecular migration from manganese to a co-ordinated cycloheptatriene, perhaps from within a complex of the type $[MnPh(\eta^4\text{-}C_7H_8)(CO)_3]$.

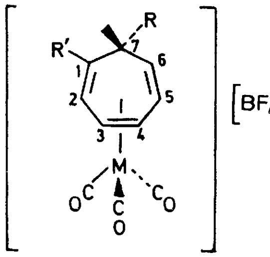


Although phenylrhenium pentacarbonyl also reacted with cycloheptatriene, in refluxing octane, complex (1b) was only a minor product, that in largest yield being $[Re(1\text{—}5\text{-}\eta\text{-}C_7H_9)(CO)_3]$ (2b), together with some $[Re_2(CO)_{10}]$. The ^1H n.m.r. spectrum of (1b) is similar to that of (1a), though shifted downfield somewhat, suggesting that in the rhenium complex the phenyl substituent is also in the *endo*-6 position. It is interesting to note that in the ^1H n.m.r. spectrum of (2b) the four aliphatic protons appeared as a symmetrical narrow multiplet (*ca.* 0.3 p.p.m. wide at 100 MHz), in contrast to the published spectrum[13] of the manganese derivative (2a) which displays a very broad, unsymmetrical, multiplet (*ca.* 1.2 p.p.m. at 60 MHz) for the analogous four protons.

The ability of various other σ-bonded groups to migrate to cycloheptatriene was investigated. No products were isolated from reactions of $[MnR(CO)_5]$ (R = Me or $SiMe_3$) with the triene, but a low yield of (1c) was obtained from benzylmanganese pentacarbonyl. Complexes (1) were, however, produced equally well from the acyls $[M(CO)_5(COR)]$ (M = Mn, R = Ph or CH_2Ph; M = Re, R = Ph). There was no evidence for products involving RCO group migration to the ring, in contrast to earlier work with butadiene[10] and *o*-styryldiphenylphosphine.[11]

Mixtures of isomeric products were obtained in low yield from reactions of the substituted cycloheptatrienes $C_7H_7(R\text{-}7)$ (R = Me or Ph) with $[MnPh(CO)_5]$. These mixtures could not be separated by column chromatography or vacuum sublimation, but ^1H n.m.r. spectra, although complex, suggest that two isomers of $[Mn\{1\text{—}5\text{-}\eta\text{-}C_7H_7(R)(Ph)\}(CO)_3]$ (R = Me or Ph) are present in each case. This is perhaps a result of the cycloheptatriene initially co-ordinating with the substituent *exo* or *endo* with respect to the metal.

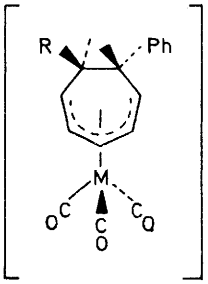
In dichloromethane at reflux, hydride abstraction from (1a) occurred readily on treatment with triphenylmethyl tetrafluoroborate to give the substituted cycloheptatriene complex $[Mn(1\text{—}6\text{-}\eta\text{-}C_7H_7Ph)(CO)_3][BF_4]$ (3) in high yield. The usual *exo*-hydride abstraction by $[CPh_3][BF_4]$ can in principle lead to either or both of the isomers (3a) and (3b) of the manganese salt, and the ^1H n.m.r. spectrum does indicate the presence of two isomers. Although we were unable to separate these isomers, stirring the salt at room temperature in dichloromethane for several hours led to substantial enrichment in an isomer with n.m.r. signals [τ 2.6 (m, 5 H), 3.1 (m, 2 H), 5.4 (m, 2 H), 7.5 (m, 1 H) (CD_3NO_2 solution)] attributable to symmetric (3a). A satisfactory n.m.r. spectrum could not be obtained for the other isomer, but the structure (3b) is strongly indicated by the nature of the products obtained on treating (3) with nucleophiles.



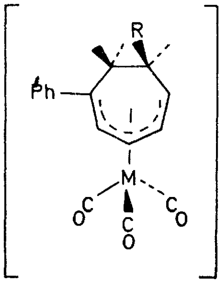
(3a) R = Ph, R' = H
(3b) R = H, R' = Ph

Reactions of various nucleophiles R^- (R = H, D, Me, or OMe) with the salt (3) gave, as expected, two isomers of formula $[Mn\{1\text{—}5\text{-}\eta\text{-}C_7H_7(R)(Ph)\}(CO)_3]$. Repeated chromatography and vacuum sublimation allowed the isolation in each case of at least one isomer in a quite pure state, and both isomers for R = Me. For R = H, D, and Me the isolated isomer was identified by n.m.r. spectroscopy as (1a), (4), and (5) respectively, corresponding to R^- attack at the 1 or 6 position of (3a), while for R = Me and OMe the products (6) and (7) were separated, attributable to attack at the 6 position of isomer (3b).

Complexes (4) and (5) showed five dienyl protons in their n.m.r. spectra, and for R = D the *exo*-R configuration expected to follow intermolecular nucleophilic attack was confirmed by the similarity of the spectra of (1a) and (4), except for the absence in the latter of the signal assigned to the *exo*-7 proton of (1a). Comparison of the spectrum of (5) with that of $[Mn\{1\text{—}5\text{-}\eta\text{-}C_7H_8(Me\text{-}6\text{-}exo)\}(CO)_3]$[13] (given in the Table) provides further



(4) R = D
(5) R = Me



(6) R = Me
(7) R = OMe

confirmation of the stereochemistry assigned, for the spectra differ substantially only in the lack of an *endo*-proton signal in the former. Complexes (6) and (7) were clearly identified by their n.m.r. spectra, each of which was almost identical to that of the appropriate [Mn-$\{1\text{—}5\text{-}\eta\text{-}C_7H_8(R\text{-}6\text{-}exo)\}(CO)_3$] (R = Me or OMe)[13] derivative, except for the modification resulting from phenyl substitution at C^1.

EXPERIMENTAL

All the experiments were carried out under nitrogen with carefully dried solvents. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer, ^1H n.m.r. spectra on Varian HA100 or T-60 spectrometers, and mass spectra for molecular weights on an A.E.I. MS902 instrument operating at 70 eV ionizing potential.* The complexes [$MR(CO)_5$] were prepared by treating the respective pentacarbonylmetal anions with either benzoyl or phenylacetyl chloride, followed by decarbonylation of the acyl derivative thereby obtained.[14]

Reaction of Cycloheptatriene (*cht*) *with* [$MR(CO)_5$].—(*a*) The complex [$MnPh(CO)_5$] (5.0 g, 17 mmol) and cht (5.0 g, 54 mmol) were heated in heptane (200 cm^3) at reflux for 20 h giving a yellow solution. Removal of solvent at reduced pressure followed by chromatography of the residue (alumina, eluting with light petroleum) gave in order of elution (*i*) [$Mn_2(CO)_{10}$] (0.7 g, 21%), identified by i.r., (*ii*) [$Mn(C_7H_9)(CO)_3$][12] (2a) (90 mg, 2%) identified by i.r. and mass spectroscopy, and (*iii*) cream *crystals* of [Mn-$(C_7H_8Ph)(CO)_3$] (1a) (2.5 g, 49%) (Found: C, 61.4; H, 4.2%; *M*, 308. $C_{16}H_{13}MnO_3$ requires C, 62.3; H, 4.2%; *M*, 308).

(*b*) The complex [$RePh(CO)_5$] (0.86 g, 2.13 mmol) and excess of cht (2 cm^3, *ca.* 20 mmol) were heated in octane (150 cm^3) at reflux for 16 h. Chromatography as above then gave in order of elution (*i*) [$Re_2(CO)_{10}$] (0.10 g, 15%) identified by i.r., (*ii*) white *crystals* of [$Re(C_7H_9)(CO)_3$] (2b) (0.30 g, 40%) (Found: C, 33.2; H, 2.5%; *M*, 362. $C_{10}H_9O_3Re$ requires C, 33.1; H, 2.5%; *M*, 362), and (*iii*) white *crystals* of [$Re(C_7H_8Ph)(CO)_3$] (1b) (0.124 g, 14%) (Found: C, 43.7; H, 3.1%; *M*, 438. $C_{16}H_{13}O_3Re$ requires C, 43.7; H, 3.0%; *M*, 438).

(*c*) The complex [$Mn(CH_2Ph)(CO)_5$] (0.50 g, 2 mmol) and cht (0.60 g, 6.5 mmol) were heated in heptane (80 cm^3) at reflux for 17 h. Chromatography as above gave (*i*) [$Mn_2(CO)_{10}$] (80 mg, 14%) identified by i.r. and (*ii*) a yellow *oil*, [$Mn(C_7H_8CH_2Ph)(CO)_3$] (1c) (20 mg, 4%) (Found: *M*, 322. $C_{17}H_{15}MnO_3$ requires *M*, 322), ν(CO) at 2 018s, 1 951s, and 1 940s cm^{-1} (in hexane).

Reaction of 7-*Methylcycloheptatriene with* [$MnPh(CO)_5$].—The reactants [0.50 g (5 mmol) and 0.50 g (2 mmol), respectively] were heated in hexane (80 cm^3) at reflux for 2 weeks. Chromatography gave in order of elution (*i*) [$Mn_2(CO)_{10}$] (50 mg, 12%) identified by i.r., (*ii*) yellow solid [$Mn(C_7H_8Me)(CO)_3$][12] (10 mg, 2%) identified by i.r. and mass spectroscopy, and (*iii*) a yellow *solid* isomeric mixture of [$Mn\{C_7H_7(Me)(Ph)\}(CO)_3$] (80 mg, 15%) (Found: C, 63.1; H, 4.8%; *M*, 322. $C_{17}H_{15}MnO_3$ requires C, 63.4; H, 4.7%; *M*, 322), which sublimed at *ca.* 70 °C (10^{-2} mmHg).

Reaction of 7-*Phenylcycloheptatriene with* [$MnPh(CO)_5$].—The reactants [1.5 g (9 mmol) and 1.4 g (5 mmol), respectively] were heated in heptane (150 cm^3) at reflux for 20 h. Chromatography with light petroleum yielded in order of elution (*i*) [$Mn_2(CO)_{10}$] (0.30 g, 17%) identified by i.r., and (*ii*) a yellow *oil*, [$Mn(C_7H_7Ph_2)(CO)_3$] (0.45 g, 25%) (Found: C, 67.6; H, 4.7%; *M*, 384. $C_{22}H_{17}MnO_3$ requires C, 68.8; H, 4.4%; *M*, 384), distilled at *ca.* 70 °C (10^{-2} mmHg).

Reaction of [$Mn(C_7H_8Ph)(CO)_3$] (1a) *with* [CPh_3][BF_4].—Complex (1a) (1.25 g, 4 mmol) and [CPh_3][BF_4] (1.6 g, 5 mmol) were heated in dichloromethane (35 cm^3) at reflux for 3 h, precipitating a yellow powder, identified as an isomeric mixture of [$Mn(C_7H_7Ph)(CO)_3$][BF_4] (3) (1.2 g, 77%) (Found: C, 47.6; H, 3.2. $C_{16}H_{12}BF_4MnO_3$ requires C, 48.7; H, 3.3%), after washing with hexane and drying under high vacuum.

Reaction of [$Mn(C_7H_7Ph)(CO)_3$][BF_4] (3) *with Nucleophiles*.—(*a*) MeLi. A sample of (3) (0.35 g, 0.9 mmol) suspended in anhydrous diethyl ether at 0 °C was treated with a diethyl ether solution of MeLi (1.5 mmol) and stirred for 1.5 h, followed by 12 h at room temperature. The suspension so formed was hydrolysed, extracted with diethyl ether (50 cm^3), and the extract dried over Mg[SO_4], solvent then being removed at reduced pressure. The residue was chromatographed and a yellow band, eluted with light petroleum, collected in two fractions. Rechromatography of each of these fractions allowed isolation of two isomers of [$Mn\{C_7H_7(Me)(Ph)\}(CO)_3$] in order of elution (*i*) pale yellow *crystals* of (5) (0.10 g, 35%) (Found: C, 63.3; H, 4.8%; *M*, 322. $C_{17}H_{15}MnO_3$ requires C, 63.3; H, 4.7%; *M*, 322) and (*ii*) yellow *crystals* of (6) (0.08 g, 27%) (Found: C, 63.8; H, 5.1%; *M*, 322), each purified by sublimation at *ca.* 50 °C (10^{-2} mmHg).

(*b*) Na(OMe). Samples of (3) (0.30 g, 0.8 mmol) and Na(OMe) (0.06 g, 1 mmol) were stirred in dried methanol (40 cm^3) at room temperature for 20 min. Removal of solvent, followed by chromatography, gave a yellow *solid* isomeric mixture of [$Mn\{C_7H_7(Ph)(OMe)\}(CO)_3$] (0.14 g, 56%) (Found: C, 61.3; H, 4.5%; *M*, 338. $C_{17}H_{15}MnO_4$ requires C, 60.4; H, 4.4%; *M*, 338). Repeated chromatography of the mixture allowed isolation of isomer (7) in a relatively pure state.

(*c*) Na[BH_4]. A sample of (3) (0.30 g, 0.8 mmol) was mixed with Na[BH_4] (0.40 g, 11 mmol) and distilled water was added (50 cm^3). The mixture was stirred at room temperature until no orange solid remained (*ca.* 2.5 h). The products were then extracted with diethyl ether and dried over Mg[SO_4]. Chromatography gave a white solid mixture of isomers of [$Mn(C_7H_8Ph)(CO)_3$] (0.11 g, 47%) (Found: C, 62.4; H, 4.9%; *M*, 308. $C_{16}H_{13}MnO_3$ requires C, 62.3; H, 4.2%; *M*, 308). Repeated chromatography allowed isolation of pure (1a).

(*d*) Na[BD_4]. A sample of (3) (0.25 g, 0.7 mmol) was treated with Na[BD_4] (0.20 g, 5 mmol) as above, giving an isomeric mixture of [$Mn\{C_7H_7(Ph)(D)\}(CO)_3$] (0.12 g, 60%) [Found: C, 62.3; H(D), 4.9%; *M*, 309. $C_{16}H_{12}DMnO_3$ requires C, 62.1; H(D), 4.9%; *M*, 309]. Repeated chromatography allowed isolation of pure (4) as pale yellow *crystals*.

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* 1 eV ≈ 1.60 × 10^{-19} J; 1 mmHg ≈ 13.6 × 9.8 Pa.

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