Transformations of a μ_2-Vinyl Ligand at a Dimanganese Centre and the Flexibility of μ_2-Acyl Ligands; *X*-Ray Crystal Structures of $[(Ph_3P)_2N][Mn_2(\mu_2\text{-}H)\{\mu_2\text{-}C(O)CPh:CHPh\}(\mu_2\text{-}PPh_2)(CO)_6]$, $[Mn_2\{\mu_2\text{-}C(O)CPh:CHPh\}(\mu_2\text{-}PPh_2)(CO)_6(CNBu^t)_2]$, and $[Mn_2\{\sigma:\eta^3\text{-}P(Ph)_2CH:CH_2\}(CO)_7(PEt_3)]$

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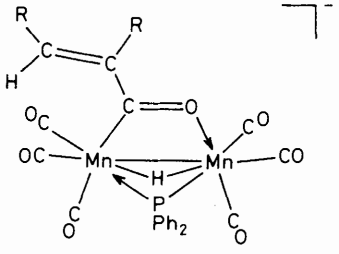
$[Mn_2(\mu_2\text{-}\sigma:\eta^2\text{-}CR:CHR)(\mu_2\text{-}PPh_2)(CO)_7]$ (R = H or Ph) reacts with 2-electron donor ligands to give μ_2-acyl complexes or products containing the $P(Ph)_2CR:CHR$ ligand; these correspond, respectively, to insertion of CO or PPh_2 into the σ-bond between the metal and the μ_2-vinyl group.

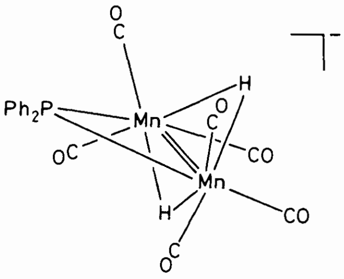
The chemistry of organic ligands bound to dinuclear metal centres is of interest in relation to the catalysis of organic reactions by metal surfaces or by metal clusters, and is currently under intensive investigation.[1—5] In this communication we describe some unusual transformations of a μ_2-vinyl ligand at a dimanganese centre. Although many complexes containing μ_2-vinyl ligands are now known the range of chemical reactions reported for this ligand is limited.[6—8]

$[Mn_2(\mu_2\text{-}\sigma:\eta^2\text{-}CR:CHR)(\mu_2\text{-}PPh_2)(CO)_7]$
(1), R = H
(2), R = Ph

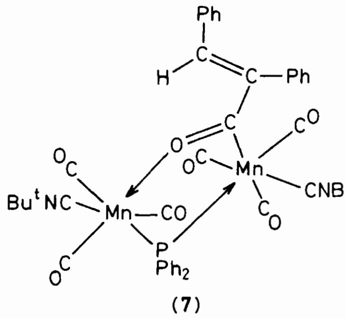
$[Mn_2(\mu_2\text{-}PPh_2)(CO)_8]^-$
(6)



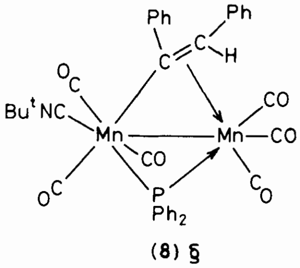
(3) R = H
(4) R = Ph



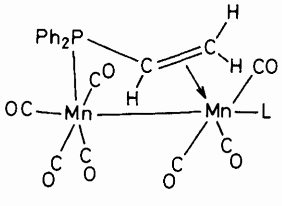
(5) §



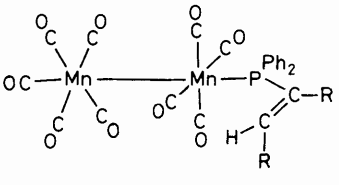
(7)



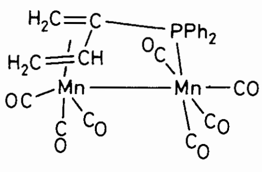
(8) §



(9) L = CNBu^t
(10) L = PEt$_3$



(11a) R = H
(11b) R = Ph §



(12) §

Reaction of $[Mn_2(\mu_2\text{-}\sigma:\eta^2\text{-}CR:CHR)(\mu_2\text{-}PPh_2)(CO)_7]$ [R = H (**1**); R = Ph (**2**)][9] with $NaBH_4$ in tetrahydrofuran (thf) or MeCN at room temperature gives, as the major product, the μ_2-acyl complexes $[PPN][Mn_2(\mu_2\text{-}H)\{\mu_2\text{-}C(O)CR:CHR\}(\mu_2\text{-}PPh_2)(CO)_6]$ [PPN = $(Ph_3P)_2N$] [R = H (**3**); R = Ph (**4**)].† Minor products are the dimanganese anions $[Mn_2(\mu_2\text{-}H)_2(\mu_2\text{-}PPh_2)(CO)_6]^-$ (**5**)† and $[Mn_2(\mu_2\text{-}PPh_2)(CO)_8]^-$ (**6**).[10]

Complex (**4**) has been characterised by a single crystal *X*-ray determination (Figure 1).‡ The acyl ligand spans the Mn–Mn vector, bonding through C(1) to Mn(2) and through O(1) to Mn(1). The Mn–Mn distance, 2.813(2) Å, is typical for a single Mn–Mn bond,[11] as is required in (**4**) by the E.A.N. (effective atomic number) rule. The geometry of the Mn–Mn–C–O ring (Figure 1) is similar to that found in analogous systems.[3,12] The hydride ligand was not located in the refinement, but on the basis of its chemical shift, δ −11.60, and the folded geometry of the C(1)–O(1)–Mn(1)–P(1)–Mn(2) ring it is assumed to occupy a bridging site *trans* to both C(22) and C(13).

Reaction of (**2**) with Bu^tNC in refluxing hexane gives the μ_2-acyl complex $[Mn_2\{\mu_2\text{-}C(O)CPh:CHPh\}(\mu_2\text{-}PPh_2)(CO)_6(CNBu^t)_2]$ (**7**)† and, as a minor product, the substituted μ_2-vinyl complex $[Mn_2(\mu_2\text{-}\sigma:\eta^2\text{-}CPh:CHPh\}(\mu_2\text{-}PPh_2)(CO)_6\text{-}$

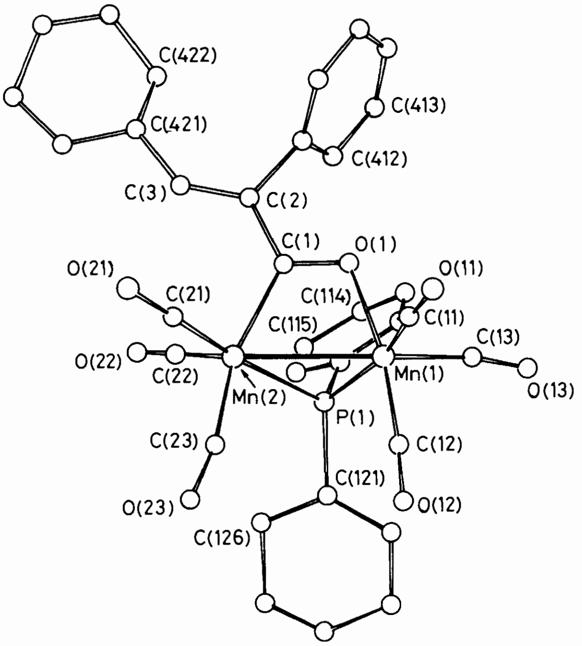


Figure 1. Molecular structure of $[PPN][Mn_2(\mu_2\text{-}H)\{\mu_2\text{-}C(O)CPh:CHPh\{\text{-}(\mu_2\text{-}PPh_2)(CO)_6]$ (**4**). Important bond parameters are: Mn(1)–Mn(2) 2.812(1), Mn(1)–O(1) 2.050(3), Mn(2)–C(1) 2.006(4), C(1)–O(1) 1.264(5) Å; ∠Mn(1)–P(1)–Mn(2) 76.3(1), Mn(1)–O(1)–C(1) 108.0(2), Mn(2)–C(1)–O(1) 116.9(3)°.

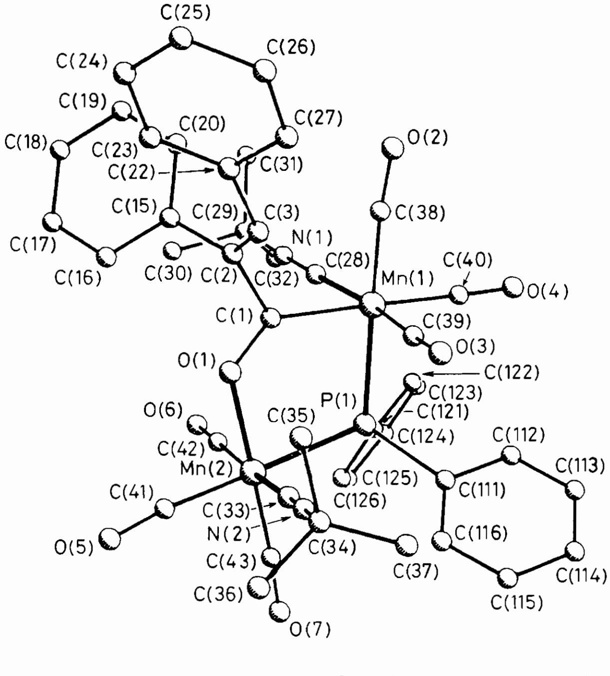


Figure 2. Molecular structure of $[Mn_2\{\mu_2\text{-}C(O)CPh:CHPh\}(\mu_2\text{-}PPh_2)(CO)_6(CNBu^t)_2]$ (**7**). Important bond parameters are: Mn(1)–Mn(2) 3.820(2), Mn(2)–O(1) 2.052(4), Mn(1)–C(1) 2.032(7), C(1)–O(1) 1.238(6), C(1)–C(2) 1.523(9), C(2)–C(3) 1.499(8) Å; ∠Mn(1)–P(1)–Mn(2) 106.5(1), Mn(2)–O(1)–C(1) 130.5(5), Mn(1)–C(1)–O(1) 127.4(5)°.

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† Selected spectroscopic data [i.r. (ν_{CO}) measured in CH_2Cl_2, (**3**)—(**5**), or hexane, (**7**)—(**11**), solution; ^1H and ^{13}C n.m.r. in $CDCl_3$ solution; couplings in Hz]: (**3**), ν_{CO} 1999m, 1966s, 1903s, and 1876m cm^{-1}; ^1H n.m.r. δ −12.06 [d, *J*(PH) 33.7, M_2H]. (**4**), ν_{CO} 1998m, 1966s, 1904s, and 1876m cm^{-1}; ^1H n.m.r. δ 6.30 [dd, *J*(PH) 1.6, *J*(HH) 7.8, 1H, CPh : C*H*Ph] and −11.59 [d, *J*(PH) 31.4, M_2H]; ^{13}C n.m.r. 309.3 p.p.m. [d, *J*(PC) *ca.* 6, R*C*O]. (**5**), ν_{CO} 2005m, 1972s, 1893sh, and 1889s cm^{-1}; ^1H n.m.r. δ −17.52 [d, *J*(PH) 49.7, M_2H_2]. (**7**), ν_{RNC} 2176m and 2156m cm^{-1}; ν_{CO} 2020s, 1999vs, 1952s, and 1920vs cm^{-1}; ^1H n.m.r. δ 6.46 (s, 1H, CPh : C*H*Ph), 1.09 (s, 9H, $CNBu^t$), and 0.91 (s, 9H, $CNBu^t$); ^{13}C n.m.r. 323.2 p.p.m. (s, R*C*O). (**8**), ν_{RNC} 2161m cm^{-1}; ν_{CO} 2028m, 2001s, 1964m, 1954m, 1941m, and 1929sh cm^{-1}; ^1H n.m.r. δ 4.94 [d, *J*(PH) 8.7, 1H, CPh : C*H*Ph] and 1.08 (s, 9H, $CNBu^t$). (**9**), ν_{RNC} 2139m cm^{-1}; ν_{CO} 2041s, 1995s, 1984m, 1969s, 1955s, 1948m, and 1916m cm^{-1}; ^1H n.m.r. δ 2.88, 1.86, and 1.66 (each m, 1H, $CH:CH_2$); 1.00 (s, 9H, $CNBu^t$). (**10**), ν_{CO} 2048s, 1981m, 1975m, 1965s, 1937m, and 1906m cm^{-1}; ^1H n.m.r. δ 2.50, 2.09, and 1.24 (each m, 1H, $CH:CH_2$); 1.92 (m, 6H, CH_2CH_3) and 1.10 (m, 9H, CH_2CH_3). (**11a**), ν_{CO} 2090m, 2011m, 1994s, 1972m, and 1939m cm^{-1}; ^1H n.m.r. δ 6.85 [ddd, *J*(PH) 24.2, *J*(H^1H^2) 17.8, *J*(H^1H^3) 12.0, 1H, C*H* : CH_2], 6.25 [ddd, *J*(PH) 38.3, *J*(H^2H^3) 1, 1H, *cis*-CH : CH_2], 5.32 [ddd, *J*(PH) 19.5, 1H, *trans*-CH : CH_2]. (**11b**), ν_{CO} 2091m, 2011m, 1996s, 1974m, and 1938m cm^{-1}; ^1H n.m.r. δ 6.62 [d, *J*(PH) 8.0, 1H, CPh : C*H*Ph]. Satisfactory elemental analyses were obtained for all compounds except (**3**) which could not be isolated from the reaction mixture.

‡ *Crystal_data*: (**4**), $C_{69}H_{52}Mn_2NO_7P_3$, M = 1209.87, triclinic, space group $P\bar{1}$, a = 10.129(3), b = 17.533(5), c = 17.446(5) Å, α = 98.05(4), β = 101.95(4), γ = 93.02(4)°, U = 2990.6 Å^3, Z = 2, D_c = 1.359 g cm^{-3}. R = 0.0521 and R_w = 0.0566 for 6160 unique data with $3 < \theta < 25°$ and $F > 6\sigma(F)$, Philips PW1100 diffractometer, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å; all non-hydrogen atoms anisotropic except for the C atoms of a disordered phenyl ring.

(**7**), $C_{43}H_{39}Mn_2N_2O_7P$, M = 836.65, triclinic, space group $P\bar{1}$, a = 10.609(2), b = 10.844(3), c = 20.426(2) Å, α = 87.04(2), β = 82.80(1), γ = 65.05(2)°, U = 2113.8 Å^3, Z = 2, D_c = 1.441 g cm^{-3}. R = 0.074 and R_w = 0.087 for 5046 unique data with $1.5 < \theta < 62.5°$ and $F > 5\sigma(F)$, Syntex $P2_1$ diffractometer, $\lambda(\text{Cu-}K_\alpha)$ = 1.5418 Å; all non-hydrogen atoms anisotropic except for the phenyl C atoms.

(**10**), $C_{27}H_{28}Mn_2O_7P_2$, M = 636.34, monoclinic, space group $P2_1/n$, a = 15.459(4), b = 16.355(4), c = 11.735(3) Å, β = 93.67(4)°, U = 2960.9 Å^3, Z = 4, D_c = 1.427 g cm^{-1}. R = 0.0748 and R_w = 0.0738 for 1725 unique data with $3 < \theta < 25°$, $F > 6\sigma(F)$, Philips PW1100 diffractometer, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å and Mn_2P_2 anisotropic. Owing to crystal decomposition during data acquisition three crystals were needed to collect a complete data set.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

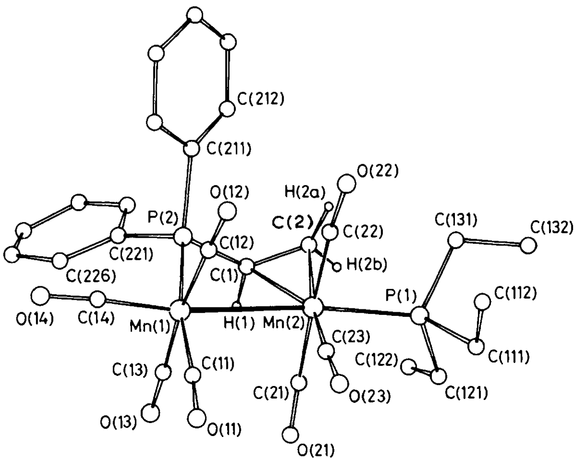

Figure 3. Molecular structure of $[Mn_2\{\sigma:\eta^3\text{-}P(Ph)_2CH:CH_2\}(CO)_7(PEt_3)]$ (**10**). Selected bond lengths are: Mn(1)–Mn(2) 2.989(3), Mn(1)–P(2) 2.290(5), Mn(2)–P(1) 2.291(5), Mn(2)–C(1) 2.229(15), Mn(2)–C(2) 2.237(15), C(1)–C(2) 1.424(21), C(1)–P(2) 1.789(15) Å.

$(CNBu^t)]$ (**8**).†§ Complex (**7**) has been characterised by a single crystal *X*-ray determination‡ (Figure 2). As in (**4**) the acyl ligand bridges the Mn–Mn vector bonding through C(1) to Mn(1) and through O(1) to Mn(2). The metal atoms in (**7**), however, are not within bonding distance, the Mn · · · Mn separation in (**7**) [3.820(2) Å] being *ca.* 1 Å longer than that found in (**4**) [2.813(2) Å] and *ca.* 1.26 Å longer than that in (**5**) [2.557(3) Å].§ Such a separation is unusually large for a dinuclear system bridged by μ-acyl[13] and/or μ-phosphido[14] ligands and illustrates the flexibility with respect to bite angle of both these groups. This longer Mn · · · Mn distance is accommodated with remarkably little change in the other bond distances of the Mn(1)–Mn(2)–C(1)–O(1) ring, but has a profound effect on the interbond angles. For example, the Mn–C(1)–O(1) angle in (**4**), 117.1(4)°, increases to 127.4(5)° in (**7**) and the Mn–O(1)–C(1) angle from 108.0(4)° in (**4**) to 130.5(5)° in (**7**).

The absence of a third bridging ligand in (**7**) allows the Mn(1)–C(1)–O(1)–Mn(2)–P(1) ring to adopt an approximately planar conformation rather than the folded arrangement found for (**4**). The carbon side chain of the acyl ligand in (**7**) is rotated through *ca.* 70° about the C(1)–C(2) bond as compared to its orientation in (**4**) (Figures 1 and 2) presumably to minimise the net steric interactions within the acyl ligand and between the side chain of this ligand and the carbonyl and/or isonitrile ligands on the metal.

Reactions of (**1**) and (**2**) with 2-electron donor ligands do not inevitably lead to the formation of μ_2-acyl complexes and, in some instances, the insertion of the μ_2-PPh_2 ligand (rather than CO) into the σ-bond between the metal and the μ_2-vinyl ligand is preferred. Thus reaction of (**1**) with Bu^tNC or Et_3P gives the complexes $[Mn_2\{\sigma:\eta^3\text{-}P(Ph)_2CH:CH_2\}(CO)_7L]$ [L = $CNBu^t$ (**9**);† L = PEt_3 (**10**)]†. Complex (**10**) has been characterised by an *X*-ray study‡ (Figure 3), which confirms that the vinyl ligand has migrated to the phosphorus atom of the phosphido bridge with rupture of one of the Mn–P bridge bonds. Bond parameters within the $Ph_2PCH:CH_2$ ligand, Figure 3, are typical of such systems.[15] As in all the other complexes described here, the incoming nucleophile is bound to the metal rather than to the organic ligand suggesting that, for this system, nucleophilic attack at the metal, and not at the organic ligand,[6—8] is the preferred reaction pathway. This has been confirmed for H^- attack by the use of $NaBD_4$ in place of $NaBH_4$ in the preparation of (**4**). Deuterium is incorporated into the μ_2-H site but not into the μ_2-acyl ligand.

Reaction of (**1**) and (**2**) with CO proceeds in a similar fashion to that of (**1**) with Bu^tNC or Et_3P but an additional molecule of CO is taken up to give $[Mn_2\{P(Ph)_2\text{-}CR:CHR\}(CO)_9]$ [R = H (**11a**);† R = Ph (**11b**)§] with displacement of the vinyl group from the co-ordination sphere of both metal atoms.

Incorporation of the μ_2-PPh_2 bridge into an organic ligand is not a reaction which is unique in this system to the μ_2-vinyl group. Thus reaction of $[Mn_2(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)(CO)_8]$ with butadiene gives, as one of several reaction products, the complex $[Mn_2(\mu_2\text{-}C_4H_5PPh_2)(CO)_7]$ (**12**)†§ in which loss of the μ-H and a C–H atom has occurred.

Reaction of (**2**) with other 2-electron donor ligands such as PMe_2Ph gives products which, from their spectroscopic properties, appear different in type from any of those reported in this communication and these are under investigation.

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§ Structure confirmed by an *X*-ray study to be reported elsewhere.