ortho-Metallation at Dimetallic Centres: Syntheses and *X*-Ray Characterizations of $Os_2(O_2CMe)_2[Ph_2P(C_6H_4)]_2Cl_2$ and $Rh_2(O_2CMe)_2[Ph_2P(C_6H_4)]_2(2MeCO_2H)$

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The complexes $M_2(O_2CMe)_4X_2$ (M = Os, X = Cl; M = Rh, X = MeOH) react with triphenylphosphine in acetic acid, leading to partial replacement of acetate groups by triphenylphosphine ligands in which *ortho*-metallation has occurred at one of the phenyl rings on each phosphine; the isolated products, $M_2(O_2CMe)_2[Ph_2P(C_6H_4)]_2X_2$, (M = Os, X = Cl; M = Rh, X = $MeCO_2H$) have been characterized by *X*-ray crystallography, showing that each complex has a central M_2L_8 core consisting of the dimetal unit bridged, in a *cisoid* arrangement, by two acetate groups and two *ortho*-metallated triphenylphosphine ligands.

Although *ortho*-metallation reactions are by no means uncommon, to the best of our knowledge, only one previous example of an *ortho*-metallation reaction involving a multiply-bonded dimetal unit has been reported in the literature.[1,2] Stereochemically, the products of such reactions would appear to be very favourable, so the lack of many successful reports of their preparation has been surprising. We have now been able to extend the range of such compounds considerably, and report here the occurrence of *ortho*-metallation reactions across both diosmium and dirhodium bonds.

The discovery of the osmium compound, $Os_2(O_2CMe)_2[Ph_2P(C_6H_4)]_2Cl_2$, occurred in the course of attempts to prepare simple adducts of the $[Os_2(O_2CMe)_4]^{2+}$ core. Gentle warming of $Os_2(O_2CMe)_4Cl_2$ with triphenylphosphine (1:2 mol ratio) in acetic acid gives rise to a black solution. Addition of diethyl ether to the cooled reaction mixture results in the slow deposition of black, square-prismatic crystals in moderate yield (*ca.* 20%). The crystalline material is insoluble in all common solvents and thus was, of necessity, characterized only by *X*-ray crystallography.†

The structure consists of a binuclear diosmium core bridged by *cisoid* acetate groups and triphenylphosphine ligands, in which *ortho*-metallation has occurred at one of the phenyl rings of each phosphine (see Figure 1). In this complex the axial sites are occupied by chloride ions. The osmium-to-osmium distance, 2.271(1) Å, is the shortest Os–Os distance yet reported.[3—6] In view of this it is perhaps not surprising that the magnetic moment of this compound, measured in the solid state is essentially zero, in contrast to the significant moments reported for the parent carboxylates, $Os_2(O_2CR)_4Cl_2$.[4,5] Interestingly, the reduction in the $Os{\equiv}Os$ bond length does not occur at the expense of a lengthening of the bond to the axial ligand. The Os(1)–Cl(1) distance, 2.372(2) Å, is also much reduced from that reported previously for the carboxylates [2.417(3) Å in $Os_2(O_2CPr)_4Cl_2$[4] to 2.448(2) Å in $Os_2(O_2CMe)_4Cl_2$].[6] However, the presence of the phosphine ligands results in a deformation of the Os(1′)–Os(1)–Cl(1) angle [161.08(5)°] from the close approximation to linearity observed for the carboxylates.[5,6] The shortening of the metal–metal bond results in the distortion of both types of bridging ligand, giving torsion angles P(1)–Os(1′)–Os(1)–C(16) = 20.3° and O(1)–Os(1′)–Os(1)–O(2) = 17.1°. In addition there is significant variation in the metal–oxygen distances, Os(1)–O(1′) = 2.223(5), Os(1)–O(2) = 2.105(5) Å, although the metal to phosphorus and carbon distances, 2.345(2) and 2.080(7) Å, respectively, are normal.

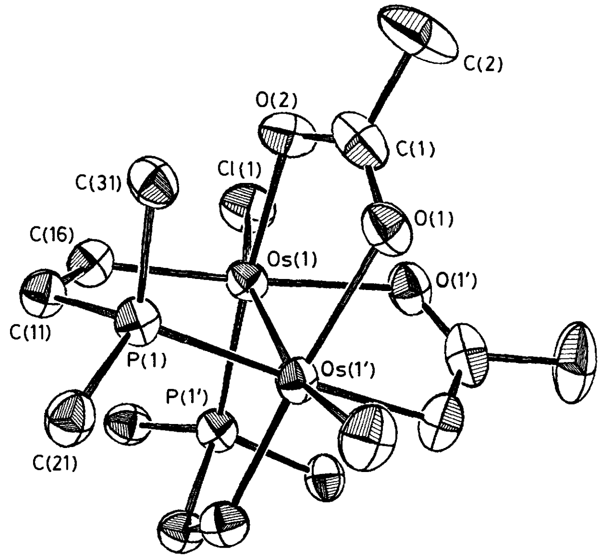

Figure 1. An ORTEP drawing at the 50% probability level of the molecular structure of $Os_2(O_2CMe)_2[Ph_2P(C_6H_4)]_2Cl_2$; only the α carbon atoms of the phenyl rings are shown. Selected bond distances (Å) and angles (°) are: Os(1)–Os(1′) 2.271(1), Os(1)–Cl(1) 2.372(2), Os(1)–O(1′) 2.223(5), Os(1)–O(2) 2.105(5), Os(1)–P(1′) 2.345(2), Os(1)–C(16) 2.080(7), P(1)–C(11), 1.797(7), P(1)–C(21) 1.825(7), P(1)–C(31) 1.839(7), C(11)–C(16) 1.390(9), O(1)–C(1) 1.249(9), O(2)–C(1) 1.281(9), C(1)–C(2) 1.522(11); Cl(1)–Os(1)–Os(1′) 161.08(5), P(1)–Os(1′)–Os(1) 87.54(4), C(16)–Os(1)–Os(1′) 100.7(2), O(1)–Os(1′)–Os(1) 82.2(1), O(2)–Os(1)–Os(1′) 94.6(1).

In an effort to determine the generality of this reaction we have investigated the process in a variety of alkylcarboxylic acids, and have successfully synthesized a number of compounds of type $Os_2(O_2CR)_2[Ph_2P(C_6H_4)]_2Cl_2$ (R = Et, Pr, Bu).[7]

There seemed no reason why this sort of reaction should be restricted to the diosmium carboxylates and we are investigating other similar dinuclear compounds. The reaction of $Rh_2(O_2CMe)_4{\cdot}2MeOH$ under similar conditions gave red-

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† *Crystal data:* for $Os_2(O_2CMe)_2[Ph_2P(C_6H_4)]_2Cl_2$, M = 1092.0, monoclinic, space group $C2/c$, a = 16.304(6), b = 14.212(3), c = 19.259(9) Å, β = 109.34(3)°, U = 4210(1) Å^3, D_c = 1.722 g cm^{-3}, μ(Mo-K_α) = 62.76 cm^{-1}, Z = 4, λ = 0.710 73 Å, crystal dimensions 0.3 × 0.3 × 0.2 mm^3, R = 0.030 and R_w = 0.040 for 2747 reflections with $F > 3\sigma(F)$ collected at 25 °C on an Enraf-Nonius CAD-4 diffractometer. For $Rh_2(O_2CMe)_2[Ph_2P(C_6H_4)]_2(2MeCO_2H)$, M = 968.6, monoclinic, space group $C2/c$, a = 10.111(3), b = 19.653(10), c = 21.033(9) Å, β = 97.63(4)°, U = 4142(1) Å^3, D_c = 1.553 g cm^{-3}, μ(Mo-K_α) = 9.10 cm^{-1}, Z = 4, λ = 0.710 73 Å, crystal dimensions 0.4 × 0.25 × 0.15 mm^3, R = 0.046 and R_w = 0.070 for 2508 reflections with $F > 3\sigma(F)$ collected at 25 °C on a Syntex $P\bar{1}$ diffractometer.

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.

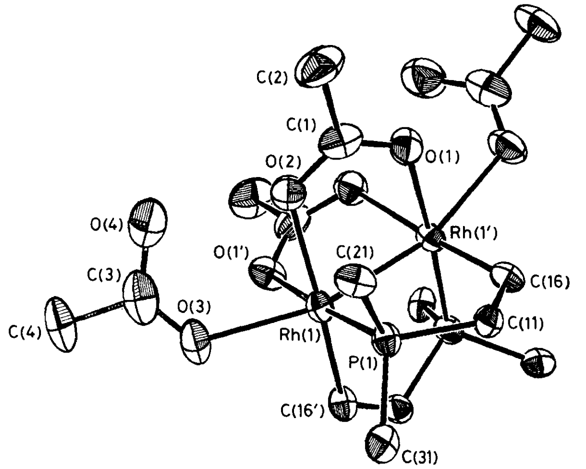

Figure 2. An ORTEP drawing at the 50% probability level of the molecular structure of $Rh_2(O_2CMe)_2[Ph_2P(C_6H_4)]_2(2MeCO_2H)$, only the α carbon atoms of the phenyl rings are shown. Selected bond distances (Å) and angles (°) are Rh(1)–Rh(1') 2.508(1), Rh(1)–P(1) 2.210(2), Rh(1)–C(16') 1.996(6), Rh(1)–O(1') 2.136(4), Rh(1)–O(2) 2.190(4), Rh(1)–O(3) 2.342(5), P(1)–C(11) 1.811(6), P(1)–C(21) 1.832(6), P(1)–C(31) 1.830(7), C(11)–C(16) 1.384(9), O(1)–C(1) 1.252(8), O(2)–C(1) 1.294(8), C(1)–C(2) 1.536(9), O(3)–C(3) 1.232(9), O(4)–C(3) 1.323(10), C(3)–C(4) 1.522(10), O(2) · · · O(4) 2.527; O(3)–Rh(1)–Rh(1') 163.6(1), P(1)–Rh(1)–Rh(1') 88.31(5), C(16)–Rh(1')–Rh(1) 97.5(2), O(1)–Rh(1')–Rh(1) 87.8(1), O(2)–Rh(1)–Rh(1') 82.7(1).

purple crystals in good yield (*ca.* 55%) and *X*-ray characterization† showed that the product is a dirhodium compound with a similar structure to that described above (see Figure 2). In this case the Rh–Rh distance, 2.508(1) Å, is longer than that reported for any of the dirhodium tetracarboxylates,[8] only the complexes $Rh_2(O_2CMe)_2(dmg)_2(PPh_3)_2$[9] (dmg = dimethylglyoximato) and $Rh_2(O_2CH)_2(phen)_2Cl_2$[10] (phen = 1,10-phenanthroline), with Rh–Rh distances of 2.618(5) and 2.576 Å, in which there are only two bridging ligands, having longer rhodium–rhodium bonds.

Surprisingly, despite the larger bite angle, both ligands still exhibit a twist distortion, with torsion angles, P(1)–Rh(1)–Rh(1')–C(16) = 12.2° and O(1)–Rh(1')–Rh(1)–O(2) = 17.3°. In this complex the axial ligands are molecules of acetic acid, the Rh(1)–O(3) distance being 2.342(5) Å and the angle O(3)–Rh(1)–Rh(1')[2] is again non-linear, 163.6(1)°. In addition, the axial ligand is hydrogen bonded to one of the oxygen atoms of the bridging acetate, O(2) · · · O(4) = 2.527 Å. It is probably this hydrogen bonding interaction which leads to the greater Rh(1)–O(2) distance, 2.190(4) Å, compared to 2.136(4) Å for Rh(1)–O(1').

Investigations are continuing to determine the full extent of these reactions.

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References

1 T. J. Barder, S. M. Tetrick, R. A. Walton, F. A. Cotton, and G. L. Powell, *J. Am. Chem. Soc.*, 1983, **105**, 4090.
2 T. J. Barder, F. A. Cotton, G. L. Powell, S. M. Tetrick, and R. A. Walton, *J. Am. Chem. Soc.*, in the press.
3 F. A. Cotton and J. L. Thompson, *J. Am. Chem. Soc.*, 1980, **102**, 6437.
4 T. A. Stephenson, D. A. Tocher, and M. D. Walkinshaw, *J. Organomet. Chem.*, 1982, **232**, C51.
5 T. Behling, G. Wilkinson, T. A. Stephenson, D. A. Tocher, and M. D. Walkinshaw, *J. Chem. Soc., Dalton Trans.*, 1983, 2109.
6 F. A. Cotton, A. R. Chakravarty, D. A. Tocher, and T. A. Stephenson, *Inorg. Chim. Acta*, submitted for publication.
7 F. A. Cotton, A. R. Chakravarty, and D. A. Tocher, unpublished work.
8 F. A. Cotton and R. A. Walton, 'Multiple Bonds Between Metal Atoms,' Wiley, New York, 1982.
9 J. Halpern, E. Kimura, J. Molin-Case, and C. S. Wong, *J. Chem. Soc., Chem. Commun.*, 1971, 1207.
10 H. Pasternak and F. Pruchnik, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 591.