Acyl Group Flipping in Heterodimetallic Complexes; *X*-Ray Crystal Structures of $[(\eta^5\text{-}C_5H_5)MoMn\{\mu\text{-}C(O)C_6H_{11}\}(\mu\text{-}PPh_2)(CO)_5]$ and $[(\eta^5\text{-}C_5H_5)MoMn\{\mu\text{-}C(O)\text{-}CH_2CH_2CH_3\}(\mu\text{-}PPh_2)(CO)_6]$

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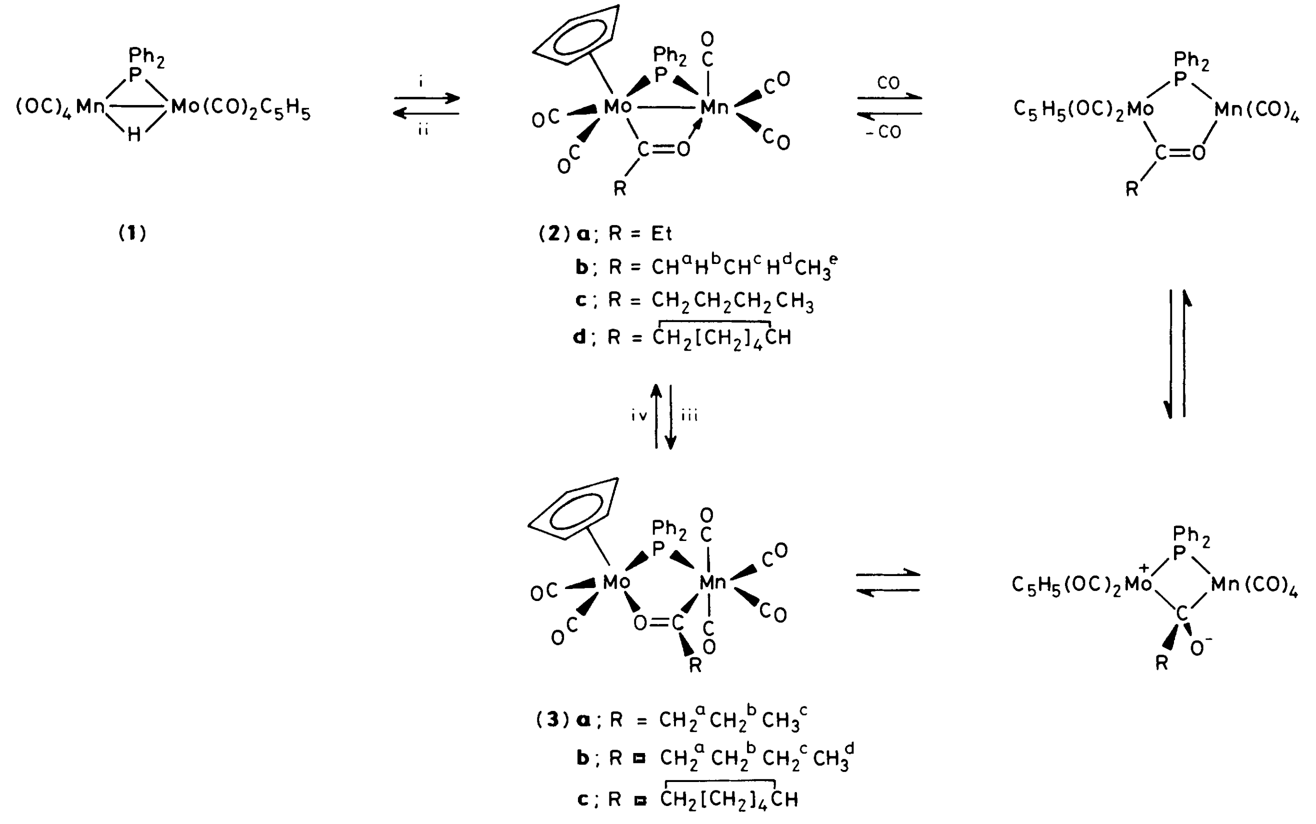
Photolytic reaction of the heterodimetallic complex $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6]$ with alkenes gives μ-acyl complexes shown by an *X*-ray analysis of $[(\eta^5\text{-}C_5H_5)MoMn\{\mu\text{-}C(O)C_6H_{11}\}(\mu\text{-}PPh_2)(CO)_5]$ to contain the Mo–C–O–Mn grouping; reaction with CO results in reversible metal–metal bond cleavage and flipping of the μ-acyl co-ordination to Mo–O–C–Mn, as shown by an *X*-ray analysis on $[(\eta^5\text{-}C_5H_5)MoMn\{\mu\text{-}C(O)CH_2CH_2CH_3\}(\mu\text{-}PPh_2)(CO)_6]$.

The η^2-co-ordination of μ-acyl ligands through carbon and oxygen to one or more metal centres is a feature of various mechanisms which have been proposed for the Fischer–Tropsch reaction.[1] In this communication we describe a heterodimetallic system in which μ-acyl ligands can be induced to flip reversibly (Scheme 1) by addition or removal of CO under mild conditions and report *X*-ray structure analyses of the two products. This flipping reaction, which is the first observed for an acyl ligand bridging two different metals, could provide a model for the migration of a μ-acyl ligand on a metal surface. A related flipping reaction in a triosmium complex has been reported but this is not influenced by CO nor were the structures of the two μ-acyl isomers investigated by *X*-ray analysis.[2]

Photolytic reaction of a hexane : benzene solution of the heterodimetallic complex, $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6]$ (**1**),[3] with a variety of alkenes (ethene, propene, but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene, cyclohexene) at



Scheme 1. i, *h*ν in hexane : benzene (3 : 1), 18 °C, with ethene, propene, but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene, or cyclohexene; ii, benzene, N_2, 45 °C; iii, benzene, CO (1 atm), 18 °C; iv, hexane : CH_2Cl_2 (10 : 1), N_2, 18 °C.

room temperature gives the complexes (**2a**—**d**)† (Scheme 1) in yields ranging from 17% [(**2c**), but-1-ene] to 83% [(**2b**), propene].

X-Ray structure analysis, Figure 1, shows that the acyl ligand in complex (**2d**) spans the Mn–Mo vector, bonding through C(1) to Mo(1) and through O(1) to Mn(1) with a geometry similar to that found in analogous acyl complexes[4—7] and a Mn–Mo distance of 2.963(2) Å, typical for a single Mn–Mo bond.[3]‡ The characteristic acyl CO stretching frequency of 1494 cm^{-1} observed in the i.r. spectrum of (**2d**) provides confirmatory evidence that the bonding of the ligand approximates more closely to the μ-acyl rather than the alternative μ-oxycarbene representation.[8]

Spectroscopic studies on complexes (**2a**—**d**)† indicate that their structures in solution are similar to that found for (**2d**) in the solid state. Most significant is the acyl carbon resonance for (**2b**) at δ 298.5 in the ^{13}C n.m.r. spectrum, showing characteristic *cis* coupling[9] to the phosphido bridge [*J*(PC)13.7 Hz].

On stirring a solution of (**2b**) in benzene for 1 h under 1 atm CO at room temperature the red complex $[(\eta^5\text{-}C_5H_5)MoMn\{\mu\text{-}C(O)CH_2CH_2CH_3\}(\mu\text{-}PPh_2)(CO)_6]$ (**3a**)† was formed in *ca.* 95% conversion, as shown by i.r. spectroscopy. *X*-Ray structure analysis, Figure 2, shows that the acyl ligand again bridges the Mn–Mo vector with an intermetal separation of 3.99 Å which is *ca.* 1 Å longer than in (**2d**).‡ Addition of a molecule of CO thus results in breaking of the Mn–Mo bond but, in addition, the carbon atom of the μ-acyl ligand is now bonded to Mn(1) and the oxygen atom to

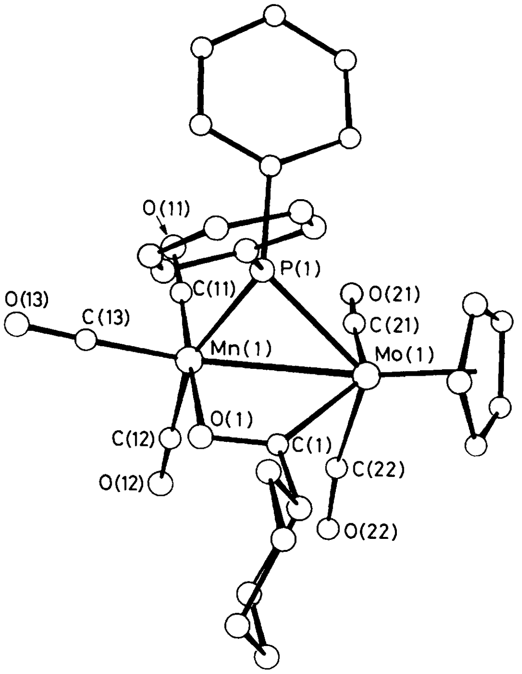


Figure 1. The molecular structure of $[(\eta^5\text{-}C_5H_5)MoMn\{\mu\text{-}C(O)\text{-}C_6H_{11}\}(\mu\text{-}PPh_2)(CO)_5]$ (**2d**). Mn(1)–Mo(1) 2.963(2); Mn(1)–P(1) 2.265(3); Mo(1)–P(1) 2.488(3); Mn(1)–C(11) 1.759(11); Mn(1)–C(12) 1.824(12); Mn(1)–C(13) 1.770(12); Mo(1)–C(21) 2.012(11); Mo(1)–C(22) 1.999(12); Mo(1)–C(of C_5H_5 ring, aver.) 2.339(10); Mo(1)–C(1) 2.200(10); Mn(1)–O(1) 2.027(6); C(1)–O(1) 1.256(10) Å. Mn(1)–P(1)–Mo(1) 76.9(1); Mo(1)–C(1)–O(1) 118.1(6); Mn(1)–O(1)–C(1) 109.3(6)°.

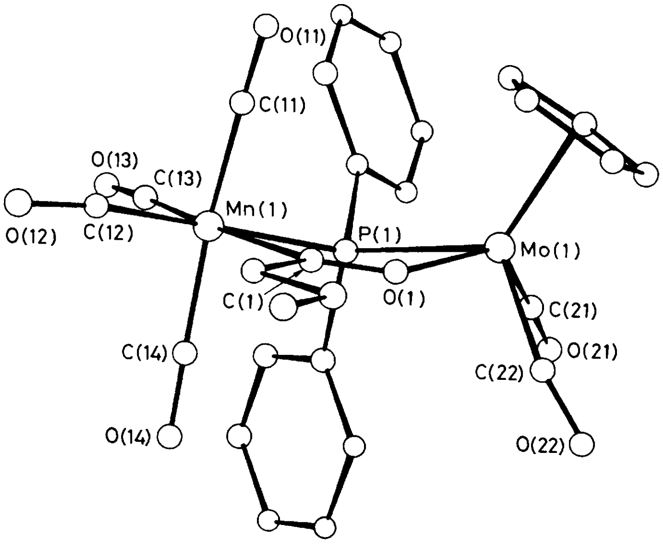


Figure 2. The molecular structure of $[(\eta^5\text{-}C_5H_5)MoMn\text{-}\{\mu\text{-}C(O)CH_2CH_2CH_3\}(\mu\text{-}PPh_2)(CO)_6]$ (**3a**). Mn(1) ··· Mo(1) 3.99; Mn(1)–P(1) 2.388(6); Mo(1)–P(1) 2.510(5); Mn(1)–C(11) 1.76(3); Mn(1)–C(12) 1.762(21); Mn(1)–C(13) 1.81(3); Mn(1)–C(14) 1.792(21); Mo(1)–C(21) 1.897(21); Mo(1)–C(22) 1.907(23); Mo(1)–C (of C_5H_5 ring, aver.) 2.318(17); Mn(1)–C(1) 2.043(19); Mo(1)–O(1) 2.162(12); C(1)–O(1) 1.252(19) Å. Mn(1)–P(1)–Mo(1) 108.9(2); Mn(1)–C(1)–O(1) 123(1); Mo(1)–O(1)–C(1) 138(1)°.

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† *Selected spectroscopic data:* [i.r. (ν_{CO} cm^{-1}) measured in hexane solution; ^1H, ^{13}C, and ^{31}P n.m.r. in $CDCl_3$ solution, ^{31}P shifts relative to $P(OMe)_3$ at 0 p.p.m. with upfield shifts negative; *J* in Hz]. (**2b**), ν_{CO} 2023s, 1968m, 1946m, 1922m, 1913sh [1510w, $\nu_{C(O)R}$]; ^1H n.m.r. δ 2.19 [ddd, $J(H^aH^b)$ 16.3, $J(H^aH^d)$ 8.3, $J(H^aH^c)$ 6.8, 1H, H^a], 1.57 [ddd, $J(H^bH^c)$ 8.7, $J(H^bH^d)$ 5.6, 1H, H^b], 1.13 [ddqd, $J(H^cH^d)$ 14.1, $J(H^cH^e)$ 7.3, 1H, H^c], 0.85 [ddqd, $J(H^dH^e)$ 7.3, 1H, H^d], 0.55 [t, 3H, $CH_3{}^e$]; ^{13}C n.m.r. δ 298.5 [d, $^2J(PC)$ 13.7, C(O)R], 63.6, 17.6, 13.5 [s, $CH_2CH_2CH_3$].

(**2d**), ν_{CO} 2021s, 1965m, 1946m, 1919m, 1910sh [1494w, $\nu_{C(O)R}$]; ^1H n.m.r. δ 2.1—0.3 [m, 11H, C_6H_{11}]; ^{13}C n.m.r. δ 300.8 [d, $^2J(PC)$ 14.0, C(O)R], 69.4 [s, $C(O)\mathit{C}HC_5H_{10}$], 29.1, 26.2, 25.8, 25.4, 25.1 [s, $C(O)CH\mathit{C}_5H_{10}$]; ^{31}P n.m.r. δ 3.54 p.p.m. [s, μ-PPh_2].

(**3a**), ν_{CO} 2057m, 1993m, 1965m, 1961sh, 1953s, 1891m, [1505w, $\nu_{C(O)R}$]; ^1H n.m.r. δ 3.08 [t, *J* (H^aH^b) 6.9, 2H, $CH_2{}^a$], 1.40 [m, *J* (H^bH^c) 7.2, 2H, $CH_2{}^b$], 0.81 [t, 3H, $CH_3{}^c$], ^{13}C n.m.r. δ 330.3 [s, C(O)R], 67.4, 18.4, 13.6 [s, $\mathit{C}H_2\mathit{C}H_2\mathit{C}H_3$].

(**3b**), ν_{CO} 2058m, 1993m, 1966s, 1961sh, 1953s, 1892m; ^1H n.m.r. δ 3.10 [t, $J(H^aH^b)$ 7.1, 2H, $CH_2{}^a$], 1.35 [m, *J* (H^bH^c) 7.1, 2H, $CH_2{}^b$], 1.18 [m, $J(H^cH^d)$ 7.1, 2H, $CH_2{}^c$], 0.87 [t, 3H, $C\mathit{H}_3{}^d$].

(**3c**), ν_{CO} 2055m, 1992m, 1964s, 1961sh, 1951m, 1891m, [1488w, $\nu_{C(O)R}$]; ^1H n.m.r. δ 3.43 [m, 1H, $C(O)C\mathit{H}C_5H_{10}$], 1.9—0.8 [m, 10H, $C(O)CHC_5\mathit{H}_{10}$]; ^{13}C n.m.r. δ 334.7 [s, $\mathit{C}(O)R$], 71.9 [s, $C(O)\mathit{C}HC_5H_{10}$], 28.1—25.2 [m, 5C, $C(O)CH\mathit{C}_5H_{10}$]; ^{31}P n.m.r. δ −70.2 p.p.m. [s, μ-PPh_2].

‡ *Crystal data:* (**2d**) $C_{29}H_{26}MnMoO_6P$, $M = 652.37$, monoclinic, space group $P2_1/c$, $a = 9.118(3)$, $b = 14.632(4)$, $c = 20.687(3)$ Å, $\beta = 101.25(4)°$, $U = 2706.9$ Å^3, $D_c = 1.600$ g cm^{-3}, $Z = 4$, $F(000) = 1320$, $\mu(Mo\text{-}K_\alpha) = 9.41$ cm^{-1}, $I/\sigma(I) \geqslant 3.0$, θ range 3—25°, $R = 0.0501$, $R_w = 0.0476$ for 2133 absorption-corrected diffractometer data.

(**3a**) $C_{27}H_{22}MnMoO_7P$, $M = 640.32$, monoclinic, space group $P2_1/n$, $a = 28.669(6)$, $b = 9.807(2)$, $c = 9.588(2)$ Å, $\beta = 93.23(2)°$, $U = 2691.45$ Å^3, $D_c = 1.57$ g cm^{-1}, $Z = 4$, $F(000) = 1288$, $\mu(Mo\text{-}K_\alpha) = 9.48$ cm^{-1}, $I/\sigma(I) \geqslant 3.0$, θ range 3—25°, $R = 0.0607$, $R_w = 0.0586$ for 1284 absorption-corrected diffractometer data. The crystals of (**2d**) and (**3a**) were obtained by recrystallisation from hexane : CH_2Cl_2 (1 : 1) under, respectively, N_2 and CO atmospheres.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

Mo(1), which is the opposite of the co-ordination in (**2d**). The geometry of the Mo–O–C–Mn group is similar to that found in analogous dimetallic complexes;[5,10—12] the Mo–O–C–Mn–P ring is approximately planar rather than folded as in (**2d**).

On the basis of spectroscopic studies it was determined that the solution structures of (**3a—c**) [(**3b**) and (**3c**) are formed on treatment of (**2c**) and (**2d**) respectively with CO] are similar to the solid state structure found for (**3a**). Particularly significant is the acyl CO stretching band in the i.r. spectrum [1505 cm^{-1} for (**3a**)] and the zero ^{31}P–^{13}C coupling for the acyl ^{13}C n.m.r. resonance [δ 330.3 for (**3a**)] as expected for *cis*-oriented acyl carbon and phosphido groups at Mn. Further, the observation that the methylene protons in (**3a**) are equivalent in the ^{1}H n.m.r. spectrum, unlike the diastereotopic methylene protons in (**2b**), reflects the increased symmetry in the environment of the n-propyl group at Mn in (**3a**) compared to that at Mo in (**2b**).

The reactions of (**1**) with alkenes to give (**2**) and of (**2**) with CO to give (**3**) are readily reversible under thermal conditions. Thus on stirring complex (**3a**) in 10:1 hexane : dichloromethane under N_2 at 18 °C for 24 h a product mixture of (**2b**) : (**3a**) of *ca.* 30 : 70 is obtained. Furthermore, whilst a solution of (**2b**) in benzene under N_2 at 18 °C is indefinitely stable, heating the solution to 45 °C gives a product mixture of (**1**) : (**2b**) of *ca.* 90 : 10 after 3 h. Such facile ejection of an alkene molecule from a μ-acyl ligand has not been previously observed. Indeed, the complexes $[(\eta^5\text{-}C_5H_5)FeMn\{\mu\text{-}C(O)Me\}(\mu\text{-}PPh_2)(CO)_5]$ and $[(\eta^5\text{-}C_5H_5)_2FeMo\{\mu\text{-}C(O)Me\}(\mu\text{-}PPh_2)(CO)_3]$, which are closely related to (**3**) (and in which in each case the acyl carbon is bonded to Fe) are not reported to undergo the first step of CO loss and the formation of metal–metal bonded derivatives.[10,11]

The first step in the formation of (**3**) from (**2**) may be the displacement of the Mn–Mo bond by CO as shown in Scheme 1. The ease with which the metal–metal bond in the structurally related complex $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}I)(\mu\text{-}PPh_2)(CO)_5]$ is broken on stirring under CO, a reaction which is reversed on photolysis, provides precedent for such a step.[13] This could then be followed by formation of a metal–metal bonded oxycarbene complex from which (**3**) would be readily obtained.

The ready interconversion of (**2**) and (**3**) indicates that the thermodynamic stability of the two acyl bonding modes is comparable. This suggests that the oxophilicity of Mo and Mn in these complexes is similar and sensitive to a small change in the ligand environment.

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