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A New Class of Reactive, Transition Metal–Metal Doubly-bonded Organodimetallic Complexes: Synthesis, Structure, and Reactivity of $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}X)_4$ (R = Me, Et; X = Cl, Br)

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Reduction of $(\eta\text{-}C_5Me_4R)TaX_4$ (R = Me, Et; X = Cl, Br) with two equivalents of sodium amalgam in toluene affords the reactive tantalum–tantalum doubly-bonded species $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}X)_4$ in 70% yield; the solid-state structure of $(C_5Me_5)_2Ta_2(\mu\text{-}Br)_4$ consists of a Ta=Ta double bond, 2.748(2) Å in length, bridged symmetrically by four bromide ligands.

The study of the synthesis and structure of transition metal–metal multiple bonds is one of the important research areas in contemporary inorganic chemistry,[1] and there is increasing interest in the reactivity of these novel species. The most prevalent metal–metal bonded dinuclear complexes are those with bridged or unbridged metal–metal quadruple or triple bonds, while species with metal–metal double bonds are rare.[1] Metal–metal bonded dinuclear complexes of the early transition metals are also comparatively rare,[1,2] particularly for organodimetallic complexes. Here we report the synthesis of a novel organodimetallic, early transition metal–metal doubly-bonded complex which exhibits a rich and diverse chemistry.[3]

The mononuclear tantalum compound $(\eta\text{-}C_5Me_4R)TaX_4$ (1; R = Me or Et; X = Cl, Br) is readily reduced by sodium amalgam (2 equiv.) in toluene with efficient stirring to afford the ditantalum species $(\eta\text{-}C_5Me_4R)_2Ta_2X_4$ (2) in 70—75% isolated yield (Scheme 1). Analytical and spectroscopic data†

are consistent with their formulation as organoditantalum(III) complexes, and the mass spectra exhibit parent ions consistent with tetrahalo dimers. The u.v.–visible spectrum of forest-green (2) in diethyl ether shows several absorption maxima, with low-energy transitions for (2a) at 726 nm (ε = 3030 l mol^{-1} cm^{-1}) and, for (2c) at 794 nm (ε = 2925 l mol^{-1} cm^{-1}); these transitions are consistent in frequency and molar absorptivity with a metal–metal bond-associated transition but display the opposite trend in band shifting with halide substitution of metal–metal localized electronic transitions in unbridged, quadruply-bonded metal–metal complexes.[4] The i.r. and ^{1}H n.m.r. spectra of isolated (2) show the absence of bridging or terminal hydride ligands from either intramolecular peralkylcyclopentadienyl ligand metallation or intermolecular solvent C–H bond activation. The ^{1}H n.m.r. spectra of these diamagnetic species are unusual in that the ring Me protons are found significantly downfield [in C_6D_6: (2a), δ 2.41; (2c) 2.57] of the usual region (δ 1.9—2.3)† for high valent mono(permethylcyclopentadienyl) complexes;[5] this downfield chemical shift may be the result of magnetic anisotropy associated with a Ta–Ta double bond and not the low-valent[5a] nature of (2). The ^{1}H n.m.r. spectra of (2c) and

‡ The C$_5$Me$_5$ ^{1}H n.m.r. chemical shifts in C_6D_6 for the Ta^V precursors (C$_5$Me$_5$)TaBr$_4$ and (C$_5$Me$_5$)TaCl$_4$ are δ 2.26 and 2.15, respectively.
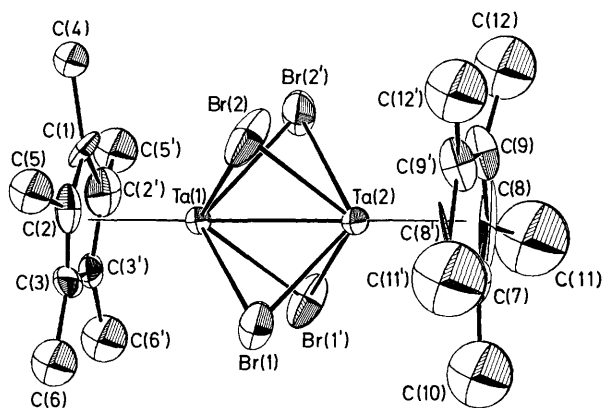
Figure 1: ORTEP diagram for $(C_5Me_5)_2Ta_2(\mu\text{-Br})_4$ (**2c**). A crystallographically-imposed mirror plane lies approximately in the plane of the Figure, with symmetrically-related atoms designated by a prime. Key bond distances [Å; standard deviation = (*) for carbon atoms at fixed positions] and angles (°) not specified in text: Ta(1)–Br(1) 2.622(4), Ta(1)–Br(2) 2.621(5), Ta(2)–Br(1) 2.589(5), Ta(2)–Br(2) 2.631(6), Ta(1)–C(1) 2.29(4), Ta(1)–C(2) 2.28(5), Ta(1)–C(3) 2.43(*), Ta(2)–C(7) 2.40(*), Ta(2)–C(8) 2.31(*), Ta(2)–C(9) 2.40(*), C(1)–C(2) 1.43(7), C(2)–C(3) 1.42(*), C(3)–C(3') 1.43(*), C(7)–C(8) 1.54(*), C(8)–C(9) 1.36(*), C(9)–C(9') 1.46(*); Br(1)–Ta(1)–Br(1') 74.1(3), Br(1)–Ta(1)–Br(2) 73.9(2), Br(2)–Ta(1)–Br(2') 73.2(5), Br(1)–Ta(2)–Br(1') 75.2(3), Br(1)–Ta(2)–Br(2) 74.3(2), Br(2)–Ta(2)–Br(2') 72.9(4).

(**2d**) show no change in signal multiplicity or line shape to $-70\,°C$ $(C_6D_5CD_3)$, and spectra of the C_5Me_4Et analogues (**2b**) and (**2d**) show the presence of a mirror plane through the equivalent cyclopentadienyl groups and thus a symmetric solution structure.

$$2(C_5Me_4R)TaX_4 + 4Na \longrightarrow (C_5Me_4R)_2Ta_2X_4$$
$$\quad\quad (1) \quad\quad\quad\quad\quad\quad\quad\quad (2)$$
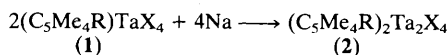
Scheme 1. a; X = Cl, R = Me. **b**; X = Cl, R = Et. **c**; X = Br, R = Me. **d**; X = Br, R = Et.

A single crystal X-ray diffraction study§ was undertaken to determine the nature of the tantalum–tantalum interaction and the number of bridging (either two[2,6,7] or four[2,8]) and terminal halide ligands present in the solid-state structure. The latter possibility was shown to be the correct one for (**2c**), as the resulting molecular structure (Figure 1) consists of four bromine atoms bridging a ditantalum centre with a Ta–Ta distance [2.748(2) Å] consistent with a tantalum–tantalum double bond.[2] The acute Ta–Br–Ta angles [av. 63.3(1)°] and obtuse Br–Ta–Br angles for nonadjacent bromides [av.
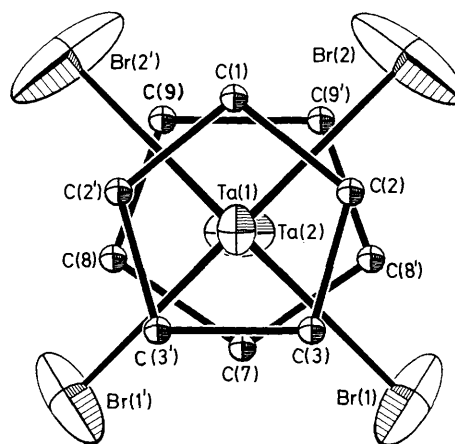
§ *Crystal data* for (**2c**): $C_{20}H_{30}Br_4Ta_2$, $M = 951.54$, monoclinic, space group $P2_1m$, $a = 8.296(5)$, $b = 14.338(6)$, $c = 10.829(10)$ Å, $\beta = 106.11(6)°$, $U = 1237.5$ Å³, $Z = 2$, $D_c = 2.55$ g cm⁻³, $\lambda(Mo\text{-}K_\alpha) = 0.71073$ Å, $\mu(Mo\text{-}K_\alpha) = 151.4$ cm⁻¹. Intensity data from two quadrants were collected on an Enraf–Nonius CAD-4 diffractometer, 2271 independent reflections after averaging $(2 \leqslant 2\theta \leqslant 50°)$, 973 observed with $I \geqslant 3\sigma(I)$. The data were corrected for Lorentz, polarization, and absorption (empirical absorption method) effects and the structure was solved with a combination of direct (MULTAN) and difference methods using the Enraf-Nonius SDP-VAX program package. Anisotropic least-squares refinement on all atoms except the C_5Me_5 methyl carbons (which were refined isotropically), C(3) and the C_5Me_5 carbon atoms on Ta(2) (placed in fixed positions and not refined), and the methyl protons (calculated and placed in fixed positions) gave final agreement factors of $R = 0.072$ and $R_w = 0.097$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Figure 2: ORTEP diagram of $(C_5Me_5)_2Ta_2(\mu\text{-Br})_4$ (**2c**) viewed approximately down the Ta(1)–Ta(2) axis. The crystallographically-imposed mirror plane, perpendicular to the plane of the Figure, passes through C(1), Ta(1), Ta(2), and C(7). Methyl carbons are omitted and the ring carbon thermal ellipsoids are reduced in size for clarity.

116.6(2)°] are in accord with a strong metal–metal interaction, and the double bond formulation is consistent with the observed solution diamagnetism of these d^2–d^2 dimers. The centroids of the C_5Me_5 groups are essentially colinear with the Ta=Ta bond axis (Figure 2), with the C_5Me_5 centroid–Ta(1) and C_5Me_5 centroid–Ta(2) vectors bent 8.7 and 3.3°, respectively, from the metal–metal bond axis. The somewhat lower accuracy in the determination of the carbon positions in the C_5Me_5 group attached to Ta(2), particularly C(8), could not be resolved by either slower scan rates at room temperature or repeated low-temperature data collection attempts at -50, -100, and $-120\,°C$ (because of either a phase change or microscopic crystal cracking at low temperature), but the significant structural results are unchanged. A relatively unreactive diniobium[9] analogue of (**2**), prepared by hydrogenolysis of $(C_5Me_5)NbMe_2Cl_2$, and a reactive divanadium[10] analogue, prepared by reductive dimerization, are of unknown but possibly similar molecular structure.

A qualitative M.O. ordering for these ditantalum species, with the z-axis along the tantalum–tantalum bond and the μ-halides in the xz and yz planes, utilizes the d_{z^2} in metal–metal σ-bonding and the d_{xy} in δ-bonding; the d_{xz}, d_{yz}, and $d_{x^2 - y^2}$ orbitals are used in μ-halide bonding. This orbital overlap implies a $\sigma^2\delta^2$ configuration for the double bond, but metal–metal bond order assignments are problematic in cases with bridging ligands[1a] because of extensive ligand orbital mixing into the relevant dinuclear molecular orbitals, so more sophisticated calculations are necessary to determine the orbital ordering and constitution. The isostructural, diamagnetic, d^3–d^3 organodimolybdenum(III) compound[8a,b] $[\eta\text{-}C_5H_4(CHMe_2)]_2Mo_2(\mu\text{-Cl})_4$ has a metal–metal single bond and, presumably, a $\sigma^2\delta^2\delta^{*2}$ electronic configuration.

The reactivity exhibited by (**2**) with a variety of reagents is also consistent with the tantalum–tantalum double bond formulation. Addition of H_2 (25 °C, 410 kPa) results in a rare[11] example of dihydrogen oxidative addition across the ditantalum centre and formation of a $Ta_2(\mu\text{-H})_2$ species. For X = Cl, the dihydrogen addition product is the known $(C_5Me_4R)_2Ta_2(\mu\text{-H})_2Cl_4$,[12] while in the case of X = Br a mixture of products, believed to be $(C_5Me_4R)_2Ta_2(\mu\text{-}H)_xBr_{6-x}$ on the basis of i.r. and ¹H n.m.r. spectroscopy, are obtained. Compound (**2**) reacts irreversibly with halogenated solvents such as CH_2Cl_2 to yield the mononuclear Ta^V precursors (**1**). Olefination reactions[3] result in either mononuclear alkene complexes or dinuclear μ-vinyl(μ-hydride)

complexes from intermolecular vinylic C–H bond activation. But-2-yne yields the mononuclear product $(C_5Me_5)Ta(MeC\equiv CMe)Br_2$, the bromide analogue of a known alkyne complex.[13] Trialkylphosphines, such as PMe_3, result in metal–metal bond cleavage and a variety of products, including $(C_5Me_4R)Ta(PMe_3)X_3$. By contrast, the reported $(C_5Me_5)_2Nb_2Cl_4$[9] does not react with H_2 or alkenes. We are continuing to explore the reactivity of these new organoditantalum doubly-bonded species.

References

1 F. A. Cotton and R. A. Walton, 'Multiple Bonds Between Metal Atoms,' Wiley, New York, 1982; F. A. Cotton and R. A. Walton, in 'Structure and Bonding,' eds. M. J. Clarke, *et al.*, Springer-Verlag, Berlin, 1985, vol. 62; M. H. Chisholm, in 'Reactivity of Metal-Metal Bonds,' ed. M. H. Chisholm, ACS Symposium Series 155, American Chemical Society, Washington, DC, 1981, pp. 17—39.

2 L. Messerle, *Chem. Rev.*, in the press.

3 C. Ting and L. Messerle, *J. Am. Chem. Soc.*, 1987, **109**, 6506.

4 M. D. Hopkins, W. P. Schaefer, M. J. Bronikowski, W. H. Woodruff, V. M. Miskowski, R. F. Dallinger, and H. B. Gray, *J. Am. Chem. Soc.* 1987, **109**, 408.

5 (a) J. M. Mayer and J. E. Bercaw, *J. Am. Chem. Soc.*, 1982, **104**, 2157; (b) L. Messerle, P. Jennische, R. R. Schrock, and G. Stucky, *ibid.*, 1980, **102**, 6744; (c) C. D. Wood, S. J. McLain, and R. R. Schrock, *ibid.*, 1979, **101**, 3210.

6 M. R. Churchill, S. A. Julis, and F. J. Rotella, *Inorg. Chem.*, 1977, **16**, 1137.

7 F. H. Kohler, R. de Cao, K. Ackermann, and J. Sedlmair, *Z. Naturforsch., Teil B*, 1983, **38**, 1406.

8 (a) M. L. H. Green, A. Izquierdo, J. J. Martin-Polo, V. S. B. Mtetwa, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1983, 538; (b) P. D. Grebenik, M. L. H. Green, A. Izquierdo, V. S. B. Mtetwa, and K. Prout, *J. Chem. Soc., Dalton Trans.*, 1987, 9; (c) A. P. Sattelberger, R. B. Wilson, and J. C. Huffman, *J. Am. Chem. Soc.*, 1980, **102**, 7111.

9 P. A. Belmonte, F. G. N. Cloke, K. H. Theopold, and R. R. Schrock, *Inorg. Chem.*, 1984, **23**, 2365.

10 M. S. Hammer, C. Ting, and L. Messerle, unpublished results.

11 A. P. Sattelberger, R. B. Wilson, and J. C. Huffman, *Inorg. Chem.*, 1982, **21**, 4179; A. J. Scioly, M. L. Luetkens, R. B. Wilson, J. C. Huffman, and A. P. Sattelberger, *Polyhedron*, 1987, **6**, 741.

12 P. A. Belmonte, R. R. Schrock, and C. S. Day, *J. Am. Chem. Soc.*, 1982, **104**, 3082.

13 G. Smith, R. R. Schrock, M. R. Churchill, and W. J. Youngs, *Inorg. Chem.*, 1981, **20**, 387.