Synthesis of Dimetal Compounds from Metal Carbene Complexes; *X*-Ray Crystal Structures of Two Forms of $[(OC)_4Mn\{\mu\text{-}(1\text{-}\sigma,1\text{-}2\text{-}\eta\text{-}C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}O)\}Pt(PMe_3)_2]$

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Summary The complexes $[M\{C(OMe)R\}(CO)_5]$ (M = Cr, Mo, or W; R = Me or Ph) and $[Mn\{C(OMe)Ph\}(CO)_2(\eta\text{-}C_5H_5)]$ react with d^{10} species (Pt^0, Pd^0, or Ni^0) to afford heteronuclear dimetal compounds with bridging carbene ligands; *X*-ray diffraction studies on a product from $[Mn_2(CO)_9(C{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2)]$ and $[Pt(C_2H_4)(PMe_3)_2]$ have identified two isomers of $[MnPt(\mu\text{-}C_4H_5O)(CO)_4(PMe_3)_2]$ with a (1-σ, 1-2-η-C:CH) group bridging a Pt–Mn bond.

Perfluoropropene and $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) afford $[(cod)Pt\{\mu\text{-}C(CF_3)_2\}Pt(cod)]$, possibly *via* attack of $[Pt(cod)_2]$ on a transient ylide species $[Pt^+C^-(CF_3)_2(cod)]$.[1] Formation of a metal–metal bond in this manner, and the synthesis of metalla-cycles from d^{10} or d^8 metal complexes and electrophilic olefins, acetylenes, and ketones,[2] suggests that mononuclear metal carbene (or ylide)[3] compounds might afford heteronuclear dimetal species with bridging carbene ligands on treatment with suitable low valent metal complexes. Hitherto there has been no general synthetic route to compounds containing the structural unit $[M(\mu\text{-}CR^1R^2)M']$, yet such dimetal species should yield an extensive chemistry. It has been recently demonstrated that tungsten carbyne compounds bond to platinum(0) complexes.[4]

Carbene complexes $[M\{C(OMe)R\}(CO)_5]$ (M = Cr, Mo, or W; R = Me or Ph)[5] react (−20 to 25 °C) with [Pt-

$(C_2H_4)_3]$,[6] to which two equiv. of PMe_3 have been previously added, to give (60—90%) orange, crystalline dimetal compounds $[(OC)_5M\{C(OMe)R\}Pt(PMe_3)_2]$, *e.g.* (**1**; M = Cr, R = Ph), m.p. 122—124 °C [ν_{CO}(cyclohexane), 2 027vs, 1 972m, 1 937vs, 1 892m, and 1 878m cm^{-1}; n.m.r. ($CDCl_3$): ^1H, τ, 2·8 (m, 5H, Ph), 6·29 (s, 3H, OMe), 8·38 {d, 9H, PMe, J(P–H) 8 and J(Pt–H) 20 Hz}, and 8·67 {d, 9H, PMe, J(P–H) 10 and J(Pt–H) 42 Hz}. ^{31}P, 14·4 p.p.m. (rel. to H_3PO_4 external) {d, J(P–P) 4 and J(Pt–P) 2441 Hz} and 22·0 {d, J(P–P) 4 and J(Pt–P) 4513 Hz}]; (**2**; M = Mo, R = Ph), m.p. 80—82 °C (decomp.) [ν_{CO}, 2 042vs, 1 977s, 1 938vs, and 1 903vs,br cm^{-1}; n.m.r.: ^1H, τ, 2·4—3·1 (m, 5H, Ph), 6·29 (s, 3H, OMe), 8·34 {d, 9H, PMe, J(P–H) 8 and J(Pt–H) 23 Hz}, and 8·65 {d, 9H, PMe, J(P–H) 11 and J(Pt–H) 44 Hz}; ^{31}P (−30 °C), 14·0 p.p.m. {d, J(P–P) 9 and J(Pt—P) 2607 Hz} and 22·8 {d, J(P–P) 9 and J(Pt–P) 4423 Hz}]; and (**3**; M = W, R = Me), m.p. 123—125 °C [m/e 728 (M^+); ν_{CO} 2 036s, 1 956m, 1 926s, 1 908sh, and 1 900s cm^{-1}; n.m.r.: ^1H, τ, 6·44 (s, 3H, OMe), 6·93 {d of d, CMe, J(P–H) 6 and 12, and J(Pt–H) 8 Hz}, 8·44 {d, 9H, PMe, J(P–H) 10 and J(Pt–H) 46 Hz}, and 8·45 {d, 9H, PMe, J(P–H) 8 and J(Pt–H) 20 Hz}; ^{31}P, 15·8 p.p.m. {d, J(P–P) 17 and J(Pt–P) 2377 Hz} and 17·8 {d, J(P–P) 17, J(Pt–P) 4465, and J(W–P) 12 Hz}].

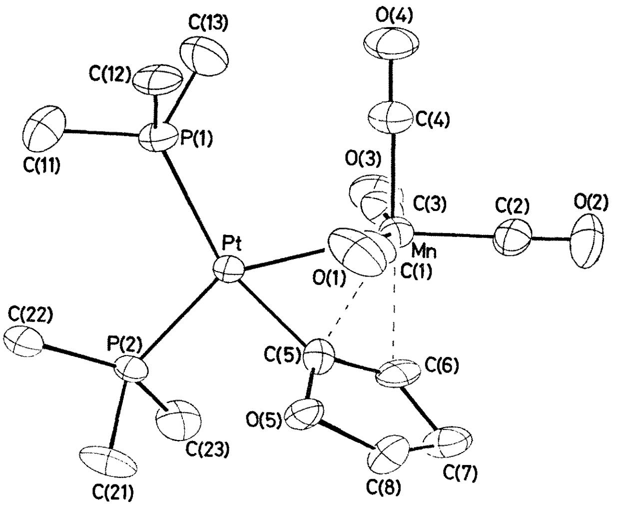

FIGURE 1. Molecular structure of the yellow complex $[(OC)_4Mn\{\mu\text{-}(1\text{-}\sigma, 1\text{-}2\text{-}\eta\text{-}C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}O)\}Pt(PMe_3)_2]$. Bond lengths: Mn–Pt, 2·658(2); Pt–C(5), 1·98(1); Mn–C(5), 2·22(1); Mn–C(6), 2·28(1), C(5)–C(6), 1·32(2); Pt–P(1), 2·293(4); and Pt–P(2), 2·267(3) Å; ∠Pt–C(5)–C(6), 132(1)°.

Formation of dimetal complexes is not limited to the chromium sub-group. The manganese compound $[Mn\{C(OMe)Ph\}(CO)_2(\eta\text{-}C_5H_5)]$[5] reacts with $[Pt(C_2H_4)_3]$, $[Pd(dba)_2]$ (dba = dibenzylidene acetone), and $[Ni(cod)_2]$, all treated with two mol of PMe_3, to give crystalline complexes $[(\eta\text{-}C_5H_5)(OC)_2Mn\{\mu\text{-}C(OMe)Ph\}M(PMe_3)_2]$ (**4**; M = Pt), 60%, orange, m.p. 151 °C (decomp.) [ν_{CO} 1 871s and 1 814s cm^{-1}; ^{31}P n.m.r. (C_6D_6), 16·3 p.p.m. {d, J(P–P) 12 and J(P–Pt) 2451 Hz} and 22·3 {d, J(P–P) 12 and J(P–Pt) 4663 Hz}]; (**5**; M = Pd), 25%, orange, m.p. 124 °C [ν_{CO} 1 870s and 1 817s cm^{-1}; ^{31}P n.m.r. (C_6D_6), 27·3 and 29·0 p.p.m. {AB quartet, J(P–P) 8 Hz}]; and (**6**; M = Ni), 30%, purple, m.p. 80 °C (decomp.) [ν_{CO} 1 863s and 1 806s cm^{-1}].

In an attempt to obtain a $[Pt(PMe_3)_2]$ adduct of the dimanganese carbene complex $[(OC)_5Mn{\cdot}Mn(C{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O)(CO)_4]$,[7] a novel reaction with $[Pt(C_2H_4)_3]$ and PMe_3 (1:2) was observed, affording (15%) a mixture of red and yellow crystals with identical spectra [ν_{CO} (hexane) 2 011s, 1 937s, 1 913s, and 1 903s cm^{-1}; ^1H n.m.r. (C_6D_6) τ, 5·8—6·2 (m, 2H, OCH_2), 6·29 (m, 1H), 7·81 (m, 2H, CH_2), 8·70 {d, 9H, Me, J(P–H) 9 and J(Pt–H) 24 Hz}, and 8·87 {d, 9H, Me, J(P–H) 10 and J(Pt–H) 32 Hz}]. In order to identify these yellow and red crystals, *X*-ray diffraction studies were carried out.

The yellow crystals are triclinic, a = 9·429(5), b = 12·113(4), c = 9·729(6) Å, α = 93·97(4), β = 115·45(4), γ = 98·83(3)°, space group $P\bar{1}$, Z = 2, U = 980·0 $Å^3$, D_m = 1·96, D_c = 1·98 g cm^3, F(000) = 562, μ(Mo-K_α) = 83·6 cm^{-1}. For the 3357 independent reflections [$I \geqslant 2\sigma(I)$], R 0·047 (R' 0·056).

The red crystals are monoclinic, a = 9·356(5), b = 12·844(9), c = 15·989(9) Å, β = 98·14(4)°, space group $P2_1/n$, Z = 4, U = 1902·0 $Å^3$, D_m = 2·02, D_c = 2·04 g cm^{-3}, F(000) = 1124, μ(Mo-K_α) = 86·1 cm^{-1}. For the 2658 independent reflections [$I \geqslant 2\sigma(I)$], R 0·035 (R' 0·047).

Both structures were solved including location of hydrogen atoms by conventional heavy-atom methods from data collected at −73 °C on a Syntex $P2_1$ four-circle diffractometer to $2\theta \leqslant 50°$, Mo-K_α (λ = 0·71069 Å).†

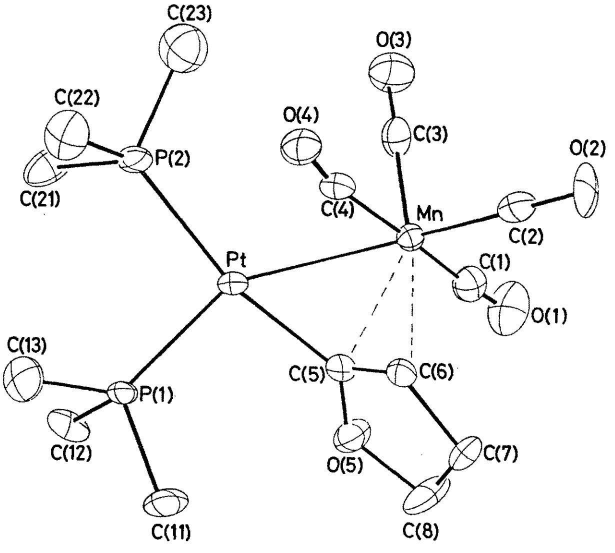

FIGURE 2. Molecular structure of the red complex $[(OC)_4Mn\{\mu\text{-}(1\text{-}\sigma,1\text{-}2\text{-}\eta\text{-}C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}O)\}Pt(PMe_3)_2]$. Bond lengths: Mn–Pt, 2·693(1); Pt–C(5), 2·014(9); Mn–C(5), 2·18(1); Mn–C(6) 2·253(9); C(5)–C(6), 1·37(1); Pt–P(1), 2·267(3); and Pt–P(2), 2·231(1) Å; ∠Pt–C(5)–C(6), 127(1)°.

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† 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.

The results establish that the red and yellow crystals are isomers of a complex $[MnPt(\mu\text{-}C_4H_5O)(CO)_4(PMe_3)_2]$ (**7**) (Figures 1 and 2) which differ in the orientation of the $Mn(CO)_4$ groups with respect to bonding to a 'vinylplatinum' group. During the course of reaction the carbene has lost a hydrogen atom at C(6), and the remaining proton on this atom accounts for the n.m.r. resonance at τ 6·29.

Compounds (**1**)—(**7**) complete the Scheme of ref. 4, involving the complexing of d^{10} metals with reactants containing the groups C=C, C=M, and M=M. Moreover, the above dimetal compounds have synthetic potential for reactions at the metal centres or at the bridging group.

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