Like **2**, diene **4**–TFA proved to be rather unstable.[5a] Upon standing at room temperature, the olefinic signals in its 300-MHz NMR spectrum (room temperature, pure D_2O) gradually diminished while a new AB pattern emerged at δ 5.9, 6.1 (J = 12.2 Hz), highly characteristic of the Claisen rearrangement product **5** ($t_{1/2}$ = 5 days at 23 °C). Aqueous solutions of **5**–TFA could readily be obtained in this fashion.[9]

p-Aminobenzoate synthase (PABS) is structurally and functionally similar to anthranilate synthase.[10] The native enzyme consists of two subunits designated PABS-I and PABS-II. PABS-I can convert chorismate to PABA in the presence of NH_4^+ but requires an amidotransferase (PABS-II) in order to use glutamine as the nitrogen source. Recent biochemical and immunological studies further indicate that AS and PABS may both have evolved from a common ancestral gene.[11]

PABS-I was obtained from a plasmid-containing strain of *E. coli* BN116 which produced ca. 50-fold greater concentrations of the enzyme.[12] From a fluorescence assay similar to that for AS-I,[5,13] freshly prepared (±)-**4**–TFA was found to be an effective substrate for PABS-I. In the absence of NH_4^+, **4**–TFA was converted to PABA with a V_{max} of 667 (pmol/min)/unit enzyme.[14] With added $(NH_4)_2SO_4$ (33 mM), V_{max} increased to 788 (pmol/min)/unit enzyme (K_M = 16 μM). By comparison, chorismate and NH_4^+ formed PABA with a V_{max} of 52 (pmol/min)/unit enzyme (K_M = 12 μM). These data appear to establish **4** as an intermediate between chorismate and PABA. However, no PABA was formed by the action of the enzyme (plus NH_4^+) on synthetic isochorismic acid ((±)-**3**).[15]

Yields of PABA from **4** never exceeded ca. 10% and product formation was nonlinear with time and enzyme concentration. Controls showed that buffered solutions of **4** were rearranging nonenzymically to **5**, pure samples of which effectively blocked the conversion of either **1** or **4** to PABA. This observation was strickingly reminiscent of the enzymatic chemistry of **2** with AS-I.[5a]

The multistep biosynthesis of L-PAPA from **1** in *Streptomyces venezuelae* is catalyzed by the enzyme system arylamine synthase.[16] Partially purified enzyme preparations[16] were unstable, even in the cold, and required added glutamine to convert chorismate to L-PAPA at pH 8.5 (50 μM Tris-HCl buffer, 20 μM MgCl$_2$, 5 μM NAD$^+$). Gratifyingly, both **4**–TFA and **5**–TFA were readily converted to L-PAPA in the absence of glutamine, although substrate concentration ranges were too low in relation to apparent K_M values to give meaningful kinetic parameters.[17] Controls with boiled and precipitated protein clearly indicated that product formation was enzyme catalyzed. It was noteworthy that aged samples of arylamine synthase continued to form L-

PAPA from **5**–TFA long after all catalytic activity toward **1** was lost. Future efforts to purify the component enzymes and make accurate kinetic measurements on our synthetic intermediates may reveal other fascinating similarities between AA, PABA, and L-PAPA biogenesis.

The Multiply Bonded Octachlorodiosmate(III) Anion [Os₂Cl₈]²⁻. The First Example of a Homoleptic Halide Complex of This Type for the Platinum Metals

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Received April 1, 1985

Central to the development of the field of metal–metal multiple bond chemistry has been the isolation of, structure determination of, study of the bonding in, and reactivity studies of the homoleptic halide anions of the type $[M_2X_8]^{n-}$ (X = Cl, Br, or I).[2-4] These species contain metal–metal bonds of orders 3.5 or 4 and have been encountered previously only for the cases where M = Mo, W, Tc, or Re.[2-4] We can now report an important extension of this chemistry to the platinum metals, through the isolation and structural characterization of the octachlorodiosmate(III) anion, the first example of such a halide complex to contain a metal–metal triple bond. The existence of this novel species is of importance both from the point of view of heralding a new chapter in the expansion of multiple-bond chemistry and in the discovery of a hitherto unknown class of complex halo anions of the platinum metals.

The diosmium(III) carboxylates of the type $Os_2(\mu-O_2CR)_4Cl_2$ (R = CH_3, C_2H_5, n-C_3H_7, or CH_2Cl) constitute an important group of triply bonded complexes that have short Os–Os bonds.[5,6] These species have been described as possessing a ground state that can be represented as having contributions from the $\sigma^2\pi^4\delta^2\delta^{*2}$ and $\sigma^2\pi^4\delta^2\pi^{*1}\delta^{*1}$ configurations,[5,7] although, more recently, a description involving only the triplet state $\sigma^2\pi^4\delta^2\pi^{*1}\delta^{*1}$ has been advocated.[8] Previously, Wilkinson, Stephenson, and co-workers[5]

(8) NMR (methanol-d_4, 300 MHz) δ 6.85 (br s, H-2), 6.50 (d, H-6, J = 9.5 Hz), 5.90 (d, H-5, J = 9.5 Hz), 5.49 (d, one OC=CH, J = 2 Hz), 5.06 (d, H-3, J = 14 Hz), 4.7–4.8 (HOD plus the other OC=CH), 4.30 (d, H-4, J = 14 Hz); IR ν_{max} (KBr) 3430, 2930, 2860, 1680, 1645, 1445 cm^{-1}; UV λ_{max} 272 nm (ϵ 5230, H_2O).

(9) We are attempting to isolate and characterize aminoprephenate **5** in pure form. It would appear that **5** is more stable than prephenic acid, which rapidly decomposes in acid ($t_{1/2}$ = 40 min at 37 °sC, pH 5.8) and can only be isolated as a salt: Zamir, L. O.; Tiberio, R.; Jensen, R. A. *Tetrahedron Lett.* **1983**, *24*, 2815.

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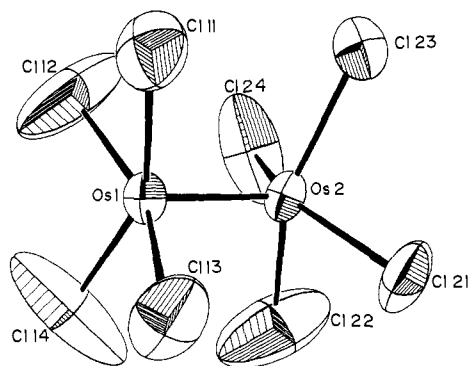
Figure 1. ORTEP view of the $[Os_2Cl_8]^{2-}$ anion. The thermal ellipsoids are drawn at the 50% probability level. There are two disordered orientations of the osmium–osmium bond. The two osmiums shown refined to an occupancy of 63.7 (4)% with an Os–Os distance of 2.195 (2) Å. The other vector is approximately perpendicular to this with a bond distance of 2.170 (3) Å. The Os–Cl bond lengths range from 2.178 (8) to 2.357 (6) Å with a weighted mean of 2.29 (2) Å. The Os–Os–Cl angles average to 103.3 (7)° with a range of 99.2 (3)–105.8 (2)°.

found that the acetate complex $Os_2(O_2CCH_3)_4Cl_2$ reacts with concentrated hydrohalic acids HX (X = Cl or Br) to produce the hexahaloosmate(IV) anions $[OsX_6]^{2-}$. Under strictly nonaqueous conditions we find that such reactions can yield $[Os_2X_8]^{2-}$ (X = Cl or Br). Thus, reflux for 1.5 h of a suspension of $Os_2(O_2CC-H_3)_4Cl_2$ (1.0 g, 1.45 mmol) in 50 mL of anhydrous ethanol that had previously been saturated with HCl gas gave a dark green solution. This was filtered and the filtrate treated with 3 g (5.23 mmol) of (PPN)Cl (PPN = bis(triphenylphosphine)iminium) dissolved in ethanol. This led to the precipitation of the silvery-green complex $(PPN)_2Os_2Cl_8$ in high yield. The product was filtered off, washed with ethanol and diethyl ether, and recrystallized from ethanol/dichloromethane (1:1); yield 85%.[9] The use of HBr(g) in place of HCl(g) gave $(PPN)_2Os_2Br_8$ in 90% yield.[10]

The chloro complex $(PPN)_2Os_2Cl_8$ behaves as a 1:2 electrolyte in acetonitrile ($\Lambda_m = 225$ Ω^{-1} cm^2 mol^{-1} for $c_m = 1 \times 10^{-3}$ M) and its ^1H NMR spectrum (recorded in CD_2Cl_2 from δ +19 to δ −21 ppm) shows only resonances due to the phenyl protons of the PPN cation (δ ca. 7.6). The electronic absorption spectrum of a CH_2Cl_2 solution of this complex (λ_{max} 729 (ϵ 180) and 466 nm (ϵ 130)) in the region 900–350 nm is quite different from the related spectrum of the $[OsCl_6]^{2-}$ anion.[11] Cyclic voltammetric measurements[12] on solutions of $(PPN)_2Os_2Cl_8$ in 0.2 M n-Bu$_4$NPF$_6$–CH$_2$Cl$_2$ show the presence of a one-electron couple at $E_{1/2} = +1.25$ V vs. Ag/AgCl, corresponding to an oxidation, and an irreversible reduction at $E_{p,c} = -0.85$ V vs. Ag/AgCl.[13] For solutions of this complex in 0.1 M n-Bu$_4$NPF$_6$–CH$_3$CN the couple at ca. +1.25 V becomes irreversible ($E_{p,a} = +1.25$ V at $\nu = 200$ mV/s) and the irreversible reduction process shifts to −0.75 V vs. Ag/AgCl.

The structural identity of $(PPN)_2Os_2Cl_8$ has been confirmed by an X-ray crystal structure determination,[14,15] and the structure

of the $[Os_2Cl_8]^{2-}$ anion is shown in Figure 1. Like salts of other $[M_2X_8]^{n-}$ anions, there is a disorder in which the Os–Os unit randomly occupies alternate pairs of faces within a nearly cubic array of halides.[2,3,16,17] The thermal ellipsoids associated with the chlorine atoms are rather large. This suggests either that they exhibit excess thermal vibration or that these atoms do not occupy exact sites in the cell.[18] We hope to resolve this problem in the near future by carrying out structure determinations at low temperatures. The Os–Os distance associated with the major orientation (64% occupancy) is 2.195 (2) Å, while that of the minor orientation (while less accurately determined) is a little shorter than this; such a disparity in M–M bond length has been encountered in the structures of other $[M_2X_8]^{n-}$ species when this type of disorder exists.[2] The remarkable feature of this distance is its shortness relative to distances in other structurally characterized triply bonded diosmium(III) species, where the distances range from 2.27 to 2.39 Å.[3,19,20] Like the ortho-metalated diosmium(III) complexes $Os_2(O_2CR)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ (R = CH$_3$ or C$_2$H$_5$), which also possess short Os–Os bonds (2.27 Å) and are essentially diamagnetic,[20] the $[Os_2Cl_8]^{2-}$ anion may well have a diamagnetic triply bonded $\sigma^2\pi^4\delta^2\delta^{*2}$ ground-state configuration of the type that characterizes complexes that contain the Re_2^{4+} core.[2,3,21,22] Overlap of the osmium 5d orbitals may be optimized in these octahalo derivatives, thereby leading to such a short distance. The other structural feature of special note concerns the rotational conformation that exists within the $[Os_2Cl_8]^{2-}$ anion. In the case of $[Tc_2Cl_8]^{3-}$, $[Re_2X_8]^{2-}$ (X = Cl or Br), $[Mo_2X_8]^{4-}$ (X = Cl or Br), and $[W_2Cl_8]^{4-}$, the two MX$_4$ units are eclipsed with respect to one another.[2,3,16,17] This is of course expected for anions which possess M–M bond orders of 3.5 or 4, since the δ component to the bonding is maximized in the rigorously eclipsed conformation.[2] For a molecule that possesses the triply bonded $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration there is no electronic barrier to rotation and, for $[M_2X_8]^{n-}$ systems where X represents a ligand (such as Cl$^-$) with modest steric requirements, a staggered rotational geometry might be expected. Our isolation of $[Os_2Cl_8]^{2-}$ has provided the first opportunity to test this hypothesis. To our surprise we find that the mean twist angle is only 13.9 (4.5)° within the Os(1)–Os(2) unit and 10.3 (6.2)° for Os(3)–Os(4). The large standard deviation suggests that there is no preferred conformation and that crystal packing may control the exact angle. While the latter explanation may well suffice, it is also appropriate to remember that plots of X$\cdots$X van der Waals energies against internuclear distances for $[M_2X_8]^{n-}$ species indicate[23] that for X = Cl we may not yet be in a region where repulsion is important and, by implication, a staggered geometry

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(10) This procedure is appropriate for the synthesis of other salts; for example, the use of (Ph$_4$As)Cl or (n-Bu$_4$N)Br in place of (PPN)Cl gives (Ph$_4$As)$_2$Os$_2$Cl$_8$ and (n-Bu$_4$N)$_2$Os$_2$Cl$_8$, respectively, when $Os_2(O_2CC_3H_7)_4Cl_2$ is used as the starting material. The bromide analogue (n-Bu$_4$N)$_2$Os$_2$Br$_8$ has also been prepared by a related procedure.

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(14) Crystal data (at 22 °C) for (PPN)$_2$Os$_2$Cl$_8$: $a = 23.142$ (5) Å, $b = 13.552$ (3) Å, $c = 23.201$ (3) Å, $\beta = 107.61$ (1)°, $Z = 4$, $\rho_{calcd} = 1.67$ g/cm^3, space group $P2_1/c$. The structure was refined using standard procedures[15] to $R = 0.070$ and $R_w = 0.073$ based on 4304 reflections with $I > 3\sigma(I)$ (9515 unique reflections collected by using Mo Kα, 2.5° < 2θ < 45°).

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Studies on the reaction chemistry of (PPN)$_2$Os$_2$Cl$_8$ have been carried out. Its reaction with refluxing 10:1 acetic acid/acetic anhydride mixtures for 12 h regenerates Os$_2$(O$_2$CCH$_3$)$_4$Cl$_2$ in 71% yield. Monodentate phosphines react almost instantaneously with (PPN)$_2$Os$_2$Cl$_8$ in ethanol at room temperature to produce the mononuclear *trans*-[OsCl$_4$(PR$_3$)$_2$]$^-$ anions in essentially quantitative yield (PR$_3$ = PMe$_3$, PEt$_3$, P-*n*-Pr$_3$, P-*n*-Bu$_3$, PMePh$_2$, PMe$_2$Ph, and PPh$_3$). These anions react further with excess phosphine in refluxing ethanol (4–6 h) to produce the yellow osmium(II) complexes OsCl$_2$(PR$_3$)$_4$ (PR$_3$ = PMe$_3$ or PMe$_2$Ph) or [Os$_2$(μ-Cl)$_3$(PR$_3$)$_6$]$^+$ (PR$_3$ = PEt$_3$, P-*n*-Pr$_3$, P-*n*-Bu$_3$, or PMePh$_2$; isolated as their PF$_6^-$ salts)[24] in yields up to 80%. These metal–metal bond cleavage reactions, as well as reactions that preserve the Os–Os multiple bond, are currently being explored. Full details will be reported in due course, along with complete details of the structural, spectroscopic, and electrochemical characterization of the triply bonded [Os$_2$X$_8$]$^{2-}$ anions.

Supplementary Material Available: Listing of atomic coordinates for the nongroup atoms and the rigid group atoms and anisotropic thermal parameters for the nongroup atoms (4 pages). Ordering information is given on any current masthead page.

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(24) This appears to be an excellent general procedure for preparing complexes of the type [Os$_2$(μ-Cl)$_3$(PR$_3$)$_6$]X, although another procedure is available.[25]

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An Example of Cyclometalation by Oxidative Addition: A Platinum(IV)–Tetramethylthiourea Complex Containing a Carbon–Metal σ Bond. Crystal Structure

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Received April 19, 1985

Thioamides and thioureas react with metals in high oxidation states not only as complexing agents but also as reductants.[3,4,6]

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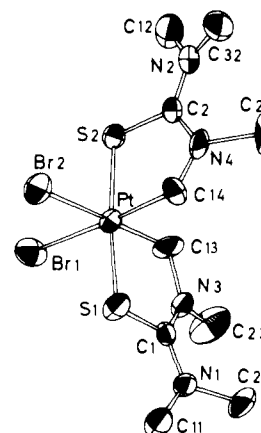

Figure 1. ORTEP illustration of the structure of the cyclometalated Pt-(tmtu*)$_2$Br$_2$ complex.

Table I. Selected Geometric Features of the Complex

distance, Å		angle, deg	
		Group I	
PtS(1)	2.313 (2)	Pt–S(1)–C(1)	98.9 (3)
S(1)C(1)	1.730 (7)	S(1)–C(1)–N(3)	116.6 (6)
C(1)N(3)	1.358 (10)	C(1)–N(3)–C(13)	122.1 (6)
N(3)C(13)	1.367 (10)	N(3)–C(13)–Pt	116.0 (5)
C(13)Pt	2.031 (7)	C(13)–Pt–S(1)	83.6 (2)
C(1)N(1)	1.326 (10)		
		Group II	
PtS(2)	2.313 (2)	Pt–S(2)–C(2)	98.4 (3)
S(2)C(2)	1.727 (8)	S(2)–C(2)–N(4)	119.8 (6)
C(2)N(4)	1.334 (10)	C(2)–N(4)–C(14)	126.6 (8)
N(4)C(14)	1.475 (10)	N(4)–C(14)–Pt	113.3 (5)
C(14)Pt	2.045 (9)	C(14)–Pt–S(2)	86.2 (2)
C(2)N(2)	1.335 (10)		

To explain this reaction, it has been proposed that the thioamide reacts in its thiol form which is oxidized to a disulfide. N-substituted derivatives that do not permit thiol–thione tautomerism are able to complex metal ions in their higher oxidation state. For example, a copper (II) complex with tetramethylthiourea (tmtu) has been isolated[5] while unsubstituted thioureas form only copper(I) complexes.

We report here the unusual behavior of tetramethylthiourea which reacts with the bridged dimer [Pt(tmtu)Br$_2$]$_2$ as an oxidizing agent to form Pt(tmtu*)$_2$Br$_2$, an octahedral Pt(IV) complex containing two metal–carbon σ bonds (tmtu* denotes the deprotonated form of tmtu).

This complex was prepared by adding tetramethylthiourea to aqueous K$_2$PtBr$_4$ in a 2/1 molar ratio. The product of the first step of this reaction has previously been identified as an orange dimer complex, [Pt(tmtu)Br$_2$]$_2$, in which the ligand acts as a bridge between the two platinum atoms.[7] Adding more ligand redissolves this complex giving a pale yellow solution which yields, upon evaporation, pale yellow crystals suitable for X-ray study.

The compound was structurally characterized by a single-crystal X-ray diffration study.[8] An ORTEP illustration of this compound is presented in Figure 1 and selected bond lengths and angles are reported in Table I. As shown in this view of the molecule, the tmtu* ligands are bonded to the platinum atom through a sulfur

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(8) The compounds crystallizes in the monoclinic space group P2$_1$ with the following cell parameters: a = 10.405 (4) Å, b = 12.418 (1) Å, c = 14.141 (8) Å, β = 108.33 (4)°, V = 1734.4 Å^3, Z = 2. The 3213 unique reflections are collected on an Enraf-Nonius CaD4 diffractometer using Mo Kα radiation. The structure was solved using the Patterson heavy-atom method which revealed the position of the Pt atom. The remaining atoms were located by successive Fourier difference syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. R_F = 0.051 and R_{wF} = 0.064. Full details will be reported at a later date.