Attempted Preparation of a Dimetallabenzyne. Preparation and Crystal Structure of $W_2(\mu\text{-}C_3Ph_3)(\mu\text{-}CPh)(NMe_2)_4$ (M–M)

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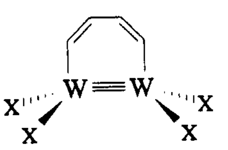
Received October 10, 1991

Summary: The reaction between 1,2-$W_2Cl_2(NMe_2)_4$ and 1,4-$Li_2C_4Ph_4$ in tetrahydrofuran yields a black crystalline compound that has been shown to be $W_2(\mu\text{-}C_3Ph_3)(\mu\text{-}CPh)(NMe_2)_4$ by single-crystal X-ray crystallography. A W–W bond of distance 2.67 Å is supported by a benzylidyne bridge and a μ-metallacyclobutadiene ligand. Each tungsten has two terminal amido ligands.

In previous studies we have reported the preparation of 1,2-dimetallahexyne compounds of formula $\overline{M_2(CH_2)_4}$-$(NMe_2)_4(M{\equiv}M)$.[1] We were intrigued by the possible existence of 1,2-dimetallabenzyne complexes (M = Mo, W) of the general formula shown in I.



X - alkyl, amide, alkoxide

I

In an attempt to prepare the first example of such a complex we carried out the reaction shown in eq 1. The product derived from this reaction is described herein.

$$\underset{\mathbf{1}}{1,2\text{-}W_2Cl_2(NMe_2)_4} + \underset{\mathbf{2}}{Li_2C_4Ph_4} \xrightarrow[\text{THF}]{22\ ^\circ\text{C}} \underset{\mathbf{3}}{W_2(C_4Ph_4)(NMe_2)_4} + 2LiCl \quad (1)$$

The molecular structure of the dark, crystalline, air-sensitive, hydrocarbon soluble product **3** obtained from reaction 1 is shown in Figure 1. Atomic coordinates are given in Table I, and selected bond distances and angles are given in Table II. **3** may be formed in two steps (eq 2). First, addition of $Li_2C_4Ph_4$ (**2**) on 1,2-$W_2Cl_2(NMe_2)_4$ (**1**) yields the metallabenzene Ia. Then we assume that reduction of the M–M triple bond takes place. This forces the cleaving of one of the C–C bonds in Ia to give, presumably via a benzvalene intermediate (IIa), the final reaction product **3**.

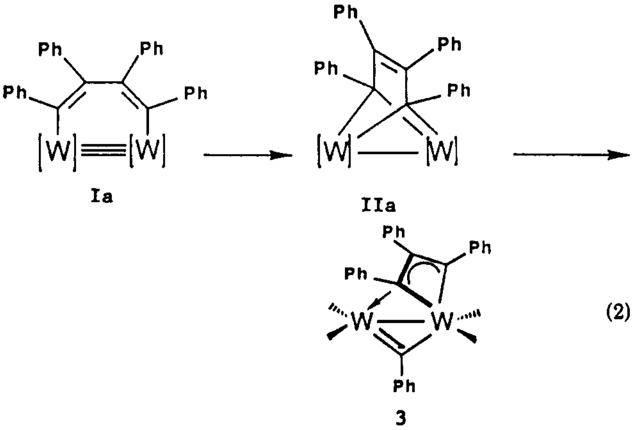


Table I. Fractional Coordinates and Isotropic Thermal Parameters for $W_2(\mu\text{-}CPh)(\mu\text{-}C_3Ph_3)(NMe_2)_4$

atom	10^4x	10^4y	10^4z	$10B_{iso}$
W(1)	6413.5 (4)	5237.9 (4)	3231.0 (3)	10
W(2)	7687.8 (4)	5632.6 (4)	2405.9 (3)	10
N(3)	5357 (7)	4251 (8)	3050 (6)	15
C(4)	4848 (10)	3750 (10)	2339 (7)	18
C(5)	5048 (10)	3868 (11)	3710 (8)	21
N(6)	6040 (7)	6055 (8)	4023 (6)	14
C(7)	6519 (10)	6419 (10)	4774 (7)	18
C(8)	4999 (10)	6386 (11)	3830 (8)	22
N(9)	8361 (7)	4751 (8)	1805 (6)	14
C(10)	9010 (9)	3932 (10)	2019 (8)	17
C(11)	8302 (10)	5027 (11)	1004 (8)	24
N(12)	8117 (8)	6912 (8)	2054 (6)	17
C(13)	9122 (10)	7129 (10)	2098 (8)	21
C(14)	7542 (10)	7870 (10)	1931 (8)	22
C(15)	6248 (9)	5732 (9)	2180 (8)	19
C(16)	5465 (9)	5970 (9)	1479 (7)	12
C(17)	5656 (9)	6086 (10)	773 (8)	18
C(18)	4921 (10)	6289 (10)	102 (7)	20
C(19)	3973 (9)	6406 (10)	149 (8)	19
C(20)	3754 (9)	6297 (10)	849 (9)	20
C(21)	4473 (9)	6085 (10)	1517 (7)	17
C(22)	7653 (9)	7824 (9)	3860 (7)	17
C(23)	7950 (11)	8796 (10)	4101 (8)	21
C(24)	8927 (11)	9023 (10)	4357 (8)	20
C(25)	9608 (9)	8264 (9)	4368 (7)	17
C(26)	9312 (10)	7289 (10)	4146 (7)	16
C(27)	8333 (9)	7057 (9)	3876 (7)	13
C(28)	8035 (9)	6009 (10)	3564 (7)	14
C(29)	8047 (9)	5078 (9)	3944 (7)	14
C(30)	7706 (9)	4419 (10)	3296 (7)	14
C(31)	7851 (9)	3300 (9)	3268 (8)	13
C(32)	8641 (9)	2821 (10)	3780 (7)	16
C(33)	8814 (9)	1804 (11)	3699 (8)	18
C(34)	8210 (10)	1239 (10)	3123 (8)	18
C(35)	7428 (10)	1714 (10)	2627 (8)	19
C(36)	7245 (9)	2718 (10)	2680 (7)	16
C(37)	8300 (9)	4814 (9)	4771 (7)	14
C(38)	7809 (9)	4004 (10)	5033 (7)	15
C(39)	8011 (10)	3760 (10)	5795 (8)	18
C(40)	8746 (10)	4295 (12)	6319 (8)	25
C(41)	9219 (9)	5057 (10)	6077 (8)	19
C(42)	9019 (9)	5315 (9)	5313 (7)	15

Although several valence bond descriptions are possible, the structural parameters and the NMR data indicate that a symmetrical structure is best representative of the product. Even though the μ-C_3Ph_3 ring appears η^2-bound to W(2) and η^3-bound to W(2), the NMR data at −80 °C in toluene indicate a time-averaged structure with equivalent NMe_2 ligands. The values of the ${}^1J_{{}^{183}W-{}^{13}C}$ coupling constants of the bridging carbyne ligand and the allylic systems of the compound are in a typical range compared with similar molecules.[2a] For a detailed discussion of probable rotation mechanisms of the C_3Ph_3 moiety, see ref 2a.

In conclusion, the attempted synthesis of a 1,2-ditungstabenzyne according to eq 1 yields an isomer $W_2(\mu\text{-}CPh)(\mu\text{-}C_3Ph_3)(NMe_2)_4$ which is an analogue of the com-

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(1) Chetcuti, M. J.; Chisholm, M. H.; Chiu, H. T.; Huffman, J. C. *Polyhedron* **1985**, *4*, 1213.

(2) (a) X = CH_2SiMe_3: Chisholm, M. H.; Heppert, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 1151; **1985**, *107*, 5116. (b) X = O-*i*-Pr: Chisholm, M. H.; Ontiveros, C. D. *Polyhedron* **1988**, *7*, 1015.

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Table II. Selected Bond Distances (Å) and Angles (deg) for $W_2(\mu\text{-CPh})(\mu\text{-C}_3Ph_3)(NMe_2)_4$

W(1)-W(2)	2.6709 (11)	W(1)-C(29)	2.354 (12)	W(2)-C(28)	2.077 (13)
W(1)-N(3)	1.953 (10)	W(1)-C(30)	2.109 (12)	W(2)-C(30)	2.267 (13)
W(1)-N(6)	1.969 (10)	W(2)-N(9)	1.996 (10)	C(28)-C(29)	1.409 (18)
W(1)-C(15)	1.960 (14)	W(2)-N(12)	1.962 (10)	C(29)-C(30)	1.439 (18)
W(1)-C(28)	2.448 (12)	W(2)-C(15)	1.983 (13)		

W(2)-W(1)-N(3)	129.7 (3)	C(29)-W(1)-C(30)	37.1 (4)
W(2)-W(1)-N(6)	129.9 (3)	W(1)-W(2)-N(9)	132.4 (3)
W(2)-W(1)-C(15)	47.7 (4)	W(1)-W(2)-N(12)	131.3 (3)
W(2)-W(1)-C(28)	47.6 (3)	W(1)-W(2)-C(15)	47.0 (4)
W(2)-W(1)-C(29)	66.9 (3)	W(1)-W(2)-C(28)	60.5 (3)
W(2)-W(1)-C(30)	55.1 (3)	W(1)-W(2)-C(30)	49.7 (3)
N(3)-W(1)-N(6)	98.8 (4)	N(9)-W(2)-N(12)	95.7 (4)
N(3)-W(1)-C(15)	99.6 (5)	N(9)-W(2)-C(15)	122.6 (5)
N(3)-W(1)-C(28)	162.5 (4)	N(9)-W(2)-C(28)	131.5 (5)
N(3)-W(1)-C(29)	129.6 (4)	N(9)-W(2)-C(30)	92.7 (4
N(3)-W(1)-C(30)	106.5 (5)	N(12)-W(2)-C(15)	105.4 (5)
N(6)-W(1)-C(15)	121.8 (5)	N(12)-W(2)-C(28)	95.9 (5)
N(6)-W(1)-C(28)	90.2 (4)	N(12)-W(2)-C(30)	153.4 (4)
N(6)-W(1)-C(29)	93.7 (4)	C(15)-W(2)-C(28)	99.0 (5)
N(6)-W(1)-C(30)	129.4 (4)	C(15)-W(2)-C(30)	90.9 (5)
C(15)-W(1)-C(28)	88.2 (5)	C(28)-W(2)-C(30)	60.2 (5)
C(15)-W(1)-C(29)	114.5 (5)	W(1)-C(15)-W(2)	85.3 (6)
C(15)-W(1)-C(30)	96.5 (5)	W(1)-C(15)-C(16)	140.3 (9)
C(28)-W(1)-C(29)	34.1 (4)	W(2)-C(15)-C(16)	134.1 (9)
C(28)-W(1)-C(30)	56.8 (5)	C(28)-C(29)-C(30)	100.2 (10)

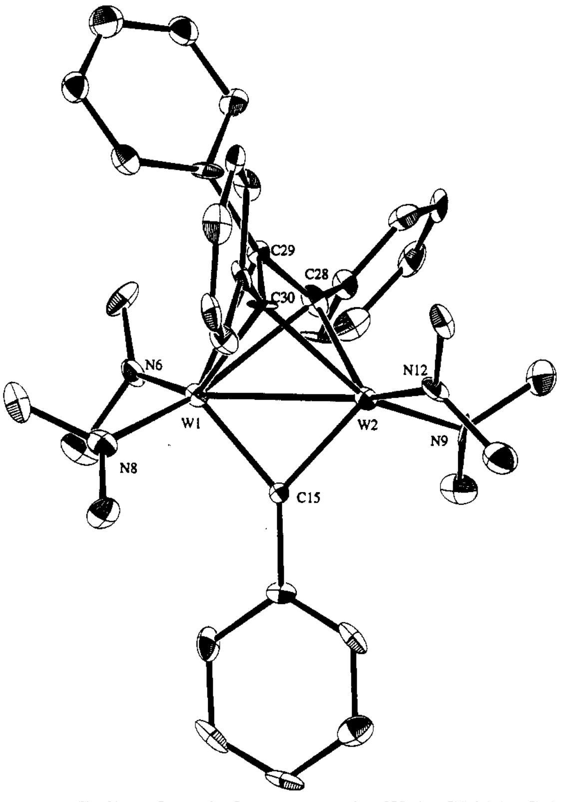

Figure 1. Ball-and-stick drawing of the $W_2(\mu\text{-CPh})(\mu\text{-C}_3Ph_3)(NMe_2)_4$ molecule showing the atom number scheme used for the central $W_2C_4N_4$ core.

Table III. Summary of Crystal Data for $W_2(\mu\text{-CPh})(\mu\text{-C}_3Ph_3)(NMe_2)_4$

empirical formula	$W_2C_{38}H_{44}N_4$
cryst color	black
cryst dimens (mm)	0.12 × 0.12 × 0.25
space group	$P2_1/c$
cell dimens	
temp (°C)	-171
a, (Å)	14.194 (6)
b (Å)	13.262 (5)
c, (Å)	18.009 (7)
β (deg)	104.88 (2)
Z (molecules/cell)	4
V (Å^3)	3276.43
d_{calcd} (gm/cm^3)	1.826
wavelength (Å)	0.71069
mw	900.47
linear absorptn coeff (cm^{-1})	71.975
detector to sample dist (cm)	22.5
sample to source dist (cm)	23.5
av *ω* scan width at half-height	0.25
scan speed (deg/min)	4.0
scan width (deg + dispersn)	2.0
individual bkgd (s)	4
aperture size (mm)	3.0 × 4.0
2*θ* range (deg)	6-45
total no. of reflectns collected	5110
no. of unique intensities	4276
no. with $F > 0.0$	4021
no. with $F > 2.33\sigma(F)$	3663
$R(F)$	0.0465
$R_w(F)$	0.0450
goodness of fit for the last cycle	1.106
max δ/σ for last cycle	0.23

pounds $X_4W_2(\mu\text{-CSiMe}_3)(\mu\text{-C}_2R_2CSiMe_3)$, where X = *i*-PrO or CH_2SiMe_3, that were synthesized from the insertion of an alkyne into one μ-$CSiMe_3$ unit of the 1,3-ditungstabutadienes $X_4W_2(\mu\text{-CSiMe}_3)_2$.[2]

Experimental Section

Dry and oxygen-free atmospheres (N_2) and solvents were used throughout. 1,2-$W_2Cl_2(NMe_2)_4$ was prepared according to literature procedures.[3] ^{1}H NMR (300 MHz) and ^{13}C NMR (75.429 MHz) were recorded on a Varian XL300 spectrometer in toluene-d_8. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Preparation of Dilithiotetraphenylbutadiene.[4] A 3.5-g (0.02 mol) sample of diphenylacetylene was placed in a small Schlenk flask and dissolved in ca. 5 mL of diethyl ether. Under a stream of nitrogen, small chips of Li (0.35 g, 0.05 mol) were added to the colorless solution. After stirring for a few minutes the color changed to yellow and later to dark red, and after ca. 30 min a yellow precipitate was formed. The reaction was stopped after 5 h and the yellow compound filtered off and washed twice with 15 mL of diethyl ether and 10 mL of *n*-hexane. Drying in vacuo for several hours yielded 3.0 g (87%) of yellow dilithiotetraphenylbutadiene.

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(3) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407.

(4) Smith, L. I.; Hoehm, H. H. *J. Am. Chem. Soc.* **1941**, *63*, 1184.

Preparation of $W_2[\mu\text{-CPh(CPh)CPh}](\mu\text{-CPh})(NMe_2)_4$. A small Schlenk tube was charged with 0.610 g (1.0 mmol) of $W_2Cl_2(NMe_2)_4$ and 0.370 g (1.0 mmol) of $Li_2(CPh)_4$. Adding 5 mL of THF at 0 °C yielded a yellow solution, which turned black a few moments later. The solution was stirred for an additional 6 h. After the solvent was removed in vacuo, the black residue was extracted with 2 × 10 mL of toluene and filtered through a fine frit. The volume of the deep red solution was concentrated to ca. 2 mL and the flask stored at −20 °C. After 24 h, black crystals were collected (400 mg, 45%). Reducing the volume to half of the amount and storing of the solution for an additional 48 h at −20 °C yielded a second crop of black crystals (140 mg, 15%). Anal. Calcd for $C_{36}H_{44}N_4W_2$: C, 48.02; H, 4.92; N, 6.22. Found: C, 47.77; H, 4.66; N, 5.82. Mp: 203 °C. ^1H NMR (toluene-d_8, 22 °C) δ: 7.96 (dd, 2 H), 7.80 (dd, 2 H), 7.58 (t, 2 H), 7.22 (t, 2 H), 7.13 (t, 1 H), 7.02 (t, 1 H), 6.99 (t, 4 H), 6.70 (t, 2 H), 6.50 (dd, 4 H), 2.89 (s, 24 H). $^{13}C\{^1H\}$ NMR δ: 335.5 ($^1J_{^{183}W-^{13}C}$ = 146 Hz (μ-CPh)), 172.9 ($^1J_{^{183}W-^{13}C}$ = 40 Hz (μ-CPh)), 157.2, 144.2, 140.2, 130.8, 130.5, 128.6, 128.3, 128.0, 127.9, 127.1, 126.5, 124.8, 123.8, 48.1 (NCH_3).

Crystallographic Studies. General operating procedures and listings of programs have been given.[5] A suitable crystal was located, transferred to the goniostat using inert atmosphere handling techniques, and cooled to −171 °C for characterization and data collection. A summary of crystal data is given in Table III.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/c$. Subsequent solution and refinement of the structure confirmed this choice.

Data were collected in the usual manner by using a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. All hydrogen atom positions were therefore calculated using idealized geometries and d(C–H) = 0.95 Å. These calculated positions were fixed for the final cycles of refinement.

A final difference Fourier was featureless, with several peaks of 1.1–1.5 e/Å^3 located at the metal site, and all other peaks less than 0.6 e/Å^3.

No absorption correction was performed.

Acknowledgment. We thank the National Science Foundation for support. R.-M.J. thanks Deutsche Forschungsgemeinschaft (DFG) for a fellowship.

Supplementary Material Available: A listing of anisotropic thermal parameters, VERSORT and stereo drawings giving the atom number scheme, and a complete listing of bond distances and bond angles (10 pages). Ordering information is given on any current masthead page.

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Synthesis of Magnesium Hydride by the Reaction of Phenylsilane and Dibutylmagnesium

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Received November 19, 1991

Summary: The reaction of phenylsilane with dibutylmagnesium in ethereal or hydrocarbon solvents in the presence of appropriate ligands, usually tetrahydrofuran (THF) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) leads to precipitation of magnesium hydride MgH_2L_x.

Magnesium hydride has generated some interest as a reducing agent for aldehydes and ketones,[1] as a hydride source in the synthesis of silane,[2] and as a potential material for use in hydrogen storage devices.[3] The hydride is usually synthesized by catalytic hydrogenation of magnesium or by reduction of $MgMe_2$ with $LiAlH_4$.[3a,4] We now report that MgH_2 can be simply prepared by the reaction of phenylsilane with dibutylmagnesium. Magnesium hydride precipitates from the reaction mixture either as a solvated hydride (from tetrahydrofuran (THF)/heptane or ethylene glycol dimethyl ether (DME)/heptane) or as a *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) adduct (from TMEDA/heptane/solutions).[5]

Experimental Section

All experiments were performed under nitrogen in a Vacuum Atmospheres drybox at room temperature or under argon using Schlenk techniques at room temperature or below. *Magnesium hydride is a highly pyrophoric, air-sensitive solid and should be handled with extreme caution.* All solvents were dried and distilled before use. Dibutylmagnesium (consisting of a 1:1 mixture of *n*-butyl/*sec*-butyl) was purchased from Alfa as a 1.07 M solution in heptane. Phenylsilane was obtained from Petrarch/Hüls America and distilled before use. TMEDA (Aldrich) was dried over CaH_2 and distilled. Proton NMR spectra were recorded on a General Electric QE-300 spectrometer; FT-IR spectra were obtained in Nujol and in THF on KBr using a Nicolet 60-SX spectrometer. GC/MS analysis was performed using a Varian 3700 gas chromatograph coupled with a VG micromass 16 mass

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[1] (a) Ashby, E. C.; Lin, J. J.; Goel, A. B. *J. Org. Chem.* 1978, *43*, 1557. (b) Carfagna, C.; Musco, A.; Pontellini, R.; Terzoni, G. *J. Mol. Catal.* 1989, *57*, 23. (c) Musco, A.; Pontellini, R.; Terzoni, G. *Inorg. Chim. Acta* 1990, *172*, 1.

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[4] (a) Ashby, E. C.; Goel, A. B. *J. Chem. Soc., Chem. Commun.* 1977, 169. (b) Ashby, E. C.; Goel, A. B. *J. Org. Chem.* 1977, *42*, 3480. (c) Goel, A. B.; Ashby, E. C. *Inorg. Chim. Acta* 1984, *87*, 61. (d) See also: McCaffrey, J. G.; Parnis, J. M.; Ozin, G. A.; Breckenridge, W. H. *J. Phys. Chem.* 1985, *89*, 4945.

[5] Earlier workers reported formation of Mg(H)OEt from the reaction of SiH_4 with $MgEt_2$ in Et_2O: Bauer, R. Z. *Naturforsch., Teil B* 1962, *17*, 201.

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