# Reactions of 1—3-η-Allyl-manganese and -rhenium Tetracarbonyls with Phosphines, Phosphites, and Triphenylarsine. The Crystal and Molecular Structure of 1—3-η-Allyldicarbonylbis(trimethyl phosphite)manganese(I)

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The complexes $[M(\eta\text{-}C_3H_5)(CO)_3L]$ [M = Mn, L = $PPh_3$, $AsPh_3$, $P(C_6H_{11})_3$, $PBu^n_3$, or $PMePh_2$; M = Re, L = $PPh_3$] and $[M(\eta\text{-}C_3H_5)(CO)_2L_2]$ [M = Mn, L = $PMePh_2$, $P(OMe)_3$, $P(OEt)_3$, or $\frac{1}{2}$ $Ph_2PCH_2PPh_2$; M = Re, L = $PPh_3$] have been prepared from $[M(\eta\text{-}C_3H_5)(CO)_4]$ using thermal or photolytic methods. Taking the allyl group as bidentate, the complexes are considered to possess pseudo-octahedral structures, the carbonyl ligands being *facial* in the tricarbonyls and *cis* in the dicarbonyls. The $^1H$ n.m.r. spectra are characteristic of $\eta^3$-allyl species and show strong $^1H$–$^{31}P$ coupling. The mass spectra of the complexes have also been obtained and fragmentation pathways suggested mainly on the basis of observed metastable peaks. Crystals of $[Mn(\eta\text{-}C_3H_5)(CO)_2\{P(OMe)_3\}_2]$ are monoclinic with $a$ = 18.618(11), $b$ = 9.218(7), $c$ = 10.607(11), β = 102.1(1)°, $Z$ = 4, and space group $P2_1/a$. 1 742 Independent reflections above background have been collected on a diffractometer and refined to $R$ 0.059. The metal atom has a distorted octahedral environment, being bonded to two mutually *trans* phosphorus atoms [Mn–P 2.175(5) and 2.219(5) Å], two *cis* carbonyls [Mn–C 1.75(2) and 1.83(2) Å], and an allyl group [Mn–C 2.223(17), 2.114(14), and 2.229(13) Å].

THE complex $[Mn(\eta\text{-}C_3H_5)(CO)_3(PPh_3)]$ has recently been isolated[1] from a phase-transfer catalysed reaction between $[MnBr(CO)_4(PPh_3)]$ and $C_3H_5Br$, and claimed to be a new compound. In fact it was first reported[2] in 1969, having been prepared by thermal reactions between $PPh_3$ and either $[Mn(\eta\text{-}C_3H_5)(CO)_4]$ or $[Mn(\sigma\text{-cyclo-}C_3H_5CO)(CO)_5]$. Apart from the two unusual products $[Mn\{\eta^3\text{-}CH(SH)C(Ph)CMe(Ph)\}(CO)_3]$[3] and $[Mn(CO)_3\{\eta\text{-}C_3F_2(CF_3)(AsMe_2)_2\}(AsMe_2)Mn(CO)_3]$[4] which contains a $\eta^3$-$C(CF_3)CCF_2$ moiety bonded to one of the metal atoms, the $PPh_3$ complex remained until very recently the sole example of a simple ligand-substituted allyl complex of the Group 7A metal carbonyls. However, Stuhl and Muetterties[5] have now reported that $[Mn(\eta\text{-}C_3H_5)(CO)_2(PR_3)_2]$ (R = Et, OMe, or $OPr^i$) and $[Mn(\eta\text{-}C_3H_5)(CO)\{P(OMe)_3\}_3]$ can be prepared from $[Mn(\eta\text{-}C_3H_5)(CO)_4]$. The effectiveness of these complexes in catalysing the hydrogenation of alkenes and alkynes was tested, and the dicarbonyl complexes shown to be the first catalyst precursors that involve a $Mn^I$–$Mn^{III}$ couple. At the time of their report we had also isolated a number of related allylmanganese tricarbonyl and dicarbonyl complexes, and in view of the catalytic potential of these complexes we have also prepared the first two allylrhenium analogues and completed a single-crystal $X$-ray structural analysis on a representative example of this class of complexes, namely $[Mn(\eta\text{-}C_3H_5)(CO)_2\{P(OMe)_3\}_2]$.

## EXPERIMENTAL

*Physical Methods.*—Infrared spectra of samples were recorded on a Perkin-Elmer 597 spectrophotometer as Nujol or hexachlorobutadiene mulls, liquid films, or as a solution in n-pentane, carbon tetrachloride, or chloroform. Hydrogen-1 n.m.r. spectra in $CDCl_3$, $CS_2$, or $CD_2Cl_2$ were obtained on JEOL PS 100 and Varian EM 360 spectrometers with tetramethylsilane as internal reference. Mass spectra were recorded using an A.E.I. MS 12 spectrometer, samples being introduced *via* an all-glass inlet system, with an ionising energy of 70 eV † being employed. In order to facilitate mass measurement some spectra were determined with the addition of perfluorokerosene as a reference. Ion abundances are expressed relative to a metal-containing base peak of 100 units. Melting points were determined using a Kofler heating block.

*Materials.*—The complexes $[Mn(\eta\text{-}C_3H_5)(CO)_4]$[6] and $[Re(\eta\text{-}C_3H_5)(CO)_4]$[7] were prepared, as previously described, by decarbonylation of $[M(\sigma\text{-}C_3H_5)(CO)_5]$. The required $[Mn(CO)_5]^-$ was normally prepared[6] from $[Mn_2(CO)_{10}]$ and sodium amalgam, but occasionally $Li[BEt_3H]$ was used in place of the amalgam and found to be very efficient in cleaving the metal–metal bond of the carbonyl.[8] The purity of these starting materials was checked by i.r. and $^1H$ n.m.r. spectroscopy.[6,7,9] Liquid phosphines and phosphites were stored over molecular sieves and vacuum-distilled before use. Solid ligands were used as received.

*Reactions.*—All thermal reactions and subsequent manipulations were performed under dry nitrogen using dried and degassed solvents. Photochemical reactions were carried out in a conventional reaction vessel fitted with a quartz water-cooled immersion well, a reflux condenser, and a cannula for admission of dry nitrogen. The irradiation source was a 100-W medium-pressure mercury arc lamp.

1—3-η-*Allyltricarbonyl*(*triphenylphosphine*)*manganese*(I)[1,2]—A mixture of $[Mn(\eta\text{-}C_3H_5)(CO)_4]$ (2 mmol) and $PPh_3$ (2 mmol) was heated in refluxing cyclohexane (25 cm$^3$) for 3 h. Removal of the solvent (25 °C, 15 mmHg) † left a pale yellow solid which was dissolved in the minimum volume of light petroleum–diethyl ether (12 : 1). Chromatography on a Florisil column (30 × 2 cm) using the same mixed solvent for elution followed by removal of the solvent gave pale yellow *crystals*, yield 53%, m.p. 159 °C (decomp.) (Found: C, 65.2; H, 4.65. $C_{24}H_{20}MnO_3P$

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† Throughout this paper: 1 eV ≈ $1.60 \times 10^{-19}$ J; 1 mmHg ≈ 13.6 × 9.8 Pa.

requires C, 65.2; H, 4.55%). N.m.r. spectrum * ($CS_2$): $\tau$ 8.31 (q of t, 2 H, $H_X$), 7.92 (overlapping q of t, 2 H, $H_M$), 6.22 (m, 1 H, $H_A$), and 2.65 (d, 15 H, $C_6H_5$); $J_{AX}$ 12.0, $J_{AM}$ 7.2, $J_{PX}$ 3.8, $J_{PM}$ 1.2, and $J_{MX}$ 1.2 Hz.

1—3-$\eta$-*Allyltricarbonyl(triphenylarsine)manganese*(I).—Reaction between $[Mn(\eta\text{-}C_3H_5)(CO)_4]$ (2 mmol) and $AsPh_3$ (4 mmol) for 8 h in refluxing cyclohexane (25 $cm^3$) followed by removal of solvent and chromatography as above gave two fractions. The first was unchanged tetracarbonyl and the second a product isolated as pale yellow *crystals*, yield 31%, m.p. 157 °C (decomp.), after removal of solvent and recrystallisation from pentane (Found: C, 59.1; H, 4.00. $C_{24}H_{20}AsMnO_3$ requires C, 59.3; H, 4.15%). N.m.r. spectrum ($CDCl_3$): $\tau$ 8.16 (d, 2 H, $H_X$), 7.57 (d, 2 H, $H_M$), 5.98 (tt, 1 H, $H_A$), and 2.64 (m, 15 H, $C_6H_5$); $J_{AX}$ 12.0 and $J_{AM}$ 7.0 Hz.

1—3-$\eta$-*Allyltricarbonyl(tricyclohexylphosphine)manganese*(I).—A similar reaction to that above using $[Mn(\eta\text{-}C_3H_5)(CO)_4]$ (2 mmol) and $P(C_6H_{11})_3$ (3 mmol) in refluxing cyclohexane (25 $cm^3$) for 4 h followed by similar work-up procedures and recrystallisation from pentane gave pale yellow *crystals*, yield 33%, m.p. 178 °C (decomp.) (Found: C, 62.6; H, 8.25. $C_{24}H_{38}MnO_3P$ requires C, 62.6; H, 8.30%). N.m.r. spectrum ($CD_2Cl_2$): $\tau$ 8.74 and 8.16 (broad m, 33 H, $C_6H_{11}$), 7.80 (dd, 2 H, $H_X$), 7.41 (dd, 2 H, $H_M$), and 5.44 (m, 1 H, $H_A$); $J_{AX}$ 12, $J_{AM}$ 7, $J_{PX}$ 6, and $J_{PM}$ *ca.* 1 Hz.

1—3-$\eta$-*Allyltricarbonyl(tri-n-butylphosphine)manganese*(I).—A mixture of $[Mn(\eta\text{-}C_3H_5)(CO)_4]$ (2 mmol) and $PBu^n{}_3$ (2 mmol) was heated in refluxing cyclohexane for 20 min. {Longer reaction times led to mixtures of $[Mn(\eta\text{-}C_3H_5)(CO)_{4-x}(PBu^n{}_3)_x]$ ($x$ = 1—3) as indicated by i.r. spectra in the $\nu$(CO) region.} The solution was reduced in volume to *ca.* 5 $cm^3$ and initially chromatographed on a Florisil column using cyclohexane as eluant. Removal of cyclohexane left an oily residue which was dissolved in the minimum volume of dichloromethane and then subjected to chromatography again. A yellow fraction eluted from the column by dichloromethane gave a yellow hygroscopic *liquid*, yield 49%, on removal of solvent (Found: C, 56.2; H, 8.55. $C_{18}H_{32}MnO_3P$ requires C, 56.5; H, 8.45%). N.m.r. spectrum ($CDCl_3$): $\tau$ 9.08 (m, 9 H, $CH_3$), 8.61 [broad m, 18 H, $(CH_2)_3$], 8.27 (dd, 2 H, $H_X$), 7.62 (dd, 2 H, $H_M$), and 6.08 (m, 1 H, $H_A$); $J_{AX}$ 12, $J_{AM}$ 7, $J_{PX}$ 5, and $J_{PM}$ *ca.* 1 Hz.

1—3-$\eta$-*Allyltricarbonyl(methyldiphenylphosphine)manganese*(I).—A mixture of $[Mn(\eta\text{-}C_3H_5)(CO)_4]$ (2 mmol) and $PMePh_2$ (2 mmol) dissolved in cyclohexane (75 $cm^3$) was photolysed at room temperature for 20 h using the method described above. Infrared evidence indicated that although some unchanged tetracarbonyl remained after this time, prolonged photolysis led to lower yields of the desired complex, the related dicarbonyl (see below) being formed together with decomposition products. The solution was filtered, reduced in volume, and chromatographed on a Florisil column using cyclohexane. The first fraction consisted of unreacted starting material. Changing to a light petroleum–diethyl ether (12 : 1) solvent allowed the elution of a yellow band which gave an oil on removal of the solvent. The oil was purified by dissolution in pentane, filtering, and evaporation of the solvent. The product was a yellow hygroscopic *liquid*, yield 36% (Found: C, 61.0; H, 4.85. $C_{19}H_{18}MnO_3P$ requires C, 60.0; H, 4.75%). N.m.r. spectrum ($CS_2$): $\tau$ 8.38 (q, 2 H, $H_X$), 8.37 (d, 3 H, $CH_3$), 7.97 (overlapping q, 2 H, $H_M$), 6.40 (m, 1 H, $H_A$), and 2.66 (m, 10 H, $C_6H_5$); $J_{AX}$ 11.8, $J_{AM}$ 7.0, $^2J_{PH}$ 7.0, $J_{PX}$ 5.0, $J_{MX}$ 1.2, and $J_{PM}$ *ca.* 1.0 Hz.

1—3-$\eta$-*Allyldicarbonylbis(methyldiphenylphosphine)manganese*(I).—A similar photolysis reaction to that above using $PMePh_2$ (8 mmol) and $[Mn(\eta\text{-}C_3H_5)(CO)_4]$ (2 mmol), and a reaction time of 72 h, followed by removal of the solvent (25 °C, 15 mmHg), gave an oily residue. This was dissolved in pentane (300 $cm^3$), filtered, and the volume of the filtrate reduced until crystallisation was evident. The filtrate was then left at 0 °C for several hours to give bright yellow *crystals*, yield 32%, m.p. 154 °C (decomp.) which were filtered off and washed with pentane (Found: C, 66.8; H, 5.60. $C_{31}H_{31}MnO_2P_2$ requires C, 67.4; H, 5.65%). N.m.r. spectrum ($CDCl_3$): $\tau$ 8.35—7.80 (m, 10 H, $CH_3$, $H_X$, and $H_M$), 6.20 (m, 1 H, $H_A$), and 2.75 (m, 20 H, $C_6H_5$).

1—3-$\eta$-*Allyl[bis(diphenylphosphino)methane]dicarbonylmanganese*(I).—A mixture of $[Mn(\eta\text{-}C_3H_5)(CO)_4]$ (4 mmol) and $Ph_2PCH_2PPh_2$ (dppm) (4 mmol) was heated in refluxing light petroleum (b.p. 80—100 °C, 50 $cm^3$) for 18 h. After filtering the hot solution, removal of the solvent left a solid which was recrystallised from a $CH_2Cl_2$–$C_2H_5OH$ (1 : 1) mixture to give orange *crystals*, yield 25%, m.p. 204 °C (decomp.) (Found: C, 66.4; H, 5.15. $C_{30}H_{27}MnO_2P_2$ requires C, 67.2; H, 5.05%).

1—3-$\eta$-*Allyldicarbonylbis(trimethyl phosphite)manganese*(I).[5]—A mixture of $[Mn(\eta\text{-}C_3H_5)(CO)_4]$ (3 mmol) and $P(OMe)_3$ (6 mmol) was heated in refluxing cyclohexane (25 $cm^3$) for 1.5 h. Removal of the solvent left a yellow oil which was chromatographed on a Florisil column using light petroleum (60—80 °C)–diethyl ether (12 : 1) as eluant. A pale yellow fraction was collected, the solvent reduced in volume, and kept at −20 °C to yield pale yellow *platelets*, yield 66%, m.p. 46 °C (Found: C, 33.5; H, 5.80. $C_{11}H_{23}MnO_8P_2$ requires C, 33.0; H, 5.80%). N.m.r. spectrum ($CDCl_3$): $\tau$ 8.62 (m, 2 H, $H_X$), 7.82 (d of m, 2 H, $H_M$), 6.40 (t, 18 H, $OCH_3$), and 5.44 (m, 1 H, $H_A$); $J_{PX}$ 14, $J_{AX}$ 11.5, $J_{PH}$ 10.5, $J_{AM}$ 7, $J_{PM}$ *ca.* 1, and $J_{MX}$ *ca.* 0.5 Hz.

1—3-$\eta$-*Allyldicarbonylbis(triethyl phosphite)manganese*(I).—A similar procedure to that above for the $P(OMe)_3$ complex gave 1.6 g of a yellow oil after chromatography. Very pale yellow *crystals*, yield 41%, m.p. 24 °C, were obtained from the oil by recrystallisation six times from pentane at −78 °C (Found: C, 42.0; H, 7.00. $C_{17}H_{35}MnO_8P_2$ requires C, 42.2; H, 7.30%). N.m.r. spectrum ($CDCl_3$): $\tau$ 8.74 (m, 20 H, $H_X$, and $OCH_2CH_3$), 7.87 (d, 2 H, $H_M$), 6.04 (m, 12 H, $OCH_2CH_3$), and 5.46 (m, 1 H, $H_A$); $J_{AM}$ 7 Hz.

1—3-$\eta$-*Allyltricarbonyl(triphenylphosphine)rhenium*(I).—A mixture of $[Re(\eta\text{-}C_3H_5)(CO)_4]$ (1 mmol) and $PPh_3$ (2 mmol) was heated in refluxing cyclohexane (25 $cm^3$) for 85 h during which time the $\nu$(CO) region of the i.r. spectrum was monitored. After this time the intensity of the $\nu$(CO) bands of a tricarbonyl product reached a maximum although some unchanged tetracarbonyl as well as some dicarbonyl product were also present. Removal of the solvent left a white solid which was dissolved in warm light petroleum–diethyl ether (12 : 1) and the solution then subjected to chromatography on a Florisil column. Further monitoring by i.r. spectroscopy allowed the separation of a product obtained as a *white powder*, yield 35%, m.p. 168 °C, after removal of the solvent (Found: C, 50.6; H, 3.95. $C_{24}H_{20}O_3PRe$ requires C, 50.3; H, 3.50%). N.m.r. spectrum

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* The allyl protons are labelled according to: M, the *syn*-protons; X, the *anti*-protons; and A, the central proton.

($CDCl_3$): τ 7.94 (d of m, 2 H, $H_X$), 7.68 (dt, 2 H, $H_M$), 6.18 (m, 1 H, $H_A$), and 2.68 (d, 15 H, $C_6H_5$); $J_{AX}$ 12, $J_{AM}$ 7, $J_{PX}$ 4, and $J_{MX}$ 1.2 Hz.

1—3-η-*Allyldicarbonylbis(triphenylphosphine)rhenium*(I).—A mixture of [$Re(\eta-C_3H_5)(CO)_4$] (1 mmol) and $PPh_3$ (6 mmol) was heated in refluxing cyclohexane (80 cm³) for 22 d. By monitoring the course of the reaction by i.r. spectroscopy, it was clear that [$Re(\eta-C_3H_5)(CO)_3(PPh_3)$] was the major product in solution. However, after 6 d a solid began to appear and the reaction was continued until the i.r. spectrum of a sample of the solution showed no further change. After cooling, the solid was filtered off, and then dissolved in hot dichloromethane–light petroleum (b.p. 80—100 °C). Evaporation of this solvent was then continued until crystals began to appear. After standing at 0 °C for several hours, the *crystals*, yield 56%, m.p. > 260 °C (decomp.) were collected, washed with pentane, and dried *in vacuo* (Found: C, 60.9; H, 4.45. $C_{41}H_{35}O_2P_2Re$ requires C, 61.0; H, 4.35%). N.m.r. spectrum ($CD_2Cl_2$): τ 9.16 (m, 2 H, $H_X$), 8.01 (d, 2 H, $H_M$), 5.86 (m, 1 H, $H_A$), and 2.43 (m, 30 H, $C_6H_5$); $J_{AM}$ 7 Hz.

*Crystal Data*.—$C_{11}H_{23}MnO_8P_2$, $M = 400.1$, Monoclinic, $a = 18.618(11)$, $b = 9.218(7)$, $c = 10.607(11)$ Å, $\beta = 102.1(1)°$, $U = 1\,780.0$ Å³, $D_c = 1.49$ g cm⁻³, $Z = 4$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,7$ Å, $\mu = 9.90$ cm⁻¹, $F(000) = 832$, space group $P2_1/a$ from systematic absences, $h0l$ with $h = 2n + 1$ and $0k0$ with $k = 2n + 1$.

A sample of [$Mn(\eta-C_3H_5)(CO)_2\{P(OMe)_3\}_2$] was recrystallised three times from pentane at −20 °C to provide crystals suitable for the *X*-ray determination. A crystal with dimensions 0.2 × 0.5 × 1.5 mm was mounted with the (101) planes perpendicular to the instrument axis of a General Electric XRD 5 diffractometer which was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum *X*-radiation was used. The stationary-crystal–stationary-counter method was used with a take-off angle of 4° and a counting time of 10 s. Individual backgrounds were taken as a function of 2θ. 1 742 Independent reflections were measured with $2\theta < 40°$ of which 1 348 with $I > 2\sigma(I)$ were used in subsequent calculations. Neither an absorption nor an extinction correction was applied.

The positions of the manganese atoms were obtained from the Patterson map, and subsequent Fourier maps gave all the remaining non-hydrogen-atom positions. These were refined and then a difference-Fourier synthesis was calculated and all hydrogen atoms were located. The positions of the allyl hydrogen atoms were allowed to refine independently while those of the methyl groups were refined as rigid groups with free rotation allowed about the C–C bond. For all hydrogen atoms, isotropic thermal parameters were refined successfully. All other atoms were given anisotropic thermal parameters and the structure was refined by full-matrix least squares to *R* 0.059. The weighting scheme employed was chosen to give similar values of $w\Delta^2$ over ranges of $F_o$ and $(\sin\theta)/\lambda$, and was $w^{\frac{1}{2}} = 1$ for $F_o < 40$ and $w^{\frac{1}{2}} = 40/F_o$ for $F_o > 40$. Calculations were made using the SHELX 76 [10] system of programs at the University of London Computer Centre. Scattering factors and dispersion corrections were taken from ref. 11. The final list of atomic positions is given in Table 1 and the bond lengths and angles in Table 2. The final difference-Fourier map showed no significant peaks, and the zero-weighted reflections showed no large discrepancies. Lists of structure factors, thermal parameters, and hydrogen-atom positions are given in Supplementary Publication No. SUP 22831 (8 pp.).*

## RESULTS AND DISCUSSION

The complexes [$M(\eta-C_3H_5)(CO)_3L$] [M = Mn, L = $PPh_3$, $AsPh_3$, $P(C_6H_{11})_3$, $PBu^n{}_3$, or $PMePh_2$; M = Re, L = $PPh_3$] and [$M(\eta-C_3H_5)(CO)_2L_2$] [M = Mn, L = $PMePh_2$, $P(OMe)_3$, $P(OEt)_3$, or ½ dppm; M = Re, L = $PPh_3$] have been prepared by carbonyl-displacement reactions employing [$M(\eta-C_3H_5)(CO)_4$] as the starting material. The manganese products are markedly susceptible to air oxidation, particularly in solution, the solids slowly turning from pale or bright yellow to brown. They can, however, be stored indefinitely under nitrogen at ambient temperatures. The two rhenium complexes appear to be air-stable as solids and much less prone to oxidation in solution.

Most syntheses could be effectively carried out thermally, but the two methyldiphenylphosphine complexes are best prepared photolytically as thermal reactions gave mixtures of products separable only with difficulty. A number of other analogous reactions have also been studied and although pure solid products have not been isolated, usually because of separation problems, i.r. evidence from the ν(CO) region clearly indicates that [$M(\eta-C_3H_5)(CO)_3L$] [M = Mn, L = unidentate dppm, unidentate $Ph_2PCH_2CH_2PPh_2$ (dppe), or $P(OMe)_3$; M = Re, L = $P(C_6H_{11})_3$ or $P(OMe)_3$], [$M(\eta-C_3H_5)(CO)_2L_2$] [M = Mn, L = $PBu^n{}_3$ or ½dppe; M = Re, L = $P(C_6H_{11})_3$ or $P(OMe)_3$], and [$Mn(\eta-C_3H_5)(CO)(PBu^n{}_3)_3$] are present in the reaction mixtures.

Of the complexes isolated in this work only [$Mn(\eta-C_3H_5)(CO)_3(PPh_3)$] [1,2] and [$Mn(\eta-C_3H_5)(CO)_2\{P(OMe)_3\}_2$] [5] have been previously reported. There are considerable disparities in the quoted melting point of the $PPh_3$ complex, found to be 159 °C (decomp.) by us and reported as either 120—125 (decomp.) [1] or 140—142 °C [2] in the literature. The two rhenium complexes [$Re(\eta-C_3H_5)(CO)_{4-x}(PPh_3)_x$] ($x$ = 1 or 2) are the first carbonyl ligand-substitution products to be obtained from [$Re(\eta-C_3H_5)(CO)_4$]. These rhenium complexes can also be prepared by activating the substitution photolytically, but the yields ($x$ = 1, 19%; $x$ = 2, 13%) are considerably poorer than those attained in thermal reactions. As anticipated, the substitution proceeds at a much slower rate for rhenium than for manganese (see Experimental section). Apart from the isolation of [$Mn(\eta-C_3H_5)(CO)_3(AsPh_3)$], all the complexes prepared contain phosphorus donor ligands and attempts to use the nitrogen donor ligands pyridine, 2,2′-bipyridyl, or 1,2-diaminoethane in analogous reactions were unsuccessful.

In a number of cases we have also prepared the manganese complexes by more direct thermal reactions between [$Mn(\sigma-C_3H_5)(CO)_5$] and phosphorus donor ligands in refluxing cyclohexane. Thus it would appear that *separate* decarbonylation of the σ-allyl to [$Mn(\eta-C_3H_5)(CO)_4$] is not essential since presumably ready

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

decarbonylation *in situ* precedes the carbonyl-substitution steps in such reactions. As we have previously found [7] that $[Re(\sigma\text{-}C_3H_5)(CO)_5]$ cannot be successfully thermally decarbonylated, but only photolytically, to give $[Re(\eta\text{-}C_3H_5)(CO)_4]$, it is not surprising that similar reactions between $[Re(\sigma\text{-}C_3H_5)(CO)_5]$ and phosphorus donor ligands in refluxing cyclohexane do not lead to the formation of $[Re(\eta\text{-}C_3H_5)(CO)_{4-x}L_x]$ ($x = 1$ or 2) analogues.

TABLE 1

Atomic co-ordinates ( $\times 10^4$) with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mn | 1 454(1) | 1 852(3) | 2 540(2) |
| P(1) | 760(2) | 2 893(5) | 3 688(4) |
| P(2) | 2 040(2) | 620(5) | 1 266(4) |
| O(1) | −91(5) | 2 438(12) | 3 199(10) |
| O(2) | 918(5) | 2 683(13) | 5 213(9) |
| O(3) | 731(6) | 4 632(12) | 3 793(11) |
| O(4) | 2 848(5) | 1 140(13) | 1 256(10) |
| O(5) | 2 111(7) | −1 106(13) | 1 416(11) |
| O(6) | 1 688(6) | 609(14) | −259(9) |
| C(1) | −653(9) | 2 972(23) | 3 819(17) |
| C(2) | 920(11) | 1 263(24) | 5 741(17) |
| C(3) | 463(11) | 5 512(20) | 2 659(19) |
| C(4) | 3 297(10) | 494(26) | 452(18) |
| C(5) | 2 448(12) | −1 810(23) | 2 576(20) |
| C(6) | 1 014(10) | −196(24) | −776(17) |
| C(7) | 988(8) | 242(18) | 2 738(13) |
| O(7) | 669(7) | −824(14) | 2 876(13) |
| C(8) | 812(9) | 2 529(17) | 1 112(16) |
| O(8) | 426(7) | 2 974(14) | 227(11) |
| C(12) | 2 254(9) | 3 664(18) | 2 665(17) |
| C(13) | 2 285(8) | 2 981(18) | 3 835(14) |
| C(14) | 2 460(8) | 1 520(18) | 4 074(14) |

The i.r. ν(CO) band frequencies of the complexes are listed in Table 3 along with weak bands at *ca.* 1 500 cm$^{-1}$ which are characteristic of $\eta^3$-allyl groups. The analogous allyl bands of $[M(\eta\text{-}C_3H_5)(CO)_4]$ are found at 1 500 cm$^{-1}$ (M = Mn) [12] and 1 495 cm$^{-1}$ (M = Re).[7] The observed ν(CO) band patterns may be rationalised if the complexes are considered to be pseudo-octahedral with the $\eta^3$-allyl group occupying two co-ordination sites as suggested independently by Stuhl and Muetterties [5] and Oudeman and Sorensen,[13] and supported by the crystal structure of $[Mn(\eta\text{-}C_3H_5)(CO)_2\{P(OMe)_3\}_2]$ reported here. A consideration of the local symmetry of the carbonyl groups and the nature of the other ligands, but without speculating on possible orientations of the $\eta^3$-allyl group, shows that the tricarbonyl complexes could exist in two isomeric forms with the three carbonyl ligands taking up either *fac* or *mer* arrangements. Both isomers should give rise to three i.r.-active ν(CO) bands. In general, the *fac* isomer may be distinguished from the *mer* by band intensity measurements, since for the former three strong absorptions are predicted [14] whereas one weak and two strong bands are expected for the latter. In solution or as liquid films all the tricarbonyl complexes display three strong ν(CO) bands, indicating the isolation of *fac* isomers of general formula $[M(CO)_3(\text{bidentate})L]$ ($C_s$ local symmetry; $2A' + A''$). The complex $[Mn(\eta\text{-}C_3H_5)(CO)_3\{P(C_6H_{11})_3\}]$ consistently shows an additional weak shoulder on the band of intermediate frequency.

All the dicarbonyl complexes display two strong ν(CO) bands ($A_1 + B_1$) consistent with a *cis*-dicarbonyl arrangement. In all of these complexes, apart from $[Mn(\eta\text{-}C_3H_5)(CO)_2(\text{dppm})]$, the band at lower frequency, assignable to the asymmetric stretching mode, is the more intense. Since the relative intensities of the two bands (assessed here by measurement of the areas under the peaks) are dependent upon the angle 2θ between the two C–O bonds,[15] according to $I_a/I_s = \tan^2\theta$ it is apparent that for these complexes the OC–M–CO angle exceeds 90°. For $[Mn(\eta\text{-}C_3H_5)(CO)_2\{P(OMe)_3\}_2]$ a value of 102° has been calculated from solution i.r. data and this compares with the value of 97.7° obtained from the single-crystal structure determination. In this bis(phosphite) complex the phosphite ligands are mutually *trans* and the carbonyl ligands are *trans* to the small-bite chelating $\eta^3$-allyl ligands; it is therefore understandable that 2θ will exceed 90°. We have no reason to suppose that this ligand arrangement is different in the other dicarbonyl complexes, apart from $[Mn(\eta\text{-}C_3H_5)(CO)_2(\text{dppm})]$, and certainly multinuclear n.m.r. evidence [5] favours this stereoisomeric arrangement for $[Mn(\eta\text{-}C_3H_5)(CO)_2\{P(OPr^i)_3\}_2]$. The phosphorus ligands cannot be mutually *trans* in $[Mn(\eta\text{-}C_3H_5)(CO)_2(\text{dppm})]$ as it contains a chelating ditertiary phosphine ligand. Since

TABLE 2

Bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| (*a*) Distances | | | |
| Mn–P(1) | 2.175(5) | Mn–P(2) | 2.219(5) |
| Mn–C(7) | 1.75(2) | Mn–C(8) | 1.83(2) |
| Mn–C(12) | 2.223(17) | Mn–C(13) | 2.114(15) |
| Mn–C(14) | 2.229(13) | | |
| P(1)–O(1) | 1.62(1) | P(2)–O(4) | 1.58(1) |
| P(1)–O(2) | 1.59(1) | P(2)–O(5) | 1.60(1) |
| P(1)–O(3) | 1.61(1) | P(2)–O(6) | 1.61(1) |
| O(1)–C(1) | 1.43(2) | O(4)–C(4) | 1.44(2) |
| O(2)–C(2) | 1.42(2) | O(5)–C(5) | 1.42(2) |
| O(3)–C(3) | 1.45(2) | O(6)–C(6) | 1.46(2) |
| C(7)–O(7) | 1.17(2) | C(8)–O(8) | 1.13(2) |
| C(12)–C(13) | 1.38(2) | C(13)–C(14) | 1.40(2) |
| (*b*) Angles | | | |
| P(1)–Mn–P(2) | 172.8(2) | | |
| P(1)–Mn–C(7) | 86.6(6) | P(1)–Mn–C(8) | 87.2(6) |
| P(1)–Mn–C(12) | 96.0(5) | P(1)–Mn–C(13) | 81.9(5) |
| P(1)–Mn–C(14) | 99.2(4) | | |
| P(2)–Mn–C(7) | 87.6(6) | P(2)–Mn–C(8) | 89.4(6) |
| P(2)–Mn–C(12) | 90.6(5) | P(2)–Mn–C(13) | 105.1(5) |
| P(2)–Mn–C(14) | 85.9(4) | | |
| C(7)–Mn–C(8) | 97.7(7) | | |
| C(7)–Mn–C(12) | 166.1(6) | C(7)–Mn–C(14) | 99.1(6) |
| C(8)–Mn–C(12) | 96.1(7) | C(8)–Mn–C(14) | 162.4(7) |
| C(12)–Mn–C(14) | 67.0(6) | | |
| Mn–P(1)–O(1) | 111.3(4) | Mn–P(2)–O(4) | 116.1(5) |
| Mn–P(1)–O(2) | 120.6(4) | Mn–P(2)–O(5) | 119.2(5) |
| Mn–P(1)–O(3) | 120.7(5) | Mn–P(2)–O(6) | 117.8(5) |
| O(1)–P(1)–O(2) | 104.7(6) | O(4)–P(2)–O(5) | 104.0(7) |
| O(1)–P(1)–O(3) | 103.6(6) | O(4)–P(2)–O(6) | 100.5(6) |
| O(2)–P(1)–O(3) | 93.0(6) | O(5)–P(2)–O(6) | 95.8(6) |
| P(1)–O(1)–C(1) | 121.6(10) | P(2)–O(4)–C(4) | 123.3(11) |
| P(1)–O(2)–C(2) | 119.7(10) | P(2)–O(5)–C(5) | 123.6(11) |
| P(1)–O(3)–C(3) | 120.7(10) | P(2)–O(6)–C(6) | 121.0(11) |
| Mn–C(7)–O(7) | 179.1(15) | Mn–C(8)–O(8) | 178.3(15) |
| C(12)–C(13)–C(14) | 124.5(15) | | |

the carbonyl ligands are still evidently *cis*, one must be *trans* to a $PPh_2$ moiety and the other essentially *trans* to a terminal carbon of the $\eta^3$-allyl ligand. It is therefore to be expected that $2\theta$ will be smaller than for the other dicarbonyl complexes. The intensity of the higher-frequency symmetric mode is found to be greater than that of the lower-frequency asymmetric mode and a value of 80° has been calculated for the OC–Mn–CO angle.

Details of the room-temperature 100-MHz $^1H$ n.m.r. spectra of these complexes are listed in the Experimental section. Some difficulties were encountered in obtaining good spectra, peaks frequently being broad with the expected splittings obscured. Since both metals have nuclei with large spins and quadrupole moments it is possible that coupling and relaxation effects could cause line broadening. However, good quality spectra showing couplings between allyl *syn* ($H_M$) and *anti* ($H_X$) protons or between $^{31}P$ nuclei and allyl *syn* protons of the order of 1 Hz can be obtained for many of the complexes once the samples have been freshly recrystallised or purified by chromatography. It seems therefore that oxidation leading to paramagnetic impurities is the cause of line broadening.

TABLE 3

Infrared data ($cm^{-1}$)

| Complex | $\nu(CO)$ | Approximate OC–M–CO angle (°) [a] | $\delta_{asym.}(CH_2)$ of $\eta$-$C_3H_5$ |
|---|---|---|---|
| $[Mn(\eta\text{-}C_3H_5)(CO)_3(PPh_3)]$ | 2 000s, 1 930s, 1 908vs [b] | | 1 508vw |
| $[Mn(\eta\text{-}C_3H_5)(CO)_3(AsPh_3)]$ | 2 005s, 1 930s, 1 910s [b] | | 1 502w |
| $[Mn(\eta\text{-}C_3H_5)(CO)_3\{P(C_6H_{11})_3\}]$ | 2 000m, 1 923m, (sh), 1 914s, 1 901s [b] | | 1 501vw |
| $[Mn(\eta\text{-}C_3H_5)(CO)_3(PBu^n{}_3)]$ | 1 997s, 1 921s, 1 898s [c] | | 1 501vw |
| $[Mn(\eta\text{-}C_3H_5)(CO)_3(PMePh_2)]$ | 1 996s, 1 919s, 1 889s [c] | | 1 502w |
| $[Re(\eta\text{-}C_3H_5)(CO)_3(PPh_3)]$ | 2 026s, 1 940s, 1 915s [b] | | |
| $[Mn(\eta\text{-}C_3H_5)(CO)_2(PMePh_2)_2]$ | 1 917s, 1 851vs [b] | 97 | |
| $[Mn(\eta\text{-}C_3H_5)(CO)_2\{P(OMe)_3\}_2]$ | 1 943s, 1 872vs [b] | 102 | 1 496w |
| $[Mn(\eta\text{-}C_3H_5)(CO)_2\{P(OEt)_3\}_2]$ | 1 939s, 1 867vs [b] | 102 | 1 496w |
| $[Mn(\eta\text{-}C_3H_5)(CO)_2(dppm)]$ | 1 930vs, 1 866s [d] | 80 | 1 500vw |
| $[Re(\eta\text{-}C_3H_5)(CO)_2(PPh_3)_2]$ | 1 926s, 1 849vs [e] | 99 | |

[a] Calculated from ratio of intensities of $\nu(CO)$ bands (ref. 15). [b] In n-pentane solution. [c] Liquid film. [d] In $CCl_4$ solution. [e] In $CHCl_3$ solution.

The room-temperature spectra are typical of $\eta^3$-allyl complexes with coupling to $^{31}P$, the spectra being interpretable as either $AM_2X_2$ or $AMM'XX'$ spin systems on $^{31}P$ decoupling. As expected, $J_{AX}$ (*ca.* 12 Hz) is always larger than $J_{AM}$ (*ca.* 7 Hz). For the phosphine complexes strong $^{31}P$–$H_X$ coupling ($J$ *ca.* 5 Hz) is also observed whereas $J_{PM}$ is much weaker (*ca.* 1 Hz). This order of magnitude of coupling constants is the reverse of that found[16] for the Group 6A complexes $[M(\eta\text{-}C_3H_5)X(CO)_2L_2]$ (M = Mo or W; X = Cl or Br, $L_2$ = dppm or dppe), where $J_{PX}$ values are less than 1 Hz whereas $J_{PM}$ values are *ca.* 3 Hz.

Some further comments on the spectrum of $[Mn(\eta\text{-}C_3H_5)(CO)_2\{P(OMe)_3\}_2]$ are appropriate. First, the magnitude of $J_{PX}$ (14 Hz) exceeds that of $J_{AX}$ (11.5 Hz) and is much greater than $J_{PX}$ of the phosphine complexes (5 Hz). Secondly, the room-temperature 100-MHz spectrum shows the methoxy-protons as a slightly split deceptively simple triplet. Harris[17] has shown that for a spin system of the type $X_9AA'X_9$ (X = H, A = P) with the nuclei of type X magnetically equivalent a simple 1 : 2 : 1 triplet will be observed when $J_{AA'} \gg |J_{AX} - J_{AX'}|$. Thus it initially seems reasonable to explain this feature on the basis of virtual coupling with the two mutually *trans* phosphorus nuclei coupling strongly with each other and the methoxy-protons coupling equally with both $^{31}P$ nuclei. The spectra of several bis(phosphine) and bis(phosphite) complexes, *e.g. trans*-$[M(CO)_4\{P(OMe)_3\}_2]$ (M = Cr, Mo, or W)[18] and *trans*-$[MX_2(PMe_3)_2]$ (M = Pd or Pt, X = halide)[19] have been assigned in this manner. The methoxy-protons of the closely related complex $[Mn(C_9H_6NO)(CO)_2\{P(OMe)_3\}_2]$ ($C_9H_6NO$ = 8-hydroxyquinolinate) also appear as a triplet at room temperature.[20] However, a more detailed study of the spectrum of $[Mn(\eta\text{-}C_3H_5)(CO)_2\{P(OMe)_3\}_2]$ suggests that virtual coupling need not be invoked to explain the spectrum. Thus the $^{31}P$-decoupled 100-MHz spectra run at −80 and at +29 °C do not show a singlet for the methoxy-protons, as would be expected for a virtually coupled system, but rather a 1 : 1 doublet of separation 10 Hz indicative of two different environments for the phosphite ligands with respect to the $\eta^3$-allyl ligand, in agreement with the solid-state structure. Furthermore, a room-temperature 60-MHz spectrum is composed of two doublets for the methoxy-protons, $^3J_{PH}$ = 10.5 Hz, showing that the central line of the triplet in the 100-MHz spectrum is produced by adventitious overlap of two of these four lines. The 100-MHz spectrum run at −80 °C clearly shows that each line of the triplet is a doublet (separation *ca.* 2 Hz), such splitting being just apparent at +29 °C but absent at +50 °C at which temperature each line of the triplet is rather broad. Also at +50 °C the methoxy-proton doublet in the $^{31}P$-decoupled spectrum is very broad, tending to collapse towards a singlet. We suggest that these features are best explained using first-order coupling. At −80 °C the complex will be stereochemically rigid, the two methoxy-proton signals being split into overlapping doublets by the proximal $^{31}P$ nuclei ($^3J_{PH}$ =

10.5 Hz), each line being further split by coupling to the distal $^{31}P$ nuclei ($^5J_{PH} = 2$ Hz). On warming, the phosphite ligands appear to lose their inequivalence with respect to the $\eta^3$-allyl group, possibly as a result of a fast rearrangement of the $\eta^3$-allyl group. Consistent with this suggestion, the allyl-proton signals are noticeably sharper at +50 than at −80 °C, although it is conceivable that favourable relaxation effects may be responsible for such sharpening of the lines. We therefore suggest that the complex may be stereochemically non-rigid above room temperature, but spectra could not be recorded above +50 °C because of the onset of decomposition.

The mass spectrum of each complex has also been obtained and the metal-containing ions observed listed in Tables 4 and 5 for the tricarbonyl and dicarbonyl complexes respectively, observed metastables also being listed. Each spectrum also contains many ions associated with ligand fragments and these are often of high intensity, but have not been considered in detail so that the individual ion abundances quoted will not approximate to the percentage of ion current carried. The rhenium-containing ions are clearly identified by the isotopic ratio $^{187}Re : ^{185}Re = 1 : 0.59$, but no such easy identification is possible for the manganese ions as $^{55}Mn$ is 100% abundant. The molecular ion is observed for all the complexes except $[Mn(\eta\text{-}C_3H_5)(CO)_2(PMePh_2)_2]$, but it is of high relative intensity only for $[Re(\eta\text{-}C_3H_5)(CO)_3(PPh_3)]$.

TABLE 4

Metal-containing ions in the mass spectra of the tricarbonyl complexes [a]

| | M, L | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mn, $PPh_3$ | | Mn, $AsPh_3$ | | Mn, $P(C_6H_{11})_3$ | | Mn, $PBu^n{}_3$ | | Mn, $PMePh_2$ | | Re, $PPh_3$ [b] | |
| Ion | *m/e* | R.I. | *m/e* | R.I. | *m/e* | R.I. | *m/e* | R.I. | *m/e* | R.I. | *m/e* | R.I. |
| $P^+$ | 442 | 7 | 486 | 5 | 460 | 4 | 382 | 10 | 380 | 10 | 574 | 90 |
| $[P-CO]^+$ | | | 458 | 5 | | | | | | | 546 | 97 |
| $[P-2CO]^+$ | | | | | | | | | 324 | 3 | 518 | 61 |
| $[P-3CO]^+$ | 358 | 100 | 402 | 100 | 376 | 100 | 298 | 100 | 296 | 100 | 490 | 38 |
| $[M(CO)_3L]^+$ | | | | | | | | | | | 533 | 100 |
| $[M(CO)_2L]^+$ | | | | | | | | | | | 505 | 32 |
| $[ML]^+$ | 317 | 47 | 361 | 33 | 335 | 10 | 257 | 8 | 255 | 28 | 449 | 88 |

Metastables (*m/e*)

| Mn, $PPh_3$ | Mn, $AsPh_3$ | Mn, $P(C_6H_{11})_3$ | Mn, $PBu^n{}_3$ | Mn, $PMePh_2$ | Re, $PPh_3$ |
|---|---|---|---|---|---|
| 358 → 317 | 486 → 402 | | 382 → 298 | 380 → 324 | 574 → 546 |
| | | | 298 → 257 | 324 → 296 | 574 → 533 |
| | | | | 296 → 255 | 546 → 518 |
| | | | | | 533 → 505 |
| | | | | | 518 → 490 |

[a] R.I. = Relative intensity. [b] Based on $^{187}Re$ isotope only.

The manganese tricarbonyl complexes show very few metal-containing ions and unexpectedly there is little evidence of stepwise carbonyl ligand loss. Indeed metastable evidence points to the fact that all three carbonyl ligands can be lost in a single step to afford $[Mn(\eta\text{-}C_3H_5)L]^+$ fragment ions which are by far the most abundant metal-containing ions for each complex. For these manganese tricarbonyl complexes there is no evidence for the presence of $[Mn(CO)_{3-x}L]^+$ ($x = 0$—2) fragment ions, so loss of allyl prior to carbonyl fragmentation is not a favoured process. The $[MnL]^+$ fragments must therefore arise from the fragmentation process (1), as shown by the presence of the appropriate metastable peaks.

$$[Mn(\eta\text{-}C_3H_5)L]^+ \longrightarrow [MnL]^+ + C_3H_5^{\cdot} \qquad (1)$$

The mass spectrum of $[Re(\eta\text{-}C_3H_5)(CO)_3(PPh_3)]$ is markedly different to those of the manganese tricarbonyl complexes, stepwise loss of carbonyl groups being a favoured process with each fragment ion being of high relative intensity and all three metastables being detected. Unlike the manganese analogues, $[Re(\eta\text{-}C_3H_5)L]^+$ is not the most abundant metal-containing ion. The most abundant ion is $[Re(CO)_3L]^+$ and the appearance of the appropriate metastable shows that the allyl fragmentation [equation (2)] is a major com-

$$[Re(\eta\text{-}C_3H_5)(CO)_3(PPh_3)]^+ \longrightarrow [Re(CO)_3(PPh_3)]^+ + C_3H_5^{\cdot} \qquad (2)$$

petitive process to that of initial carbonyl loss. Stepwise loss of carbonyl ligands from $[Re(CO)_3(PPh_3)]^+$ then follows, with $[Re(PPh_3)]^+$ thereby arising from two alternative fragmentation pathways. For the parent compound $[Re(\eta\text{-}C_3H_5)(CO)_4]$ stepwise loss of carbonyl groups with retention of the allyl group is much favoured over fragmentation of the allyl followed by stepwise carbonyl loss.[7]

Ligand fragmentation whilst still attached to the metal is not a favoured process for the tricarbonyl complexes although $[Mn(\eta\text{-}C_3H_5)(AsPh_2)]^+$ is observed as an ion of moderate intensity in the spectrum of the $AsPh_3$ complex.

From a consideration of the metastables detected in the spectra of the manganese dicarbonyl complexes $[Mn(\eta\text{-}C_3H_5)(CO)_2L_2]$ [L = $PMePh_2$, $P(OMe)_3$, or $P(OEt)_3$], the major fragmentation pathway is undoubtedly (3). Thus initial simultaneous loss of

$$\begin{tikzcd}
{} & {[Mn(\eta\text{-}C_3H_5)(CO)_2L_2]^+} \arrow[r] & {[Mn(\eta\text{-}C_3H_5)L_2]^+ + 2CO} \arrow[d] & {} \\
{} & {C_3H_5^{\cdot} + [MnL]^+} & {[Mn(\eta\text{-}C_3H_5)L]^+ + L} \arrow[l] & (3)
\end{tikzcd}$$

both carbonyl groups, $[Mn(\eta\text{-}C_3H_5)(CO)L_2]^+$ not being detected, is followed by loss of one ligand molecule before elimination of the allyl group. Loss of 1 mol of ligand only is a favoured process since $[Mn(\eta\text{-}C_3H_5)L]^+$ are the most abundant metal-containing ions in each of the three spectra and there is evidence for other ions such as $[Mn(\eta\text{-}C_3H_5)(CO)L]^+$, albeit in low abundance, showing that carbonyl and ligand loss may be competitive processes.

The mass spectrum of $[Mn(\eta\text{-}C_3H_5)(CO)_2(dppm)]$ is, as expected, somewhat different since one phosphorus cannot be lost without ligand cleavage. Fragmentation thus follows the simpler sequence (4), as confirmed by metastable observations.

$$\begin{array}{l} [Mn(\eta\text{-}C_3H_5)(CO)_2(dppm)]^+ \longrightarrow \\ \qquad [Mn(\eta\text{-}C_3H_5)(dppm)]^+ + 2CO \\ \qquad \downarrow \\ \qquad [Mn(dppm)]^+ + C_3H_5^{\bullet} \qquad (4) \end{array}$$

As in the tricarbonyl series, the rhenium dicarbonyl complex $[Re(\eta\text{-}C_3H_5)(CO)_2(PPh_3)_2]$ does not follow the same fragmentation pattern as the manganese dicarbonyl complexes. The base metal-containing peak is $[Re(\eta\text{-}C_3H_5)(CO)_2(PPh_3)]^+$ and generally the most intense ions arise from fragments containing only one $PPh_3$ ligand, *e.g.* $[Re(CO)_2(PPh_3)]^+$, $[Re(\eta\text{-}C_3H_5)(CO)(PPh_3)]^+$, and $[Re(\eta\text{-}C_3H_5)(PPh_3)]^+$. Although the loss of 1 mol of phosphine ligand is again favoured, for this complex alone of the dicarbonyls, initial loss of allyl must be a competing pathway since all possible $[Re(CO)_{2-x}(PPh_3)_2]^+$ ($x$ = 0—2) ions as well as $[Re(CO)_2(PPh_3)]^+$ are detected. Surprisingly, initial loss of carbonyl ligands appears not to be significant for this complex as the ions $[Re(\eta\text{-}C_3H_5)(CO)_{2-x}(PPh_3)_2]^+$ ($x$ = 1 or 2) are not detected. In contrast to the tricarbonyl complexes, ligand fragmentation whilst still attached to the metal is a significant feature, particularly for the dicarbonyl bis(phosphite) complexes. Ions not listed in Table 5 such as $[Mn(\eta\text{-}C_3H_5)(CO)_{2-x}\{P(OR)_3\}\{P(OR)_2\}]^+$ ($x$ = 0 or 2; R = Me or Et) and $[Mn(OMe)\{P(OMe)_3\}]^+$ are of at least moderate relative intensity. The fragmentation pathway (5) is established for the bis(trimethyl phosphite) complex by observation of the metastables, $m^*$, as shown.

$$\underset{400}{P^+} \xrightarrow[m^* = 295.8]{} \underset{369}{[P-(OR)]^+} \xrightarrow[m^* = 265.5]{} \underset{313}{[P-2CO-(OR)]^+} \qquad (5)$$

TABLE 5

Metal-containing ions in the mass spectra of the dicarbonyl complexes [a]

| | M, L | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Mn, $2PMePh_2$ | | Mn, dppm | | Mn, $2P(OMe)_3$ | | Mn, $2P(OEt)_3$ | | Re, $2PPh_3$ [b] | |
| Ion | *m/e* | R.I. | *m/e* | R.I. | *m/e* | R.I. | *m/e* | R.I. | *m/e* | R.I. |
| $P^+$ | | | 536 | 1 | 400 | 11 | 484 | 9 | 808 | 3 |
| $[P-2CO]^+$ | 496 | <0.1 | 480 | 100 | 344 | 8 | 428 | 7 | | |
| $[M(CO)_2L_2]^+$ | | | | | | | | | 767 | 7 |
| $[M(CO)_2L]^+$ | | | | | | | | | 505 | 16 |
| $[M(CO)L_2]^+$ | | | | | | | | | 739 | 8 |
| $[ML_2]^+$ | 455 | <0.1 | 439 | 18 | 303 | 1 | 387 | 1 | 711 | 4 |
| $[M(C_3H_5)(CO)_2L]^+$ | | | | | | | | | 546 | 100 |
| $[M(C_3H_5)(CO)L]^+$ | 324 | 5 | | | 248 | 1 | | | 518 | 40 |
| $[M(C_3H_5)L]^+$ | 296 | 100 | | | 220 | 100 | 262 | 100 | 490 | 38 |
| $[ML]^+$ | 255 | 18 | | | 179 | 37 | 221 | 14 | 449 | 50 |
| | Metastables (*m/c*) | | | | | | | | | |
| | | | 536 → 480 | | 344 → 220 | | 484 → 428 | | 739 → 711 | |
| | | | 480 → 439 | | 220 → 179 | | 428 → 262 | | | |
| | | | | | | | 262 → 221 | | | |

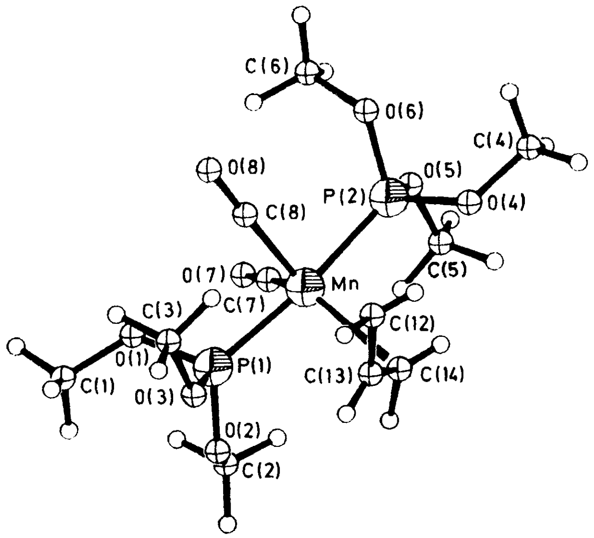
[a] R.I. = Relative intensity. [b] Based on $^{187}Re$ isotope only.

Finally, it is noticeable that no fragment ions have been detected which involve loss of two hydrogens from the allyl group whilst bound to the metal. Such ions, *e.g.* $[Re(C_3H_3)(CO)_x]^+$ ($x$ = 0—2), are of high abundance in the mass spectra of both $[Re(\sigma\text{-}C_3H_5)(CO)_5]$ and $[Re(\eta\text{-}C_3H_5)(CO)_4]$ and have been ascribed [7] to the formation of cyclopropenyl metal ions within the spectrometer.

*Crystal Structure of* $[Mn(\eta\text{-}C_3H_5)(CO)_2\{P(OMe)_3\}_2]$.—The structure (Figure) consists of discrete molecules separated by the usual van der Waals contacts. The metal atom is bonded to two mutually *trans* phosphorus atoms, two mutually *cis* carbonyl groups, and an allyl ligand. The metal atom can be regarded as having a slightly distorted octahedral co-ordination if the allyl ligand is reasonably considered to span two co-ordination positions on the manganese atom. The structure is however considerably more distorted from octahedral than the chelate acetato-complex $[Mn(CO)_2(O_2CMe)(PPh_3)_2]$,[21] and we ascribe this to the presence of the allyl ligand. Whereas the allylic hydrogens and indeed C(13) are close to the co-ordination sphere of the metal in the present molecule, in the acetato-complex only the two oxygen atoms of the acetate ligand affect the positions of the other atoms.

We have already mentioned $^1H$ n.m.r. evidence pointing to the non-equivalence of the two trimethyl phosphite ligands of the complex in solution. These ligands are also inequivalent in the solid-state structure as shown by the variation in Mn–P–O and O–P–O angles (Table 2) and by the manner in which the methoxy-groups of P(1) are markedly twisted away from the central allyl C–H bond. Furthermore, the two manganese–phosphorus distances [Mn–P(1) 2.175(5) and Mn–P(2)

2.219(5) Å] are significantly different and P(1) is further from the allyl-carbon atoms C(12) and C(14) [P(1)–Mn–C(12) 96.0(5) and P(1)–Mn–C(14) 99.2(4)°] than P(2) [P(2)–Mn–C(12) 90.6(5) and P(2)–Mn–C(14) 85.9(4)°]. The central allyl-carbon atom C(13), which must be on one side of the equatorial plane defined by Mn, C(7), and C(8), is closer to P(1) [P(1)–Mn–C(13) 81.9(5)°] than P(2) [P(2)–Mn–C(13) 105.1(5)°]. An additional cause of distortion from octahedral symmetry is close contacts involving the oxygen atoms of the trimethyl phosphite ligands and atoms in the co-ordination sphere. It seems pertinent that torsion angles of the type L–Mn–P–O are different for the two phosphorus atoms and that the three smallest angles involve P(2) rather than P(1); these are C(8)–Mn–P(2)–O(6) −6.0, C(12)–Mn–P(2)–O(4) 17.1, and C(13)–Mn–P(2)–O(4) −17.5°. We therefore suspect that these O • • • C contacts are the major cause of the disparity in the Mn–P bond lengths.



A perspective view of the molecule $[\mathrm{Mn}(\eta\text{-}C_3H_5)(CO)_2\{P(OMe)_3\}_2]$ showing the atom-numbering scheme

Both Mn–P bonds are noticeably shorter than those found in a number of other manganese(I) complexes, *e.g.* 2.260 and 2.275 Å in $[\mathrm{Mn}(CO)_2(O_2CMe)(PPh_3)_2]$,[21] 2.296 and 2.303 Å in *fac*-$[\mathrm{MnBr}(CO)_3\{PPh(OMe)_2\}_2]$,[22] and 2.262 and 2.281 Å in *cis*-$[\mathrm{Mn}(CO)_2\{PPh(OMe)_2\}_4]^+$.[23] This shortening may reflect the superior π-acceptor ability of trimethyl phosphite.

The Mn–C carbonyl bond lengths [Mn–C(7) 1.75(2) and Mn–C(8) 1.83(2) Å] are as expected and the Mn–C(7)–O(7) and Mn–C(8)–O(8) angles are very close to 180°. The C(7)–Mn–C(8) angle exceeds 90°, as predicted from i.r. ν(CO) band intensity measurements, whereas for $[\mathrm{Mn}(CO)_2(O_2CMe)(PPh_3)_2]$ [21] this angle [89.3(5)°] is hardly perturbed from a right angle.

The $\eta^3$-allyl group is symmetrically bonded to the metal, as shown by the manganese–carbon allyl distances [Mn–C(12) 2.223(17), Mn–C(13) 2.114(15), and Mn–C(14) 2.229(13) Å], the shortest bond being to the unique central C(13) atom. Amongst the $\eta^3$-allyl structures that have been studied crystallographically, many are similarly symmetric.[24] The C(12)–Mn–C(14) and C(12)–C(13)–C(14) angles of 67.0(6) and 124.5(15)° are also typical [24] of many $\eta^3$-allyl complexes. It is generally found in such complexes that the allyl $C_3$ plane is not perpendicular to the co-ordination plane of the metal, the central carbon atom being tipped away from the metal atom. In the present complex the dihedral angle between the allyl $C_3$ plane and the equatorial plane defined by Mn, C(7), and C(8) is 109.0°. The $\eta^3$-allyl group is slightly twisted with respect to this plane, C(12) and C(14) lying 0.07 and 0.21 Å respectively below, and C(13) lying 0.47 Å above the plane. No other simple $\eta^3$-allyl manganese structures appear to have been reported in the literature, so valid comparisons of Mn–C(allyl) distances with those of the present complex are not possible. These distances in $[\mathrm{Mn}_2(CO)_6\{(AsMe_2)\{C_4F_5\}(AsMe_2)_2\}]^4$ are 2.09(2), 2.07(2), and 2.13(2) Å but this complex contains a fluoro-$\eta^3$ $-CF_3C(As) \overset{\cdot\cdot\cdot}{-} C(As) \overset{\cdot\cdot\cdot}{-} CF_2$ moiety which is also part of a ring.

The mean bond distances and interbond angles involving the trimethyl phosphite ligands are unremarkable, being very similar to those in such widely different complexes as octahedral $[\mathrm{Ru}(\eta\text{-}C_3H_4Me\text{-}2)_2\{P(OMe)_3\}_2]$,[25] trigonal-bipyramidal $[\mathrm{Fe}(CO)_3\{P(OMe)_3\}_2]$,[26] and distorted-tetrahedral $[\{\mathrm{Ag}(NO_3)[P(OMe)_3]_2\}_2]$.[27] Thus in the order for the complexes of Mn, Ru, Fe, and Ag, mean distances and angles are: P–O 1.60, 1.61, 1.59, and 1.56 Å; O–C 1.44, 1.42, 1.44, and 1.42 Å; O–P–O 100.3, 99.0, 100.9, and 100.8°; P–O–C 121.6, 122.7, 121.0, and 125.3°; and M–P–O 117.6, 118.6, 117.1, and 116.7° respectively. The phosphorus co-ordination is clearly close to tetrahedral in all examples.

There are no intermolecular distances in the present complex greater than the sum of the van der Waals radii.

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