Synthesis of Cationic Heteronuclear Dimetal Compounds with Bridging Alkylidyne Ligands: *X*-Ray Crystal Structures of $[(\eta\text{-}C_5H_5)(OC)_2Mn(\mu\text{-}CC_6H_4\text{-}Me\text{-}p)Pt(PMe_3)_2]BF_4{\cdot}CH_2Cl_2$ and $[(Me_3P)(OC)_4Cr\{\mu\text{-}C(CO_2Me)Ph\}Pt(PMe_3)_2]$

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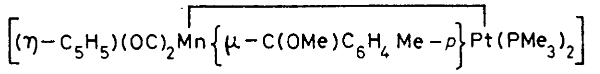
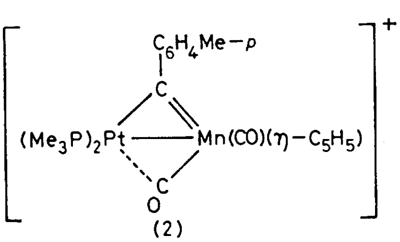
Summary The dimetal complexes $[(\eta\text{-}C_5H_5)(OC)_2M\{\mu\text{-}C(OMe)C_6H_4\text{-}Me\text{-}p\}Pt(PR_3)_2]$ (M = Mn, $PR_3 = PMe_3$; M = Re, $PR_3 = PMe_2Ph$) react with $Me_3O^+BF_4^-$ to give the salts $[(\eta\text{-}C_5H_5)(OC)_2M(\mu\text{-}CC_6H_4\text{-}Me\text{-}p)Pt(PR_3)_2]BF_4$, the manganese compound being characterised by an *X*-ray diffraction study; reaction of these salts with methoxide anion regenerates the neutral species, but in contrast treatment of the cation $[(Me_3P)(OC)_4Cr(\mu\text{-}CPh)Pt(PMe_3)_2]^+$ with methoxide affords $[(Me_3P)(OC)_4Cr\{\mu\text{-}C(CO_2Me)Ph\}Pt(PMe_3)_2]$, also characterised by *X*-ray diffraction.

We recently showed[1] that Pt^0 and other d^{10} metal compounds react with Fischer's[2] mononuclear metal carbene complexes to afford dimetal complexes with bridging carbene groups, *e.g.* $[(\eta\text{-}C_5H_5)(OC)_2Mn\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$. We now report preliminary results concerning reactions of the bridging ligand on the dimetal centre.

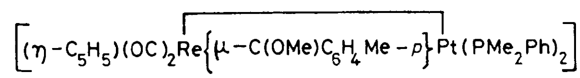
The neutral yellow complex {(**1**), m.p. 150 °C decomp.; ν_{CO} (cyclohexane), 1 869m and 1 813s cm^{-1}; ^{13}C (^1H-decoupled) n.m.r. spectrum ($CDCl_3$), μ-*C* resonance at 193·6 p.p.m. [d, *J*(PC) 73 Hz]} was prepared (80% yield) from $[Mn\{C(OMe)C_6H_4\text{-}Me\text{-}p\}(CO)_2(\eta\text{-}C_5H_5)]$ and $[Pt(C_2H_4)(PMe_3)_2]$. Treatment of (**1**), suspended in acetonitrile, with $Me_3O^+BF_4^-$ gave a deep red solution which afforded (90% yield) very dark red crystals of the salt $[(\eta\text{-}C_5H_5)(OC)_2Mn(\mu\text{-}CC_6H_4\text{-}Me\text{-}p)Pt(PMe_3)_2]BF_4$ {(**2**), m.p. 80 °C decomp.; ν_{CO} (CH_2Cl_2), 1 993s and 1 829m cm^{-1}; ^{13}C (^1H-decoupled) n.m.r. spectrum, μ-C resonance at 338·1 p.p.m. [d, *J*(PC) 71 and *J*(PtC) 757 Hz]}. The downfield chemical shift of 144·5 p.p.m. for the bridging carbon atom in (**2**), compared with the neutral complex (**1**), accords well with formation of a cationic dinuclear metal–carbyne complex. In $[PtW(\mu\text{-}CC_6H_4\text{-}Me\text{-}p)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ the corresponding signal occurs at 336.5 p.p.m. [d, *J*(PC) 59 and *J*(PtC) 747 Hz].[3] Reaction of (**3**) with $Me_3O^+BF_4^-$ in dichloromethane gives a quantitative yield of red crystals of (**4**), {m.p. 65 °C decomp.; ν_{CO} (CH_2Cl_2) 1 990s and 1 866m cm^{-1}; ^{13}C (^1H-decoupled) n.m.r. spectrum, μ-C resonance at 382·6 p.p.m. [d, *J*(PC) 66 and *J*(PtC) 730Hz]}. The cation of (**4**) is isoelectronic with the neutral compound $[PtW(\mu\text{-}CC_6H_4\text{-}Me\text{-}p)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$,[3] and the former could also be prepared by the reaction of $[Re{\equiv}CC_6H_4\text{-}Me\text{-}p\text{-}(CO)_2(\eta\text{-}C_5H_5)]BF_4$ with $[Pt(C_2H_4)(PMe_2Ph)_2]$. Since complexes (**2**) and (**4**) were of a new type, a single crystal *X*-ray diffraction study was carried out on (**2**).†


$[(\eta\text{-}C_5H_5)(OC)_2Mn\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}Pt(PMe_3)_2]$

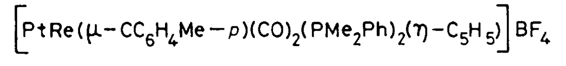
(1)



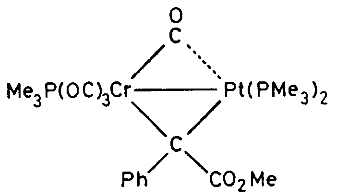
(2)


$[(\eta\text{-}C_5H_5)(OC)_2Re\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}Pt(PMe_2Ph)_2]$

(3)


$[PtRe(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]BF_4$

(4)



(5)

Crystal data: $C_{21}H_{30}BF_4MnO_2P_2Pt{\cdot}CH_2Cl_2$, *M* 798·2, monoclinic, space group $P2_1/c$, a = 10·434(4), b = 19·334(7), c = 14·901(7) Å, β = 94·42(4)°, U = 2997(2) Å^3, Z = 4, D_m = 1·76, D_c = 1·77 g cm^{-3}, $F(000)$ = 1552, μ(Mo-K_α) = 51·8 cm^{-1}. Current *R* 0·044 (R′ 0·046) for 4 223 absorption-corrected intensities [298 K, $2{\cdot}9 \leqslant 2\theta \leqslant 55°$, $I \geqslant 2{\cdot}5\sigma(I)$, Syntex $P2_1$ diffractometer, Mo-K_α (λ = 0·71069 Å)].

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† 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 molecular structure (Figure 1) reveals that the Pt–Mn bond [2·628(1) Å] is bridged by the $C{\cdot}C_6H_4\text{-Me-}p$ group [Pt–C 1·967(8), Mn–C 1·829(8) Å] and that one of the CO ligands of the $Mn(CO)_2(\eta\text{-}C_5H_5)$ group is semi-bridging to the platinum atom [$\angle$Mn·C(1)·O(1), 157·5(9)°]. The plane of the tolyl group is inclined at 43° to the $Mn(\mu\text{-}C)Pt$ plane. The Mn–(μ-C) distance is shorter than those found for the bridging carbon atoms in $[Mn_2(\mu\text{-}CH_2)(CO)_4(\eta\text{-}C_5H_4Me)_2]$ [2·013(4) Å][4] and $[Mn_2\{\mu\text{-}C(CO)C_6H_4\text{-Me-}p\}(CO)_6(\eta\text{-}C_5H_5)]$ [2·128(4) Å][5] and may be regarded as an Mn=C linkage.

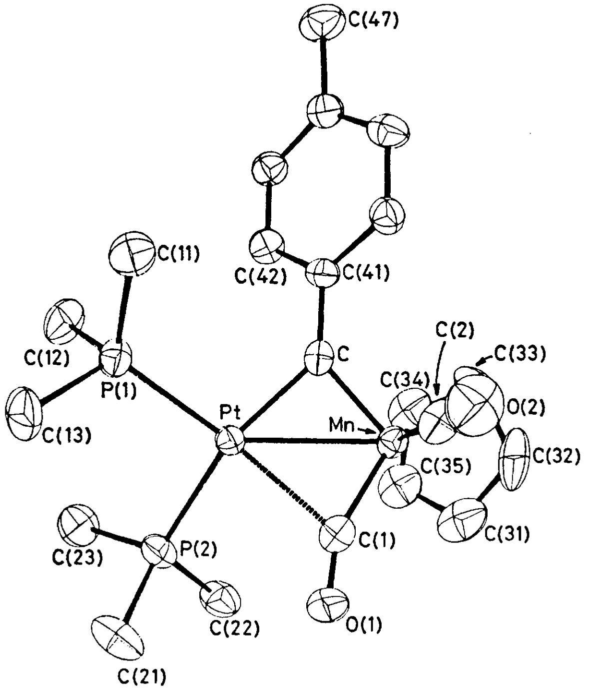

FIGURE 1. The molecular geometry of the cation $[MnPt(\mu\text{-}CC_6H_4\text{-Me-}p)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ (**2**) including the atomic numbering scheme.

The relationship between the neutral dimetal bridging carbene complexes (**1**) and (**3**), and the cationic bridging carbyne complexes (**2**) and (**4**) is emphasised by reaction of the salts with methoxide ion in methanol which regenerates (**1**) and (**3**) quantitatively. However, reaction of the salt $[(Me_3P)(OC)_4\overline{Cr(\mu\text{-}CPh)Pt}(PMe_3)_2]BF_4$ with methoxide ion follows a different course giving (50% yield) yellow crystalline $[CrPt\{\mu\text{-}C(CO_2Me)Ph\}(CO)_4(PMe_3)_3]$ [(**5**), m.p. 159—161 °C; ν_{CO} (cyclohexane), 1 992m, 1 915(sh), 1 909vs, 1 888vs (CO), and 1 626w br cm^{-1} (CO_2Me)]. Metal assisted CO transfer to the μ-CPh group with concomitant methoxide attack was confirmed by an *X*-ray diffraction study.†

Crystal data: $C_{22}H_{35}CrO_6P_3Pt$, *M* 735·5, monoclinic, space group *A*2/*a*, a = 18·27(3), b = 9·84(1), c = 31·93(5) Å, β = 106·2(1)°, U = 5·510(12) Å^3, Z = 8, D_m = 1·79, D_c = 1·77 g cm^{-3}, $F(000)$ 2 896, μ(Mo-K_α) = 54·3 cm^{-1}. Current *R* 0·12 (*R′* 0·12) for 2 292 absorption-corrected intensities [230 K, $2{\cdot}9 \leqslant 2\theta \leqslant 50°$, $I \geqslant 3\sigma(I)$, Mo-K_α (λ = 0·71069 Å)].

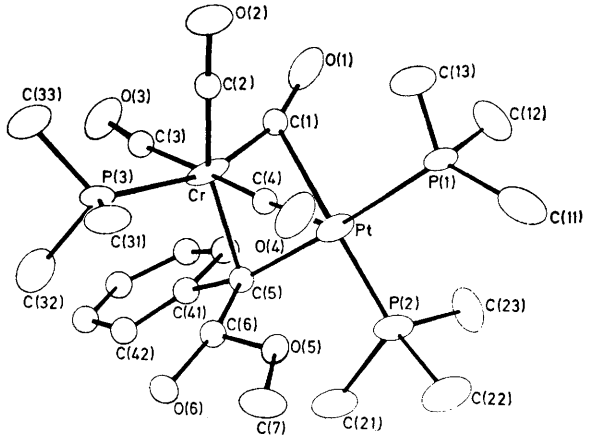

FIGURE 2. The molecular geometry of $[CrPt\{\mu\text{-}C(CO_2Me)Ph\}(CO)_4(PMe_3)_3]$ (**5**) including the atomic numbering scheme. Bond lengths: Cr–Pt, 2·646(7); Cr–C(5), 2·27(4); Pt–C(5), 1·98(4); Pt–C(1), 2·19(4); Cr–C(1), 1·75(5); and C(1)–O(1), 1·31(5) Å. Angles: Cr–C(1)–O(1), 157(4); Cr–C(1)–Pt, 84(2)°.

The molecular structure (Figure 2) determination confirms the presence of the CO_2Me group, reveals a bridging carbonyl [<Cr–C(1)–O(1) 157(4)°], and also demonstrates that the C(CO_2Me)Ph ligand asymmetrically bridges the Cr–Pt bond [Cr–C(5), 2·27(4); Pt–C(5), 1·98(4) Å]. Similar asymmetric carbene bridging has been found in $[PtW\{\mu\text{-}C(OMe)Ph\}(CO)_5(PMe_3)_2]$ [W–(μ-C), 2·48(1) Å; Pt–(μ-C), 2·04(1) Å].[6]

Other reactions of the cationic heteronuclear dimetal compounds include the synthesis of $[CrPt\{\mu\text{-}C(Ph)C_6H_4\text{-Me-}p\}(CO)_5(PMe_3)_2]$ from $[CrPt(\mu\text{-}CPh)(CO)_5(PMe_3)_2]^+$, and $[MPt\{C(CO_2Me)C_6H_4\text{-Me-}p\}(CO)_4(PMe_3)_3]$ from $[MPt\{\mu\text{-}C(C_6H_4\text{-Me-}p)\}(CO)_4(PMe_3)_3]^+$ (M = Cr or W).

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