Susceptibility of the Tungsten–Tungsten Quadruple Bond to Oxidative Addition. Structure of an HCl Adduct

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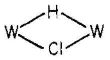
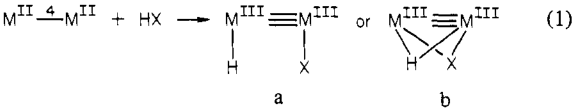
Abstract: The complex $W_2[\mu\text{-H}][\mu\text{-Cl}]Cl_2[P(n\text{-Bu})_3]_2[C_6H_5CO_2]_2$, **1**, has been prepared from the reaction between 2 equiv of benzoic acid and 1 equiv of $W_2Cl_4[P(n\text{-Bu})_3]_4$ and characterized by a single-crystal X-ray crystallographic study and NMR spectroscopy. Crystals of **1** belong to the space group $P2_12_12_1$ with $a = 22.242$ (3) Å, $b = 25.516$ (3) Å, $c = 16.467$ (4) Å, $V = 9345$ (5) Å^3, and $Z = 8$. There are two crystallographically independent molecules per asymmetric unit, and the structure has been refined to $R_1 = 0.043$ and $R_2 = 0.054$. The structures of the two independent dinuclear molecules are essentially identical, each consisting of two distorted octahedra sharing an edge. There is a central $W(O_2CC_6H_5)_2W$ unit that is planar except for the phenyl groups, and the hydrogen and chlorine atoms are placed above and below this plane forming a



plane approximately perpendicular to the former. Terminal phosphine and chlorine ligands on each tungsten atom complete the distorted octahedra. The approximate symmetry is C_s, with the approximate plane of symmetry containing the bridging ligands. The tungsten–tungsten distances are 2.423 (1) and 2.435 (1) Å, and the metal–metal bond is of formal order 3. This molecule provides the first structurally confirmed example of oxidative addition, in this case of HCl, to a tungsten–tungsten quadruply bonded dinuclear species. The bridging hydrogen atom was found in each molecule and its presence verified by ^{31}P and ^1H NMR spectra. The ^1H resonance is at 1.92 ppm, and the couplings to phosphorus atoms are $^2J_{H\text{-cisP}} = 31$ Hz and $^2J_{H\text{-transP}} = 63$ Hz.

Methods for the synthesis of compounds containing tungsten–tungsten quadruple bonds have been developed only slowly and with difficulty.[1-3] In many, if not most, cases those that work for molybdenum are unsuccessful for tungsten. In sharp contrast, the chemistry of tungsten–tungsten triple bonds is as straightforward as, and generally analogous to, that of molybdenum–molybdenum triple bonds. In a general sense, this situation can be traced to the fact that the δ component of the $W\overset{4}{-}W$ bond is weaker and more easily broken than the δ component of the $Mo\overset{4}{-}Mo$ bond,[4] whereas in both cases the σ and π components are strong and about equally resistent to chemical attack.

In attempting to understand in a chemically mechanistic way the relative instability of the $W\overset{4}{-}W$ bond, we have found that susceptibility to acids, probably by way of initial oxidative addition, eq 1, is a recurrent and presumably general property of the $W\overset{4}{-}W$ bonds. This type of reaction is well established for $Mo\overset{4}{-}Mo$ bonds, and the structures of the products are known.[5] For molybdenum, however, the process appears to be easily reversible, as first evidenced by the preparation[6] of many quadruply bonded Mo_2^{4+} complexes from $[Mo_2Cl_8H]^{3-}$.



$$M^{II}\overset{4}{-}M^{II} + HX \longrightarrow \underset{\mathrm{H}}{M^{III}}\equiv\underset{\mathrm{X}}{M^{III}} \quad \text{or} \quad M^{III}\equiv M^{III}\ (\mu\text{-H})(\mu\text{-X}) \qquad (1)$$

a b

With the $W\overset{4}{-}W$ bond, however, oxidative addition appears to be (a) thermodynamically, and perhaps also kinetically, more favored, and (b) irreversible, perhaps because the initial products readily undergo further irreversible reactions. The best-known illustration of this is the fact that under all conditions that are known to have been tried, $W(CO)_6$ reacts with acetic acid or other carboxylic acids to give *only* the trinuclear tungsten(IV) species $[W_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ without any indication that $W_2(O_2CR)_4$ compounds are ever formed,[7] whereas $Mo(CO)_6$ gives rise to $Mo_2(O_2CR)_4$ compounds. Other examples of the way in which acidic media destroy $W\overset{4}{-}W$ bonds are provided by the reaction[8] of W_2(2-oxo-6-methylpyridinato)$_4$ with HCl to give $[W_2Cl_9]^{3-}$, perhaps via an intermediate $[W_2Cl_8H]^{3-}$ ion[2] that reacts with HCl to give H_2, and by the reaction of $W_2Cl_4[P(C_4H_9)_3]_4$ with acetic acid[9] to give no $W_2(O_2CCH_3)_4$ but rather a trinuclear tungsten(IV) compound.[10] Only by treating $W_2Cl_4(THF)_4$ with $Na(O_2CCF_3)$ under nonacidic conditions was the preparation of a $W_2(O_2CR)_4$ compound finally achieved.[2]

Although the above explanation of the sensitivity of $W\overset{4}{-}W$ bonds toward acids is consistent with a variety of circumstantial evidence, there has not as yet been reported any direct evidence for the existence of an oxidative addition product of type a or b in eq 1. Sattelberger[2] has recently suggested, with some evidence, that he may have obtained $Cs_3[W_2Cl_9H]$, but provided no proof of its identity. We report here the preparation and structural characterization of $W_2(O_2CPh)_2Cl_3(H)[P(n\text{-Bu})_3]_2$, the expected product of oxidative addition of HCl to the quadruply bonded molecule $W_2(O_2CPh)_2Cl_2[P(n\text{-Bu})_3]_2$, which has well-characterized molybdenum analogues.[11,12] In each of the two crystallographically distinct molecules, the bridging hydrogen atoms were located in difference electron density maps.

Experimental Section

All chemical operations were conducted in an atmosphere of dry argon by using standard Schlenk techniques. Benzene was dried over a sodi-

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Table I. Crystallographic Data and Data Collection Procedures

formula	$W_2Cl_3P_2O_4C_{38}H_{65}$
M_r	1121.95
space group	$P2_12_12_1$
a, Å	22.242 (3)
b, Å	25.516 (3)
c, Å	16.467 (4)
V, Å^3	9345 (5)
Z	8
ρ_C, g/cm^3	1.595
μ(Cu Kα), cm^{-1}	116.2
crystal size, mm	0.20 × 0.20 × 0.15
diffractometer	Syntex P$\bar{1}$
radiation; graphite monochromated	Cu Kα (λ_α = 1.54184 Å)
collection range	$+h, +k, +l$; $0 < 2\theta < 115°$
no. of γ scans	9
transmission factors, min	0.65
max	1.00
av	0.83
maximum counting time, s	120
X-ray exposure time, h	350
no. of unique data	6862
no. of data with $I \geq 3\sigma(I)$	4636
ρ	0.07
no. of variables	784
R_1	0.043
R_2	0.054
esd	1.069
largest shift[a]	0.55
largest peak[b]	0.58

[a] Largest Δ_i/σ_i ratio in final refinement cycle. [b] Largest peak in a final difference Fourier, e/Å^3.

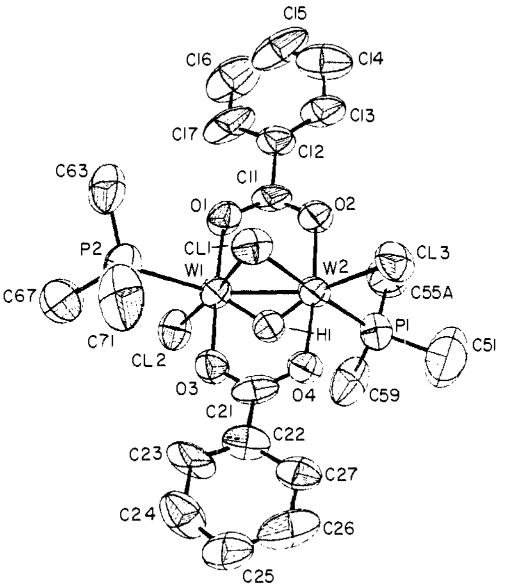

Figure 1. ORTEP diagram of molecule 1 with thermal ellipsoids at the 40% probability level.

um-potassium amalgam and methanol over magnesium metal; the solvents were purged with nitrogen and distilled immediately before use. $W_2Cl_4[P(n\text{-}Bu)_3]_4$ was prepared by the method of Sharp and Schrock.[9]

Preparation of Crystalline $W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2[P(n\text{-}Bu)_3]_2(C_6H_5CO_2)_2$. Thrice chromatographed (hexane on Florisil) $W_2Cl_4[P(n\text{-}Bu)_3]_4$ (1.32 g, 1 mmol) and benzoic acid (0.244 g, 2 mmol) were placed in an air-free three-neck flask fitted with a condenser. Benzene (15 mL) was added and the stirred mixture heated to reflux for 5 min. After cooling, 12 mL of benzene was removed by distillation and the reaction mixture cooled to −15 °C. Addition of cold (−15 °C) methanol (10 mL) and vigorous stirring resulted in precipitation of a brick-red crystalline material (0.25 g) whose empirical formula was shown to be not that of the expected $W_2Cl_2[P(n\text{-}Bu)_3]_2(C_6H_5CO_2)_2$ but of its hydrogen chloride oxidative-addition product $W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2[P(n\text{-}Bu)_3]_2(C_6H_5CO_2)_2$. After filtration, recrystallization from warm methanol afforded small, slightly air-sensitive crystals of which a few were found to be suitable for an X-ray structure analysis.

NMR Spectra. ^1H (C_6D_6; reference Me_4Si): 0.8 (m, CH_3), 1.2 (m), 1.46 (m), 1.75 (m, CH_2), 1.92 (dd with J = 31, 63 Hz, μ-H), 7.2 (m), 7.4 (m), 8.62 (m, C_6H_4). $^{31}P\{^1H\}$ (C_6D_6; reference 85% H_3PO_4): 12.0 (d, J = 21 Hz), −8.0 (d, J = 21 Hz).

X-ray Structure Determination. A single well-formed, regularly shaped crystal was sealed in a capillary with degassed epoxy cement. Preliminary data collection on an Enraf-Nonius CAD-4 automated diffractometer using Mo Kα radiation indicated a problem with poor diffraction at $2\theta > 30°$, and we chose to collect data using Cu Kα radiation on a Syntex P$\bar{1}$ diffractometer. Despite the increased absorption of Cu radiation by tungsten-containing crystals, the greater intensity of reflections and considerably superior quality of the data resulted in a much-improved structure.

Least-squares refinement of 15 intense reflections in the range $20° \leq 2\theta \leq 30°$ gave an orientation matrix for calculation of setting angles and cell parameters. An orthorhombic cell, later shown by systematic absences and successful refinement to belong to the acentric space group $P2_12_12_1$, was used. The cell parameters are presented in Table I. A total of 6862 unique reflections were measured, of which 4636 had intensity I exceeding $3\sigma(I)$ and were considered observed. The data set was corrected for Lorentz and polarization effects, and an empirical absorption correction based on the ψ-scan method (ψ = 0–360° every 10° for χ values near 90°) was made.

The structure was solved by Patterson and Fourier methods and refined[13] by full-matrix least squares. A Patterson synthesis provided the four independent tungsten positions consistent with the expected value of $Z = 8$ on the basis of the unit-cell volume. Three cycles of isotropic refinement produced values of $R_1 = 0.237$ and $R_2 = 0.301$, where R_i are defined as

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$$

As a result of subsequent difference Fourier syntheses, all non-hydrogen atoms were located, but some of the n-butyl chains showed signs of disorder. Secondary positions at C(55), C(78), and C(87) were included with occupancies of 0.4, 0.4, and 0.25, respectively, and the atoms C(57) and C(58) were included at fixed positions. At this stage the hydrogen atom position in each molecule was readily identified; however, H(1) was somewhat off center, with W(1)–H(1) = 1.82 Å and W(2)–H(1) = 1.29 Å. Refinement of this atom position afforded a more reasonable location with W(1)–H(1) = 1.534 (1) Å and W(2)–H(1) = 1.447 (1) Å. Positional and thermal parameters for H(1) and H(2) were then fixed and their contributions included in F_c values. With inclusion of anisotropic thermal parameters for well-behaved atoms, the refinement gave convergence at $R_1 = 0.0435$ and $R_2 = 0.055$. The other enantiomorph of the structure was then tested. It gave $R_1 = 0.0427$ and $R_2 = 0.054$ and was retained as the marginally better model. The error in an observation of unit weight was 1.07, and the largest shift/error ratio in the final cycle was 0.55. A final difference synthesis exhibited peaks as high as 0.58 e/Å^3 in the region of the less-well-behaved butyl chains, but attempts at additional refinement of the disorder were unsuccessful. Final positional parameters are given in Table II. A table of thermal parameters is available as supplementary material, as are values of observed and calculated structure factor amplitudes.

Results and Discussion

The asymmetric unit consists of two $W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2[P(n\text{-}Bu)_3]_2(C_6H_5CO)_2$ molecules, neither of which is subject to any crystallographically imposed symmetry. Virtual C_s symmetry does exist, however, for each molecule, with the $(Cl)(PR_3)W(\mu\text{-}H)(\mu\text{-}Cl)W(PR_3)(Cl)$ atoms lying approximately in one plane and the benzoato groups on opposite sides. Figures 1 and 2 present ORTEP drawings of the two independent molecules and define the atomic numbering scheme excluding the β- through γ-butyl carbon atoms and the minor disordered atoms, C(55B) and C(87B). These figures also emphasize the local distorted octahedral geometry about each tungsten atom. Pertinent bond distances and angles are listed in Table IIIA, while the less important ones are available as supplementary material (Table IIIB).

Each molecule may be described as a $W_2Cl_2[P(n\text{-}Bu)_3]_2(C_6H_5CO_2)_2$ unit that has C_{2h} symmetry to which is added a bridging hydrogen atom and a bridging chlorine atom. The addition of these two atoms annuls all symmetry elements except the plane of symmetry in which they lie along with the $W_2Cl_2P_2$

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(13) Calculations were performed by using a PDP 11/60 computer and the Enraf-Nonius Structure Determination Package with programs written chiefly by Frenz and Okaya.

Table II. Positional Parameters and Their Estimated Standard Deviations for $W_2[\mu\text{-}H][\mu\text{-}Cl]Cl_2[P(n\text{-}Bu)_3]_2[C_6H_5CO_2]_2$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
W(1)	−0.39106 (4)	−0.40452 (4)	−0.43980 (6)	C(54)	−0.667 (2)	−0.266 (2)	−0.222 (3)
W(2)	−0.44861 (3)	−0.32589 (4)	−0.41224 (7)	C(55A)	−0.381 (2)	−0.240 (2)	−0.251 (3)
W(3)	−0.61570 (4)	−0.41021 (4)	−0.93224 (6)	C(55B)	−0.439 (3)	−0.226 (3)	−0.265 (5)
W(4)	−0.57321 (3)	−0.32382 (4)	−0.90687 (6)	C(56)	−0.383 (2)	−0.200 (2)	−0.278 (3)
Cl(1)	−0.4414 (2)	−0.3597 (2)	−0.5528 (3)	C(57)	−0.340 (0)	−0.164 (0)	−0.238 (0)
Cl(2)	−0.3386 (2)	−0.4538 (2)	−0.3420 (4)	C(58)	−0.296 (0)	−0.148 (0)	−0.260 (0)
Cl(3)	−0.5101 (2)	−0.2556 (2)	−0.4687 (4)	C(59)	−0.4456 (11)	−0.3308 (12)	−0.187 (2)
Cl(4)	−0.5752 (2)	−0.3591 (2)	−0.0485 (4)	C(60)	−0.392 (2)	−0.360 (1)	−0.179 (2)
Cl(5)	−0.5260 (2)	−0.2456 (2)	0.0362 (5)	C(61)	−0.4020 (15)	−0.4034 (11)	−0.098 (2)
Cl(6)	−0.6594 (2)	−0.4658 (2)	0.1666 (4)	C(62)	−0.3300 (15)	−0.4210 (14)	−0.092 (2)
P(1)	−0.4564 (3)	−0.2878 (3)	−0.2727 (4)	C(63)	−0.3091 (14)	−0.4434 (11)	−0.629 (2)
P(2)	−0.3684 (3)	−0.4679 (3)	−0.5579 (4)	C(64)	−0.250 (1)	−0.441 (1)	−0.585 (2)
P(3)	−0.6291 (3)	−0.4786 (2)	−0.0477 (4)	C(65)	−0.205 (2)	−0.417 (2)	−0.655 (2)
P(4)	−0.5697 (3)	−0.2839 (2)	−0.7672 (4)	C(66)	−0.144 (2)	−0.409 (2)	−0.609 (3)
O(1)	−0.3183 (5)	−0.3574 (5)	−0.4662 (9)	C(67)	−0.3413 (13)	−0.5344 (11)	−0.524 (2)
O(2)	−0.3727 (5)	−0.2828 (5)	−0.4406 (10)	C(68)	−0.3933 (16)	−0.5594 (10)	−0.477 (2)
O(3)	−0.4695 (5)	−0.4464 (5)	−0.4216 (9)	C(69)	−0.373 (2)	−0.617 (2)	−0.462 (3)
O(4)	−0.5229 (5)	−0.3743 (5)	−0.3961 (9)	C(70)	−0.324 (3)	−0.621 (3)	−0.430 (5)
O(5)	−0.6970 (5)	−0.3729 (6)	0.0414 (8)	C(71)	−0.4505 (17)	−0.4866 (12)	−0.614 (2)
O(6)	−0.6578 (5)	−0.2937 (5)	0.0687 (9)	C(72)	−0.4351 (17)	−0.5175 (18)	−0.671 (3)
O(7)	−0.4907 (5)	−0.3611 (5)	0.1097 (9)	C(73)	−0.4978 (16)	−0.5288 (14)	−0.725 (2)
O(8)	−0.5308 (5)	−0.4396 (5)	0.0808 (8)	C(74)	−0.543 (2)	−0.562 (2)	−0.680 (3)
C(11)	−0.3247 (8)	−0.3072 (8)	−0.459 (1)	C(75)	−0.3002 (10)	−0.9730 (9)	−0.395 (2)
C(12)	−0.2742 (9)	−0.2719 (9)	−0.492 (1)	C(76)	−0.2912 (10)	−0.9235 (11)	−0.352 (2)
C(13)	−0.2818 (10)	−0.2182 (9)	−0.502 (2)	C(77)	−0.775 (1)	−0.427 (1)	−0.193 (2)
C(14)	−0.2310 (12)	−0.1884 (12)	−0.526 (2)	C(78A)	−0.788 (2)	−0.375 (1)	−0.236 (2)
C(15)	−0.1734 (10)	−0.2143 (14)	−0.527 (2)	C(78B)	−0.801 (4)	−0.399 (4)	−0.142 (6)
C(16)	−0.1662 (12)	−0.2697 (14)	−0.516 (2)	C(79)	−0.6338 (14)	−0.5451 (8)	−0.006 (2)
C(17)	−0.2158 (10)	−0.2997 (12)	−0.498 (2)	C(80)	−0.5712 (14)	−0.5575 (11)	0.034 (2)
C(21)	−0.5203 (7)	−0.4248 (9)	−0.408 (1)	C(81)	−0.569 (2)	−0.618 (2)	0.053 (3)
C(22)	−0.5736 (8)	−0.4586 (9)	−0.405 (1)	C(82)	−0.499 (2)	−0.630 (2)	0.078 (3)
C(23)	−0.5721 (9)	−0.5091 (8)	−0.433 (2)	C(83)	−0.5671 (11)	−0.4769 (10)	−0.125 (2)
C(24)	−0.6215 (10)	−0.5404 (9)	−0.423 (2)	C(84)	−0.5632 (12)	−0.5285 (10)	−0.181 (1)
C(25)	−0.6751 (11)	−0.5234 (11)	−0.396 (1)	C(85)	−0.4937 (13)	−0.5209 (12)	−0.222 (2)
C(26)	−0.6824 (8)	−0.4681 (13)	−0.378 (2)	C(86)	−0.4884 (15)	−0.5745 (12)	−0.269 (2)
C(27)	−0.6278 (10)	−0.4335 (9)	−0.377 (1)	C(87A)	−0.629 (3)	−0.235 (3)	−0.711 (5)
C(31)	−0.7001 (8)	−0.3239 (8)	0.044 (1)	C(87B)	−0.632 (2)	−0.237 (1)	0.242 (2)
C(32)	−0.7590 (7)	−0.2988 (7)	0.019 (1)	C(88)	−0.633 (2)	−0.190 (2)	−0.796 (3)
C(33)	−0.8054 (9)	−0.3325 (9)	0.003 (1)	C(89)	−0.687 (2)	−0.140 (2)	0.262 (3)
C(34)	−0.8636 (9)	−0.3019 (12)	−0.022 (2)	C(90)	−0.725 (2)	−0.166 (2)	0.262 (4)
C(35)	−0.8651 (12)	−0.2482 (13)	−0.025 (2)	C(91)	−0.5054 (11)	−0.2447 (10)	−0.740 (2)
C(36)	−0.8128 (10)	−0.2167 (13)	−0.010 (2)	C(92)	−0.4437 (8)	−0.2759 (10)	0.245 (2)
C(37)	−0.7590 (11)	−0.2427 (10)	0.016 (2)	C(93)	−0.3914 (12)	−0.2432 (10)	−0.710 (2)
C(41)	−0.4890 (8)	−0.4123 (8)	0.101 (1)	C(94)	−0.3321 (11)	−0.2731 (12)	−0.718 (2)
C(42)	−0.4261 (8)	−0.4353 (9)	0.110 (1)	C(95)	−0.5715 (11)	−0.3310 (12)	−0.684 (2)
C(43)	−0.3766 (8)	−0.3976 (12)	0.133 (2)	C(96)	−0.6270 (11)	−0.3593 (11)	−0.668 (2)
C(44)	−0.3195 (11)	−0.4266 (16)	0.145 (2)	C(97)	−0.6157 (14)	−0.4055 (9)	−0.609 (2)
C(45)	−0.3120 (11)	−0.4788 (12)	0.128 (2)	C(98)	−0.6719 (16)	−0.4346 (11)	−0.602 (2)
C(46)	−0.3608 (12)	−0.5106 (11)	0.102 (2)	H(1)	−0.4363 (0)	−0.3782 (0)	−0.3826 (0)
C(47)	−0.4184 (10)	−0.4873 (8)	0.093 (2)	H(2)	−0.6113 (0)	−0.3672 (0)	0.1445 (0)
C(51)	−0.5296 (18)	−0.2474 (15)	−0.255 (2)				
C(52)	−0.5711 (13)	−0.2836 (14)	−0.245 (2)				
C(53)	−0.630 (3)	−0.239 (2)	−0.224 (4)				

[a] Estimated standard deviations in the least-significant digits are shown in parentheses.

set of atoms. The best least-squares planes and the angles between them, which are approximately 90°, have been calculated (Table IV, supplementary material).

With the tungsten–tungsten separations averaging 2.429 [8] Å and the average oxidation number of tungsten at +3, it is reasonable to assume the existence of a tungsten–tungsten triple bond. The W–W distance here is longer than that found in many other compounds with triple bonds, but that is probably due in part to the higher coordination number in this case. Thus, in a variety of $W_2(NR_2)_6$ and $W_2X_2(NR_2)_4$ molecules, the W–W distances are in the range 2.254 (2) to 2.301 (1) Å,[14] but in the $W_2Cl_9^{3-}$ ion[15] where each metal atom is in an octahedron of ligand atoms, the distance is 2.41 Å. On the other hand, in $W_2(O_2CNMe_2)_6$ where each metal atom has five ligand atoms at normal bonding distances plus one more at a rather long distance, the W–W bond length is still only 2.279 (1) Å, thus showing that there is no simple relation between W–W bond length and coordination number independent of other factors. In $W_4(O\text{-}i\text{-}Pr)_{14}H_2$,[16] where the H atoms bridge W–W bonds that may reasonably be regarded as double bonds, the W–W distances are 2.446 (1) Å, again illustrating the fact (which is already well established) that for metal–metal bonds, especially multiple ones, simple bond order to bond length correlations are not to be expected.

Another way to consider the W–W distance in this compound is as follows. In the molecule $W_2Cl_2[P(n\text{-}Bu)_3]_2(O_2CC_6H_5)_2$, which we have not been able to isolate, there would be a quadruple bond. We may estimate the length of this bond by adding about 0.10 Å to the Mo–Mo distance, 2.091 (3) Å in the similar molecule[12] $Mo_2Br_2[P(n\text{-}Bu)_3]_2(O_2CC_6H_5)_2$, thus obtaining about 2.19 Å. This is in the expected range.[3] The combined effect of adding the μ-H and μ-Cl atoms and reducing the W–W bond order

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Table IIIA. Important Bond Distances (Å) and Bond Angles (Deg) for $W_2[\mu\text{-H}][\mu\text{-Cl}]Cl_2[P(n\text{-Bu})_3]_2[C_6H_5CO_2]_2$[a]

Distances

molecule 1				molecule 2			
W(1)-W(2)	2.423 (1)	P(2)-C(63)	1.87 (4)	W(3)-W(4)	2.435 (1)	P(3)-C(75)	1.84 (3)
-Cl(1)	2.454 (6)	-C(67)	1.88 (3)	-Cl(4)	2.485 (7)	-C(79)	1.83 (3)
-Cl(2)	2.353 (7)	-C(71)	2.11 (5)	-Cl(6)	2.367 (7)	-C(83)	1.87 (3)
-P(2)	2.579 (8)	P(1)-C(51)	1.95 (4)	-P(3)	2.597 (8)	P(4)-C(87A)	2.05 (10)
-O(1)	2.06 (1)	-C(55A)	2.11 (6)	-O(5)	2.09 (2)	-C(87B)	1.84 (5)
-O(3)	2.07 (1)	P(1)-C(55B)	1.64 (9)	-O(8)	2.04 (1)	P(4)-C(91)	1.80 (3)
-H(1)	1.534 (1)	-C(59)	1.81 (3)	-H(2)	1.677 (1)	-C(95)	1.83 (3)
W(2)-Cl(1)	2.475 (7)	O(1)-C(11)	1.29 (3)	W(4)-P(4)	2.517 (8)	O(5)-C(31)	1.25 (3)
-Cl(3)	2.440 (6)	O(2)-C(11)	1.27 (3)	-Cl(4)	2.500 (7)	O(6)-C(31)	1.28 (2)
-P(1)	2.501 (9)	O(3)-C(21)	1.28 (3)	-Cl(5)	2.442 (6)	O(7)-C(41)	1.31 (3)
-O(2)	2.07 (1)	O(4)-C(21)	1.30 (3)	-O(6)	2.07 (1)	O(8)-C(41)	1.21 (3)
-O(4)	2.08 (1)	C(11)-C(12)	1.54 (3)	-O(7)	2.09 (1)	C(31)-C(32)	1.52 (3)
-H(1)	1.447 (1)	C(21)-C(22)	1.47 (3)	-H(2)	1.631 (1)	C(41)-C(42)	1.52 (3)

Angles

molecule 1				molecule 2			
W(2)-W(1)-Cl(1)	61.0 (2)	Cl(3)-W(2)-P(1)	91.4 (3)	W(4)-W(3)-Cl(4)	61.1 (2)	Cl(5)-W(4)-P(4)	90.4 (3)
-Cl(2)	125.2 (2)	-O(2)	88.9 (5)	-Cl(6)	125.7 (2)	-O(6)	90.8 (4)
-P(2)	139.8 (2)	-O(4)	92.3 (4)	-P(3)	141.1 (2)	-O(7)	92.6 (5)
-O(1)	88.4 (4)	-H(1)	155.9 (2)	-O(5)	87.6 (5)	-H(2)	167.7 (2)
-O(3)	87.5 (4)	P(1)-W(2)-O(2)	93.3 (5)	-O(8)	87.4 (5)	P(4)-W(4)-O(6)	93.2 (5)
W(2)-W(1)-H(1)	34.44 (3)	-O(4)	93.4 (5)	W(4)-W(3)-H(2)	41.88 (4)	-O(7)	92.1 (5)
Cl(1)-W(1)-Cl(2)	173.8 (2)	-H(1)	93.5 (2)	Cl(4)-W(3)-Cl(6)	173.0 (3)	-H(2)	79.4 (2)
-P(2)	79.1 (3)	O(2)-W(2)-O(4)	173.2 (7)	-P(3)	80.2 (2)	O(6)-W(4)-O(7)	173.7 (6)
-O(1)	85.8 (5)	-H(1)	114.3 (4)	-O(5)	85.1 (5)	-H(2)	83.1 (4)
-O(3)	88.1 (5)	O(4)-W(2)-H(1)	63.8 (4)	-O(8)	86.5 (5)	O(7)-W(4)-H(2)	94.6 (4)
-H(1)	87.8 (2)	W(1)-Cl(1)-W(2)	58.9 (2)	-H(2)	102.5 (2)	W(3)-Cl(4)-W(4)	58.5 (2)
Cl(2)-W(1)-P(2)	94.8 (3)	W(1)-H(1)-W(2)	108.69 (6)	Cl(6)-W(3)-P(3)	93.1 (3)	W(3)-H(2)-W(4)	94.77 (5)
-O(1)	93.8 (5)	W(1)-P(2)-C(63)	114 (1)	-O(5)	93.5 (5)	W(3)-P(3)-C(75)	114.9 (9)
-O(3)	92.5 (5)	-C(67)	114 (1)	-O(8)	95.0 (5)	-C(79)	111 (1)
-H(1)	98.0 (2)	-C(71)	108 (1)	-H(2)	84.2 (2)	-C(83)	113 (1)
P(2)-W(1)-O(1)	93.0 (5)	C(63)-P(2)-C(67)	105 (2)	P(3)-W(3)-O(5)	93.1 (5)	C(75)-P(3)-C(79)	102 (2)
-O(3)	87.1 (5)	-C(71)	114 (2)	-O(8)	86.4 (5)	-C(83)	106 (2)
-H(1)	150.1 (2)	C(67)-P(2)-C(71)	102 (2)	-H(2)	176.4 (2)	C(79)-P(3)-C(83)	108 (1)
O(1)-W(1)-O(3)	173.7 (6)	W(2)-P(1)-C(51)	114 (2)	O(5)-W(3)-O(8)	171.5 (6)	W(4)-P(4)-C(87A)	130 (3)
-H(1)	112.9 (5)	-C(55A)	109 (2)	-H(2)	84.7 (5)	-C(87B)	108 (2)
O(3)-W(1)-H(1)	65.4 (4)	-C(55B)	116 (3)	O(8)-W(3)-H(2)	96.1 (5)	-C(91)	119 (1)
W(1)-W(2)-Cl(1)	60.1 (2)	-C(59)	118 (1)	W(3)-W(4)-Cl(4)	60.5 (2)	-C(95)	115 (1)
-Cl(3)	146.5 (2)	C(51)-P(1)-C(55A)	110 (2)	-Cl(5)	147.2 (2)	C(87A)-P(4)-C(91)	93 (3)
-P(1)	122.1 (2)	-C(59)	108 (2)	-P(4)	122.4 (2)	-C(95)	93 (3)
-O(2)	88.1 (4)	C(55A)-P(1)-C(59)	96 (2)	-O(6)	87.1 (4)	C(91)-P(4)-C(95)	101 (2)
-O(4)	87.2 (4)	W(1)-O(1)-C(11)	118 (1)	-O(7)	87.2 (4)	W(3)-O(5)-C(31)	120 (1)
-H(1)	36.86 (4)	W(2)-O(2)-C(11)	119 (1)	-H(2)	43.35 (4)	W(4)-O(6)-C(31)	120 (1)
Cl(1)-W(2)-Cl(3)	86.4 (3)	W(1)-O(3)-C(21)	123 (2)	Cl(4)-W(4)-Cl(5)	86.8 (3)	W(4)-O(7)-C(41)	118 (1)
-P(1)	177.5 (2)	W(2)-O(4)-C(21)	122 (1)	-P(4)	177.1 (2)	W(3)-O(8)-C(41)	122 (2)
-O(2)	85.5 (5)	O(1)-C(11)-O(2)	127 (2)	-O(6)	86.3 (5)	O(5)-C(31)-O(6)	125 (2)
-O(4)	87.9 (5)	-C(12)	118 (2)	-O(7)	88.5 (5)	-C(32)	117 (2)
-H(1)	89.0 (2)	O(2)-C(11)-C(12)	114 (2)	-H(2)	103.3 (2)	O(6)-C(31)-C(32)	118 (2)
		O(3)-C(21)-O(4)	120 (2)			O(7)-C(41)-O(8)	126 (2)
		-C(22)	118 (3)			-C(42)	114 (2)
		O(4)-C(21)-C(22)	123 (2)			O(8)-C(41)-C(42)	121 (3)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

from 4 to 3 is to lengthen the bond by about 0.24 Å. This is a greater lengthening than might be expected just from the bond order reduction and probably indicates that the introduction of bridging groups tends to force the metal atoms apart.

One of the most interesting results of this study is the actual observation of the bridging hydrogen atom in each of the two independent molecules. While the detection of hydrogen atoms in the presence of heavy metal atoms is far from common, it is not unprecedented either. Thus, to cite only cases closely related to the present one, in the compound $W_2(O\text{-}i\text{-Pr})_{14}H_2$,[16] already mentioned, the hydrogen atom was observed and refined in a bridging position to give W–H distances of 1.61 (8) and 1.89 (8) Å, the average being 1.75 [20] Å. However, in this case it may not be correct to assume that the two distances ought to be equal and thus average them, since the two tungsten atoms being bridged are not equivalent. In two compounds containing the $[Mo_2Cl_8H]^{3-}$ ion, the bridging hydrogen atom has been detected and refined. In one case the two crystallographically independent values were 1.62 (1) and 1.74 (1) Å, and in the other, where there was a crystallographic symmetry plane through the bridging hydrogen atom, a value of 1.728 (2) Å was found. Thus, the four crystallographically independent W–H distances obtained in the present study, 1.534, 1.447, 1.677, and 1.631 Å, which average 1.57 [9] Å, are of reasonable magnitude.

One other structural feature worth mentioning is the structural trans effect of the μ-H atom. The W–P and W–Cl distances for those trans to the W–H bond (average W–P, 2.588 (8) Å; W–Cl, 2.441 (6) Å) are significantly longer than those that are trans to the bridging chlorine atom (average W–P, 2.509 (8) Å; W–Cl, 2.360 (7) Å) by ca. 0.08 Å. A similar but even larger effect was found in the $[Mo_2Cl_8H]^{3-}$ case[5] where the Mo–Cl bonds trans to μ-H were about 0.11 Å longer than those trans to μ-Cl.

NMR Spectra. Both ^{31}P and ^{1}H NMR spectra were studied in order to confirm the existence of the bridging hydride ligand as well as its relation to the other ligands. According to the X-ray results, it is cis to one phosphorus atom and trans to the other.

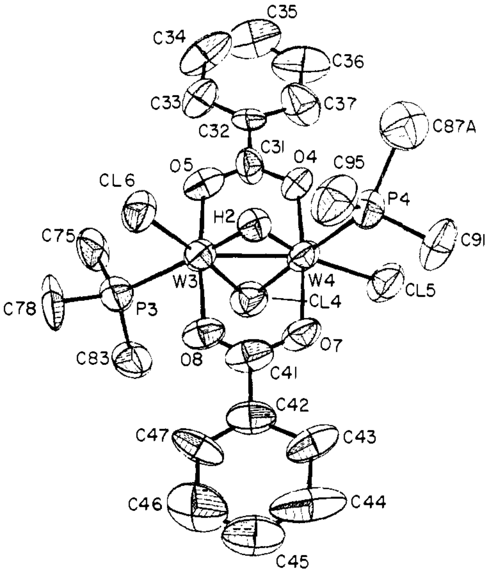

Figure 2. ORTEP diagram of molecule **2** with thermal ellipsoids at the 40% probability level.

In the ^{31}P spectrum (without decoupling of protons), two resonances were observed. One was a broad peak (width at half-height, 72 Hz) at +12.0 ppm and the other a broad doublet at −8.0 ppm with a splitting of 65 ± 5 Hz. The +12.0 ppm resonance can be assigned to the P atom cis to H, and the fact that no splitting is resolved suggests a $^2J_{\text{H-P}}$ value of ≤ 30 Hz. The doublet resonance is then assigned to the P atom trans to H, with $^2J_{\text{H-P}} \approx 65$ Hz. With broad-band ^{1}H decoupling, both of these resonances appeared as sharp doublets with $^3J_{\text{P-P}} = 21$ Hz. The decoupled spectrum also showed satellites due to coupling of the ^{183}W($I = {}^1/_2$) nuclei to ^{31}P. For the cis P atom, we found $^1J_{\text{W-P}} = 180$ Hz and $^2J_{\text{W-P}} = 79$ Hz, while for the trans P atom, we found $^1J_{\text{W-P}} = 112$ Hz and $^2J_{\text{W-P}} = 53$ Hz. The smaller couplings to the trans P atom are in accord with the greater W–P bond length (ca. 2.59 Å) as compared with that for the cis P atom (ca. 2.51 Å).

A series of off-resonance decoupling experiments were performed in which the ^{31}P spectrum was examined as the ^{1}H decoupling frequency was varied. In this way the chemical shift of the bridging ^{1}H nucleus was estimated as approximately 2 ppm, i.e., just downfield from the very large resonances due to the aliphatic hydrogen atoms of the butyl groups. With this information a search was made and the hydride resonance was found as a doublet of doublets (due to H–P couplings) centered at 1.92 ppm. The satellites due to W–H coupling were not detectable. In agreement with inferences from the undecoupled ^{31}P spectrum, the following coupling constants were observed: $^2J_{\text{H-cisP}} = 31$ Hz and $^2J_{\text{H-transP}} = 63$ Hz. These values may be compared with those previously reported[17] in WH(η^5-C_5H_5)(CO)$_2$(PMe$_3$), viz., $^2J_{\text{H-cisP}} = 24$ Hz and $^2J_{\text{H-transP}} = 68$ Hz.

Finally, although our spectrometer did not permit high-power broad-band decoupling of ^{31}P from the ^{1}H spectrum, a measurement at low power revealed significant reduction in both of the $^2J_{\text{H-P}}$ couplings, thus confirming the above analysis of the spectra.

Chemical Considerations. Our own experience, and that of others, in attempting to synthesize tungsten analogues to the well-established $Mo_2(O_2CR)_4$ compounds has made us increasingly aware that media of significant acidity are generally inappropriate for this purpose. Thus, the reaction of W(CO)$_6$ with RCO_2H in a way analogous to the preparation of $Mo_2(O_2CCH_3)_4$ from Mo(CO)$_6$ and acetic acid[18] is unsuitable for obtaining $W_2(O_2CR)_4$ compounds and affords either polymeric or high-oxidation-state tungsten trinuclear species.[7,19] Similarly, Sharp and Schrock[9] have shown that the stable molecule W_2Cl_4[P(n-Bu)$_3$]$_4$ reacts with acetic acid under forcing conditions to give an unusual trinuclear W(IV) compound. Our own current work was undertaken prior to our learning of Sattelberger's successful synthesis of $W_2(O_2CCF_3)_4$ from W_2Cl_4(THF)$_4$ and NaO_2CCF_3 under nonacidic conditions.[20] We attempted to mimic the reactions of San Filippo and Sniadoch,[11] who had demonstrated the utility of the molybdenum compound Mo_2Cl_4P(n-Bu$_3$)$_4$ in synthesizing a number of dimolybdenum tetracarboxylates and Mo_2Cl_2[P(n-Bu)$_3$]$_2$(O_2CR)$_2$ complexes with both strong and weak carboxylic acids. In addition, experiments in this laboratory have shown that the n-butylphosphine ligands in W_2Cl_4[P(n-Bu)$_3$]$_4$ can be removed under very mild conditions.[1]

In this study we chose to investigate the reactions of W_2Cl_4[P(n-Bu)$_3$]$_4$ with benzoic acid, a relatively weak acid. Initial attempts at complete displacement of halogen and phosphine ligands using a 4:1 acid:W_2Cl_4[P(n-Bu)$_3$]$_4$ ratio resulted in formation of an air-stable product that is presumably analogous to Sharp and Schrock's $W_2O_3Cl_5$(CH_3CO_2)[P(n-Bu)$_3$]$_3$ compound.[9] We then noted that the 2:1 acid:W_2Cl_4[P(n-Bu)$_3$]$_4$ reaction afforded a more promising, slightly air-sensitive red material, the composition of which we expected to be W_2Cl_2[P(n-Bu)$_3$]$_2$[$C_6H_5CO_2$)$_2$, thus getting us at least half way to our goal. However, as the structural work reported here has shown, we have not obtained W_2Cl_2[P(n-Bu)$_3$]$_2$($C_6H_5CO_2$)$_2$ but instead the product of reaction of this with 1 mol of HCl. Presumably, in most other cases the sequence of reactions does not stop even at this point, and only substances containing even more highly oxidized tungsten atoms can be obtained.

Our observation of W_2(μ-H)(μ-Cl)Cl_2[P(n-Bu)$_3$]$_2$($C_6H_5CO_2$)$_2$ is consistent with Sattelberger's report[2] that the tetracarboxylate ditungsten molecule $W_2(O_2CCF_3)_4$ is susceptible to reaction with HCl affording $W_2Cl_8H^{3-}$. While oxidative addition to metal–metal multiple bonds is well-known for both Cp_2Mo_2(CO)$_4$ (M≡M)[20] and the Chisholm-type compounds $M_2(L)_6$ (M≡M; M = Mo, W; L = OR, NR$_2$),[21] W_2(μ-H)(μ-Cl)Cl_2[P(n-Bu)$_3$]$_2$($C_6H_5CO_2$)$_2$ provides the first structural confirmation of an oxidative addition to a quadruply bonded ditungsten(II) moiety.

This work suggests that, although we were not successful in our goal of synthesizing $W_2(O_2CPh)_4$, under special conditions, such as the presence of an HCl trapping agent, this may still prove to be a route to the tetracarboxylate species and indeed a simpler and less cumbersome procedure than Sattelberger's method, and we are continuing our studies in this direction.

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Registry No. 1, 82891-95-0; W_2Cl_4[P(n-Bu)$_3$]$_4$, 73133-23-0.

Supplementary Material Available: Tables of structure factors, anisotropic thermal vibration tensors, some less important bond distances and angles, and some least-squares planes (28 pages). Ordering information is given on any current masthead page.

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