lution using 0.1 M $(Bu_4N)BF_4$ as the supporting electrolyte and an Ag–AgCl reference electrode by both the cyclic voltametric and differential-pulse techniques.

The complex exhibits a number of waves on the cyclic voltametric time scale as shown in Figure 3. A quasi-reversible oxidation wave is evident at +0.75 V (peak to peak separation, $\Delta E_p = 70$ mV) with a current ratio i_c/i_a of ca. 1. When the scan rate is increased to 2000 mV s^{-1}, the i_c/i_a ratio decreases with a concomitant increase in ΔE_p. In addition, at fast scan rates the development of a further reduction wave is observed at $E_{p,c}$ ca. +0.60 V. These observations are consistent with an equilibrium between the oxidized product and a second redox-active species that is reduced independently. A number of reduction processes are evident. There are two quasi-reversible reduction waves, at −0.23 and −0.37 V, with $\Delta E_p \approx 60$ mV for both, but with an i_a/i_c ratio $\ll 1$. Upon further increase of the scan rate, the i_a/i_c ratio approaches unity for the more facile reduction, with no apparent change in the ratio for the second reduction. This effect was also observed upon recording the voltammagram in increasingly dilute solution. The interpretation of these observations is not at this stage apparent. However, a possible explanation for the two waves is that we are observing a sequential reduction of the two ends of the asymmetric molecule. In addition to these quasi-reversible processes, two further multielectron reduction processes are observed at potentials of −1.25 and −1.47 V.

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Registry No. $Os_2Cl_3(PhNpy)_3{\cdot}0.25C_7H_8$, 93606-10-1; $Os_2(O_2CCH_3)_4Cl_2$, 81519-41-7; Os, 7440-04-2.

Supplementary Material Available: Details of the crystal structure determination and listings of bond angles, anisotropic thermal parameters, bond distances, and observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
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An Ortho-Metalation Reaction of $Os_2(O_2CCH_3)_4Cl_2$: Syntheses and Crystal Structure Characterizations of $Os_2(O_2CR)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ (R = CH_3 (1), C_2H_5 (2))

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The compounds $Os_2(O_2CR)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ (R = CH_3 (**1**), C_2H_5 (**2**)) have been prepared by the interaction of $Os_2(O_2CCH_3)_4Cl_2$ with triphenylphosphine in the appropriate carboxylic acid. Each molecule consists of a diosmium unit bridged by two cisoid carboxylato ligands and by triphenylphosphine ligands in which ortho metalation has occurred at one of the phenyl rings on each phosphine. The black crystals of the acetate, **1**, belong to the monoclinic system, space group $C2/c$, with unit cell dimensions a = 16.315 (6) Å, b = 14.210 (4) Å, c = 19.271 (9) Å, β = 109.34 (3)°, and V = 4211 (2) Å^3 with Z = 4. The propionate, **2**, crystallized in the orthorhombic space group $Pbcn$ with unit cell dimensions a = 11.901 (2) Å, b = 18.473 (5) Å, c = 17.578 (6) Å, and V = 3864 (2) Å^3 with Z = 4. The structure of **1** was refined to $R = 0.030$ ($R_w = 0.040$) while **2** gave $R = 0.027$ ($R_w = 0.039$). The $Os{\equiv}Os$ distances 2.271 (1) and 2.272 (1) Å, for **1** and **2**, respectively, are the shortest yet recorded for a diosmium complex containing a triple bond. In each case the molecule has crystallographic C_2 symmetry; the inner group of atoms, i.e., the two Os atoms and the $P_2C_2O_4Cl_2$ group bonded to them, show no higher symmetry since there is a significant twist about the Os–Os axis away from an eclipsed geometry and the Cl–Os–Os–Cl chains are far from linear, with Cl–Os–Os angles of 161.08 (5)° in **1** and 162.51 (5)° in **2**. In contrast to their $Os_2(O_2CR)_4Cl_2$ precursors, these complexes are essentially diamagnetic.

Introduction

In the developing chemistry of compounds containing multiple bonds between atoms of the transition metals,[1] two important goals have always been (1) the enlargement of the number of compounds with metals other than Mo and Re, which were first extensively exploited, and (2) the discovery of new classes of bridging ligands. For a number of years, specific objectives, both of this group and elsewhere, have been the discovery of new diosmium compounds and the preparation of complexes containing a metal–metal bond that is bridged by an ortho-metalated ligand. Since ortho-metalation reactions are by no means uncommon at single metal centers it is perhaps surprising that M_2 complexes containing bridging ortho-metalated ligands have been so elusive. The first[2] report of a complex of this type, $Re_2Cl_3(Ph_2Ppy)_2[(C_6H_5)(C_6H_4)Ppy]$,[2,3] appeared only in 1983. The ortho-metalated ligand, 2-(diphenylphosphino)pyridine, in this complex exhibited an unusual tridentate mode of coordination and therefore could not be regarded as a typical or prototypal ortho-metalated bridging ligand. In the course of our investigations into the reactivity of the recently reported osmium carboxylates,[4-7] we were able to prepare the complex $Os_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$.[8] We have now found that, in contrast to the synthesis of the rhenium complex, the synthetic method by which this diosmium compound was obtained can be readily generalized to include other carboxylic acids and transition-metal ions, and a number of ortho-metalated dirhodium complexes, $Rh_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2{\cdot}2L$,[8,9] have been prepared.

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Table I. Crystallographic Parameters for $Os_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2 \cdot CH_3CO_2H$ (1) and $Os_2(O_2CC_2H_5)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ (2)

formula	$Os_2Cl_2P_2O_6C_{42}H_{38}$	$Os_2Cl_2P_2O_4C_{42}H_{38}$
fw	1164.05	1120.04
space group	*C*2/*c*	*Pbcn*
syst abs	*hkl* ($h + k = 2n$), *h*0*l* ($l = 2n$, $h = 2n$), 0*k*0 ($k = 2n$)	0*kl* ($k = 2n$), *h*0*l* ($l = 2n$), *hk*0 ($h + k = 2n$), *h*00 ($h = 2n$), 0*k*0 ($k = 2n$), 00*l* ($l = 2n$)
a, Å	16.315 (6)	11.901 (2)
b, Å	14.210 (4)	18.473 (5)
c, Å	19.271 (9)	17.578 (6)
α, deg	90.0	90.0
β, deg	109.34 (3)	90.0
γ, deg	90.0	90.0
V, $Å^3$	4211 (2)	3864 (2)
Z	4	4
d_{calcd}, g/cm^3	1.84	1.93
cryst size, mm	0.3 × 0.3 × 0.2	0.4 × 0.2 × 0.1
μ(Mo Kα), cm^{-1}	62.8	68.6
data collcn instrum	CAD 4	CAD 4
radiation (monochromated in incident beam)	Mo Kα	Mo Kα
orientation reflcns: no.; range (2θ), deg	25; $14 < 2\theta < 38$	25; $21 < 2\theta < 34$
temp, °C	22 ± 2	22 ± 2
scan method	ω–2θ	ω–2θ
data collcn range (2θ), deg	$5 < 2\theta < 50$	$5 < 2\theta < 50$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3701, 2747	3551, 2233
no. of parameters refined	248	235
transmissn factors: max, min	99.93%; 89.36%	99.96%; 74.74%
R^a	0.030	0.027
$R_w{}^b$	0.040	0.039
quality-of-fit indicator^c	1.166	1.167
largest shift/esd, final cycle	0.32	0.31
largest peak, e/Å^3	0.97	0.96

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{observns} - N_{parameters})]^{1/2}$.

The development of this chemistry in the field of triply bonded diosmium complexes is particularly significant in view of the scarcity of such species. Apart from the tetracarboxylates[4-7] the only other complexes are $Os_2(PhCONH)_4X_2$ (X = Cl, Br)[11] and an unusual unsymmetrical complex $Os_2Cl_3(PhNpy)_3$.[12] Hence, the work presented here represents a significant development in two relatively neglected fields. It also makes a contribution to our knowledge of the reactivity of metal cluster compounds toward C–H bonds.[13]

Experimental Section

$Os_2(O_2CCH_3)_4Cl_2$ was prepared by a literature method.[6] All other reagents were purchased from normal commercial suppliers. Solvents were of analytical grade. All manipulations were carried out under a nitrogen atmosphere.

Table II. Positional Parameters and Their Estimated Standard Deviations for 1

atom	*x*	*y*	*z*	*B*,^{a} Å^2
Os(1)	0.07336 (2)	0.22416 (2)	0.27704 (1)	2.245 (5)
Cl(1)	0.2139 (1)	0.2557 (2)	0.3615 (1)	3.71 (4)
P(1)	−0.0531 (1)	0.1300 (1)	0.12992 (9)	2.42 (4)
O(1)	0.4545 (3)	0.1454 (3)	0.6711 (3)	3.2 (1)
O(2)	0.5957 (3)	0.1806 (4)	0.7016 (3)	3.3 (1)
C(1)	0.5294 (5)	0.1290 (5)	0.6701 (4)	3.7 (2)
C(2)	0.5457 (6)	0.0425 (6)	0.6299 (5)	5.6 (2)
C(11)	0.5445 (4)	0.4374 (5)	0.6695 (4)	2.5 (1)
C(12)	0.5608 (5)	0.5206 (6)	0.6372 (4)	3.6 (2)
C(13)	0.3566 (5)	0.4382 (6)	0.3358 (5)	4.4 (2)
C(14)	0.2933 (5)	0.4820 (7)	0.2791 (5)	4.3 (2)
C(15)	0.3108 (5)	0.4350 (6)	0.7471 (4)	3.7 (2)
C(16)	0.3934 (4)	0.3938 (5)	0.7717 (4)	2.6 (1)
C(21)	0.3587 (4)	0.4497 (5)	0.5817 (4)	2.9 (2)
C(22)	0.3473 (5)	0.5322 (6)	0.6181 (4)	3.8 (2)
C(23)	0.7236 (6)	0.4090 (6)	0.4167 (5)	5.1 (2)
C(24)	0.7193 (6)	0.0679 (7)	0.5146 (6)	5.8 (3)
C(25)	0.7313 (5)	0.9852 (7)	0.4780 (5)	5.5 (3)
C(26)	0.3019 (5)	0.4276 (6)	0.5120 (4)	4.0 (2)
C(31)	0.4684 (4)	0.3016 (5)	0.5568 (4)	2.7 (2)
C(32)	0.5432 (5)	0.3233 (6)	0.5377 (4)	3.6 (2)
C(33)	0.5566 (6)	0.2731 (6)	0.4802 (5)	4.8 (2)
C(34)	0.4982 (6)	0.2038 (6)	0.4413 (5)	4.5 (2)
C(35)	0.4245 (5)	0.1826 (6)	0.4616 (4)	4.2 (2)
C(36)	0.4102 (5)	0.2324 (6)	0.5195 (4)	3.4 (2)
O(40)	0.625 (2)	0.206 (2)	0.271 (2)	8.2 (7)*
O(50)	0.500	0.169 (2)	0.250	2.7 (4)*
O(60)	0.531 (1)	0.198 (2)	0.261 (1)	6.8 (6)*
C(40)	0.667 (2)	0.172 (3)	0.327 (2)	7.0 (9)*
C(50)	0.647 (3)	0.154 (4)	0.294 (3)	9 (1)*
C(60)	0.424 (2)	0.243 (2)	0.228 (1)	3.3 (5)*

[a] Starred parameters were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Synthesis of $Os_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2 \cdot CH_3CO_2H$ (1). A 0.10-g quantity of $Os_2(O_2CCH_3)_4Cl_2$ was suspended in a 15-mL volume of acetic acid. Triphenylphosphine, 0.08 g, was added and the mixture refluxed for 1 h, after which time a black solution had formed. The solution was filtered through Celite to remove any unreacted $Os_2(O_2CCH_3)_4Cl_2$ and then layered carefully with 15 mL of diethyl ether. Slow diffusion of the ether resulted in the formation of a homogeneous mass of black crystals. The compound is insoluble in organic solvents. Yield: 0.04 g (24%). Infrared spectrum (Nujol mull, CsI plates): 1520, 1412, 1341, 1311, 1227, 1189, 1157, 1126, 1104, 1089, 1022, 998, 852, 765, 751, 745, 733, 719, 690, 616, 539, 512, 510, 488, 479, 428, 334, 325, 311, 294, 288 cm^{-1}.

Preparation of $Os_2(O_2CC_2H_5)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$. A 0.12-g quantity of $Os_2(O_2CCH_3)_4Cl_2$ was suspended in 15 mL of propionic acid containing triphenylphosphine, 0.10 g. The mixture was warmed to 120 °C for 1 h after which a black solution had formed. This solution was cooled and then filtered through Celite to remove any unreacted starting materials. Careful layering with diethyl ether, 20 mL, and subsequent diffusion gave a homogeneous mass of black crystals. The compound is insoluble in organic solvents. Yield: 0.05 g (26%). Infrared spectrum (Nujol mull, CsI plates): 1559, 1519, 1405, 1302, 1230, 1181, 1154, 1126, 1092, 1084, 1023, 1009, 889, 863, 800, 746, 736, 717, 701, 689, 534, 516, 504, 489, 480, 445, 398, 322, 288, 274, 260 cm^{-1}.

Measurements. Infrared spectra were recorded on a Perkin-Elmer 785 spectrometer.

X-ray Crystallographic Procedures. The structures of **1** and **2** were determined by applying the general procedures described elsewhere.[14,15] A detailed description is available as part of the supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I.

Compound **1** crystallizes in the monoclinic space group *C*2/*c* with half the molecule as the asymmetric unit. The position of the crystallographically unique metal atom was derived from a three-dimensional Patterson map, and the remainder of the structure was

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Table III. Positional Parameters and Their Estimated Standard Deviations for **2**

atom	*x*	*y*	*z*	*B*,[a] Å^2
Os(1)	0.43512 (2)	0.08902 (1)	0.20254 (2)	2.031 (5)
Cl(1)	0.2283 (2)	0.3848 (1)	0.6277 (1)	3.62 (5)
P(1)	0.3258 (2)	0.0103 (1)	0.2775 (1)	2.68 (4)
O(1)	0.4724 (5)	0.1618 (3)	0.3652 (3)	2.8 (1)
O(2)	0.3735 (5)	0.1855 (3)	0.2616 (3)	3.3 (1)
C(1)	0.3984 (7)	0.1978 (4)	0.3293 (5)	2.9 (2)
C(2)	0.3382 (8)	0.2600 (5)	0.3661 (5)	4.4 (2)
C(3)	0.346 (1)	0.2617 (6)	0.4508 (6)	7.1 (3)
C(11)	0.5846 (7)	0.0349 (4)	0.6549 (5)	2.9 (2)
C(12)	0.6193 (9)	0.0972 (5)	0.6160 (6)	4.3 (2)
C(13)	0.5502 (9)	0.1238 (5)	0.5562 (5)	4.6 (2)
C(14)	0.4518 (8)	0.0880 (5)	0.5390 (5)	4.0 (2)
C(15)	0.4176 (7)	0.0261 (4)	0.5795 (4)	3.1 (2)
C(16)	0.5158 (6)	0.0016 (4)	0.3608 (4)	2.3 (1)
C(21)	0.2499 (8)	0.0597 (5)	0.7258 (5)	3.4 (2)
C(22)	0.6409 (8)	0.4507 (6)	0.2984 (5)	4.4 (2)
C(23)	0.5859 (9)	0.3940 (6)	0.3403 (7)	5.7 (3)
C(24)	0.644 (1)	0.3305 (6)	0.3547 (6)	5.9 (3)
C(25)	0.2564 (9)	0.1808 (5)	0.6668 (6)	4.9 (2)
C(26)	0.3122 (8)	0.1245 (5)	0.7087 (5)	3.9 (2)
C(31)	0.2181 (7)	0.0547 (5)	0.3360 (5)	3.6 (2)
C(32)	0.7023 (9)	0.4692 (7)	0.5891 (5)	5.7 (3)
C(33)	0.617 (1)	0.4390 (9)	0.5462 (7)	8.7 (4)
C(34)	0.548 (1)	0.3857 (9)	0.5756 (7)	8.2 (4)
C(35)	0.5633 (9)	0.3612 (9)	0.6504 (8)	8.4 (4)
C(36)	0.6484 (9)	0.3918 (6)	0.6948 (6)	5.2 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table IV. Some Important Bond Distances (Å) in **1** and **2**

	1	**2**
Os(1)-Os(1)	2.271 (1)	2.272 (1)
-Cl(1)	2.372 (2)	2.396 (2)
-P(1)	2.345 (2)	2.353 (2)
-O(1)	2.223 (5)	2.105 (5)
-O(2)	2.105 (5)	2.187 (5)
-C(16)	2.080 (7)	2.045 (7)
P(1)-C(11)	1.797 (7)	1.800 (8)
-C(21)	1.825 (7)	1.820 (8)
-C(31)	1.839 (7)	1.836 (8)
C(11)-C(16)	1.390 (9)	1.398 (11)
O(1)-C(1)	1.249 (9)	1.270 (9)
O(2)-C(1)	1.281 (9)	1.247 (9)
C(1)-C(2)	1.522 (11)	1.500 (11)
C(2)-C(3)		1.491 (12)

obtained by using least-squares refinement and difference Fourier maps. In the final cycles of refinement the presence of a disordered molecule of acetic acid was observed in the unit cell. This molecule was disordered over three sites about the twofold axis at ($^1/_2$, *y*, $^1/_4$). However, attempts to refine this disordered molecule led to unsatisfactory results, namely unreasonable bond lengths and angles for the solvent molecule. In the end, the atoms in question were allowed to refine freely to a chemically imperfect result, in order that the chemically more interesting parts of the structure would not be lost. There were no short intermolecular contacts between this solvent molecule and the diosmium molecule.

Compound **2** crystallizes in the orthorhombic space group *Pbcn*, with half of the molecule in the asymmetric unit. The structure of **2** was developed routinely.

Tables II and III list the atomic coordinates for **1** and **2**, respectively. Table IV contains the important bond lengths for both compounds while the notable bond angles are contained in Table V. Figures 1 and 2 depict **1** and **2**, respectively, and define the atomic labeling scheme.

Results and Discussion

The synthesis of complexes containing a metal-metal bond bridged by an ortho-metalated phenylphosphine ligand has been a longstanding, and somewhat elusive, goal. To the best of our knowledge, all attempts at planned syntheses of such species have resulted in failure. One such compound was recently obtained, namely $Re_2Cl_2(Ph_2Ppy)_2[(C_6H_5)(C_6H_4)Ppy]$,[2,3] which appeared in the course of an investigation into the reactivity of the quadruply bonded dirhenium(III) complexes $(n\text{-}Bu_4N)_2Re_2Cl_8$ and $Re_2Cl_6(PR_3)_2$ with the ligand 2-(diphenylphosphino)pyridine. In this complex the Re$\equiv$Re bond is bridged by two Ph_2Ppy ligands in the conventional manner, i.e., through the phosphorus and nitrogen atoms, while the third bridging ligand exhibits a novel tridentate coordination mode so that it is bound to one metal center through the phosphorus atom and to the other one through the nitrogen

Table V. Some Important Bond Angles (deg) in **1** and **2**

	1	**2**
Os(1)-Os(1)-Cl(1)	161.08 (5)	162.51 (5)
-P(1)	87.54 (4)	87.96 (5)
-O(1)	82.2 (1)	93.4 (1)
-O(2)	94.6 (1)	83.1 (1)
-C(16)	100.7 (2)	101.8 (2)
Cl(1)-Os(1)-P(1)	86.13 (6)	89.03 (7)
-O(1)	80.2 (1)	89.2 (2)
-O(2)	90.2 (1)	79.9 (2)
-C(16)	97.2 (2)	95.3 (2)
P(1)-Os(1)-O(1)	91.8 (1)	177.9 (2)
-O(2)	174.2 (1)	93.0 (2)
-C(16)	90.5 (2)	88.6 (2)
O(1)-Os(1)-O(2)	83.2 (2)	85.6 (2)
-C(16)	176.4 (2)	92.7 (3)
O(2)-Os(1)-C(16)	94.4 (2)	174.9 (3)
Os(1)-O(1)-C(1)	120.6 (5)	114.6 (5)
Os(1)-O(2)-C(1)	112.5 (5)	121.4 (5)
Os(1)-P(1)-C(11)	108.0 (2)	109.2 (3)
Os(1)-C(16)-C(11)	119.9 (5)	121.1 (6)
O(1)-C(1)-O(2)	124.2 (7)	122.9 (7)
P(1)-C(11)-C(16)	114.3 (5)	114.4 (6)

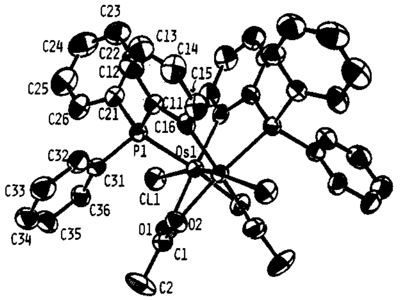

Figure 1. ORTEP drawing of $Os_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ (**1**). Atoms are represented by thermal ellipsoids at the 50% level, and the atomic labeling scheme in one crystallographically independent half of the molecule is defined.

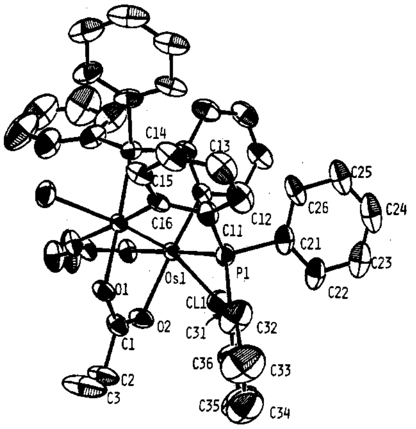

Figure 2. ORTEP drawing of $Os_2(O_2CC_2H_5)_2[(C_6H_5)P(C_6H_4)]_2Cl_2$ (**2**). Atoms are represented by thermal vibration ellipsoids at the 50% level, and the atomic labeling scheme in one crystallographically independent half of the molecule is defined.

and carbon atoms. In view of this unusual geometry it appeared doubtful that this synthesis would be of general applicability.

The discovery of the diosmium compound $Os_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2{\cdot}CH_3CO_2H$ (**1**)[8] occurred in the course of attempts to prepare simple adducts of the $[Os_2(O_2CCH_3)_4]^{2+}$ core. We now report the extension of this synthesis to the propionato analogue, $Os_2(O_2CC_2H_5)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ (**2**) and present the full characterization of each compound, including details of the X-ray structure determination in each case.

When $Os_2(O_2CCH_3)_4Cl_2$ is refluxed in acetic acid containing triphenylphosphine, it rapidly gives rise to a black solution from which a homogeneous black crystalline material can be obtained upon slow addition of diethyl ether. This material has benchtop stability for an indefinite period of time under normal conditions. It is insoluble in all organic solvents tested, nor will it dissolve in acetic acid. Indeed, it neither dissolves in nor reacts with 12 M HCl. The infrared spectrum (Nujol mull) contains bands in the region 1520–1560 cm^{-1}, which may be tentatively assigned to the ortho-metalated ligand.[16] The region 1350–1480 cm^{-1} (HCBD mull) contains several bands making the definite assignment of symmetric and asymmetric $\nu(CO_2)$ stretching frequencies impossible but is consistent with a bridging mode of coordination for the carboxylates. Bands below 300 cm^{-1} are indicative of the retention of the Os–Cl bond. As the identity of the complex could not be unequivocally established from the spectral data, it became not only desirable but imperative to employ X-ray crystallography. In this way the complex was shown to be $Os_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2{\cdot}CH_3CO_2H$, in which there are two bridging phosphine ligands, in each of which ortho metalation has occured at one ring. When the reaction described above was carried out in propionic acid as a solvent, an analogous complex $Os_2(O_2CC_2H_5)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$, in which two acetate bridging ligands have been replaced by propionato groups, was obtained. The infrared spectrum of this complex is similar to that of the acetate, and an X-ray structure determination has confirmed that the molecular geometries of the two compounds are essentially identical in their principal features.

Molecular Structures of $Os_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2{\cdot}CH_3CO_2H$ (1) and $Os_2(O_2CC_2H_5)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ (2). The important details of the two structures are similar, and hence both **1** and **2** will be discussed concurrently. The structure of each compound was solved by three-dimensional X-ray crystallographic procedures. The atomic coordinates and equivalent isotropic thermal vibration parameters for **1** and **2** are listed in Tables II and III, respectively. A diagram of each molecule is shown in Figures 1 and 2. Important bond distances and angles are listed in Tables IV and V. In each case the molecule resides on a twofold axis of symmetry that is a perpendicular bisector of the $Os{\equiv}Os$ bond.

Each structure consists of a dinuclear osmium(III) core bridged in a cisoid arrangement by two carboxylate ligands and by triphenylphosphine molecules in which ortho metalation has occurred at one phenyl ring of each phosphine. One phosphorus atom is bound to each osmium. The axial sites of each molecule are occupied by chloride ions. The geometry about each osmium ion is that of a distorted octahedron, with angles between adjacent atoms in the coordination sphere in the range 82–102°. The osmium–osmium distances at 2.271 (1) and 2.272 (1) Å are the shortest yet to be reported[5-7] for any diosmium compound containing a triple bond between the metal atoms. Surprisingly, this shortening of the $Os{\equiv}Os$ bond does not occur at the expense of increased Os–Cl bond distance. The Os(1)–Cl(1) distances, 2.372 (2) and 2.396 (2) Å for **1** and **2**, respectively, are actually reduced from those reported for the tetracarboxylates.[17] This result is doubly surprising in view of the significant deviation from linearity of the Os(1′)–Os(1)–Cl(1) bonds, 161.08 (5)° in **1** and 162.51 (5)° in **2**, which might also have been expected to weaken the bonds. The Os–O bond distances lie in the range 2.105 (5)–2.223 (5) Å, with the Os–O bonds trans to the phosphorus atoms (2.105 (5) and 2.105 (5) Å) being shorter than those trans to the carbon atoms (2.223 (5) and 2.187 (5) Å). This observation is in accord with the expected order of trans influences for M–P and M–C bonds. The Os–P distances, 2.345 (2) and 2.353 (2) Å, for **1** and **2**, respectively, are not significantly different in the two complexes, nor is the difference very large for the Os–C bonds, 2.080 (7) and 2.045 (7) Å, respectively. The deformation of the octahedral geometry in these complexes can probably be attributed to steric interactions between the non-ortho-metalated phenyl rings of the phosphine and the axial chloride ligands. This interaction together with repulsive contacts between the ortho-metalated ring of one ligand and one of the normal rings of the other one leads to severe distortions of both types of bridging ligand and to the development of significant torsion angles about the metal–metal bond. In **1** these torsion angles are P(1)–Os(1)–Os(1′)–C(16) = 20.3° and O(1)–Os(1′)–Os(1)–O(2) = 17.1°, while for **2** the torsion angles are P(1)–Os(1)–Os(1′)–C(16) = 15.6° and O(1)–Os(1)–Os(1′)–O(2′) = 15.4°.

The tetracarboxylates exhibit significant, temperature-dependent magnetic moments,[5,6] which have been ascribed to an equilibrium between a ground-state singlet electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}$ and an excited-state triplet that is either $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*1}$ or $\sigma^2\pi^4\delta^2\pi^{*2}$. In contrast, the two complexes described here are essentially diamagnetic at 295 K. Compound **1** exhibits an apparent moment of 0.29 μ_B/Os while **2** has an apparent moment of 0.07 μ_B/Os. Since these are based on room-temperature measurements only, they might be indicative of temperature-independent paramagnetism only. There are two factors that might separately or jointly account for the absence of unpaired electrons. The shorter Os–Os distances may result in good enough overlap of the 5d orbitals that a singlet ground state based on the $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration would lie well below triplet states derived from either of the following configurations: $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*1}$ or $\sigma^2\pi^4\delta^2\pi^{*2}$. It is also possible that the severe distortions of the geometry about the metal atoms may result in sufficiently drastic splitting of some of the energy levels as to cause the occurrence of essentially diamagnetic complexes. No calculations to verify these speculations have yet been undertaken.

Finally, although the synthetic route used to prepare $Re_2Cl_3(Ph_2Ppy)_2[(C_6H_5)(C_6H_4)Ppy]$ seems unlikely to be of general applicability, the synthesis described in this paper has already been extended to the preparation of the ortho-metalated dirhodium complexes, $Rh_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2{\cdot}2L$,[8,9] and our investigations into its extension to other multiply bonded transition-metal complexes are continuing.

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Supplementary Material Available: Details of the crystal structure determination and listings of bond angles, anisotropic thermal parameters, bond distances, observed and calculated structure factors, and root-mean-square amplitudes (50 pages). Ordering information is given on any current masthead page.

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(16) Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 797.

(17) 2.417 (3) Å in $Os_2(O_2CC_3H_7)_4Cl_2$[6] to 2.448 (2) Å in $Os_2(O_2CCH_3)_4Cl_2$.[7]