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Synthesis and Structural Characterization of Three Compounds with Zr(III)–Zr(III) Bonds: $Zr_2Cl_6(dppe)_2\cdot 2C_2H_4Cl_2\cdot 1.5C_6H_5CH_3$, $Zr_2Cl_6(PMe_2Ph)_4$, and $Zr_2Cl_6(PEt_3)_4$

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The syntheses and crystal and molecular structures of $Zr_2Cl_6(dppe)_2\cdot 2C_2H_4Cl_2\cdot 1.5C_6H_5CH_3$ (**1**), $Zr_2Cl_6(PMe_2Ph)_4$ (**2**), and $Zr_2Cl_6(PEt_3)_4$ (**3**) are described. They were obtained by reduction of $ZrCl_4$ with 1 equiv of sodium amalgam in the presence of the appropriate phosphine. $Zr_2Cl_6(dppe)_2\cdot 2C_2H_4Cl_2\cdot 1.5C_6H_5CH_3$ (**1**) crystallizes from toluene/dichloroethane in the triclinic space group $P\bar{1}$ with unit cell dimensions a = 15.905 (1) Å, b = 20.398 (2) Å, c = 11.859 (2) Å, α = 98.21 (1)°, β = 110.59 (1)°, γ = 97.33 (1)°, V = 3497 (2) Å^3, and d_{calcd} = 1.445 g/cm^3 for Z = 2. The structure was refined to R = 0.060 and R_w = 0.069 for 3978 reflections with $I > 3\sigma(I)$. $Zr_2Cl_6(PMe_2Ph)_4$ (**2**) crystallizes from toluene in the triclinic space group $P\bar{1}$ with unit cell dimensions a = 10.982 (5) Å, b = 11.079 (4) Å, c = 9.838 (4) Å, α = 114.12 (3)°, β = 108.33 (4)°, γ = 86.41 (4)°, V = 1034 (2) Å^3, and d_{calcd} = 1.522 g/cm^3 for Z = 1. The structure was refined to R = 0.049 and R_w = 0.072 for 1880 reflections having $I > 3\sigma(I)$. $Zr_2Cl_6(PEt_3)_4$ (**3**) crystallizes from toluene in the monoclinic space group $P2_1/n$ with unit cell dimensions a = 10.570 (2) Å, b = 14.997 (3) Å, c = 13.227 (2) Å, β = 108.54 (2)°, V = 1987 (1) Å^3, and d_{calcd} = 1.450 g/cm^3 for Z = 2. The structure was refined to R = 0.047 and R_w = 0.070 for 1815 reflections having $I > 3\sigma(I)$. All compounds are of the edge-sharing bioctahedron type, having cis phosphine ligands in the same plane as the bridging chlorides, with Zr–Zr distances of 3.104 [5], 3.127 (1), and 3.169 (1) Å for **1**, **2**, and **3**, respectively.

Introduction

The investigation of binuclear compounds of the edge-sharing bioctahedron type has led to the accumulation of a large amount of structural data[1] as well as a moderate amount of interpretative theory.[2-5] In the majority of the previously known compounds the pairs of metal atoms have formed double or triple bonds to each other and this can be viewed as an important factor contributing to the stability of the binuclear molecule as compared to that of two separate mononuclear complexes. In the case of two d^1 metal ions, which are capable of forming only a single bond, the question naturally arises as to whether binuclear molecules will be stable.

It must also be taken into consideration that for the early transition metals coordination numbers higher than 6 are common. This means that the possible formation of more than six metal-to-ligand bonds is still another factor that could militate against the edge-sharing bioctahedral structure, either by favoring the formation of seven- or eight-coordinate mononuclear complexes or by permitting alternative forms of dimerization, as in the $M_2X_8(PR_3)_4$ molecules (M = Nb, Ta) that consist of face-sharing square antiprisms.[6-9]

Only one structurally characterized example of an edge-sharing bioctahedron containing M(III) atoms from group IV has previously been reported,[10] namely $Zr_2Cl_6(PBu_3)_4$ (Bu = n-C_4H_9), in which a metal-to-metal distance of 3.182 (1) Å was found. Since the molecule is diamagnetic, the existence of a Zr–Zr bond of order 1 seems to be indicated. Because of our interest in general, comparative studies of M–M bonds within the structural context of the edge-sharing biotahedron, we have been attempting to isolate and characterize additional examples of this type of compound containing the metals Zr or Hf. Our experience to date indicates that the chemical and thermodynamic stability of such molecules is generally not great and their isolation may in general be difficult. However, we found that compounds **1** and **2**, as well as those previously reported,[10] are accessible in crystalline form and in good yield. We report here their preparation and structure.

Experimental Section

All manipulations were carried out under an argon atmosphere by using standard vacuum-line and Schlenk techniques. The solvents were freshly distilled under nitrogen from the appropriate drying agent. $ZrCl_4$, bis(diphenylphosphino)ethane (dppe), and PMe_2Ph were purchased from Strem Chemicals, and PEt_3 was obtained from Aldrich. The were used without further purification.

Preparation of $Zr_2Cl_6(dppe)_2\cdot 2C_2H_4Cl_2\cdot 1.5C_6H_5CH_3$ (1). $ZrCl_4$ (0.23 g, 1.0 mmol), dppe (0.50 g, 1.0 mmol), and 0.41% NaHg (5.62 g, 1.0 mmol) were stirred vigorously in 20 mL of toluene for 24 h. Dichloroethane (35 mL) was added to the green suspension that formed. The resulting green solution was filtered through Celite. Within minutes a crop of green prisms formed in the flask. The yield was 1.16 g (76%).

Preparation of $Zr_2Cl_6(PMe_2Ph)_4$ (2) and $Zr_2Cl_6(PEt_3)_3$ (3). Both compounds were prepared by the literature method[10] described for $Zr_2Cl_6(P$-n-$Bu_3)_4$ by using PMe_2Ph and PEt_3 instead of P-n-Bu_3. The yields were ~60%. Crystals suitable for X-ray diffraction studies were obtained from toluene solutions by layering with hexane.

X-ray Crystallography

Crystal Structure of $Zr_2Cl_6(dppe)_2\cdot 2C_2H_4Cl_2\cdot 1.5C_6H_5CH_3$ (1). A small crystal of $Zr_2Cl_6(dppe)_2\cdot 2C_2H_4Cl_2\cdot 1.5C_6H_5CH_3$ (**1**) was mounted inside a thin-walled capillary with epoxy cement. Geometric and intensity data were taken by an Enraf-Nonius CAD-4 automated diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation by using procedures described previously.[11] The unit cell was indexed on 25 strong reflections in the range 12° ≤ 2θ ≤ 25° that were located by an automatic search routine. The crystal system was found to be triclinic. The lattice dimensions were verified by axial photography. Least-squares analysis was used to refine the cell dimensions and the orientation matrix.

The intensity data were gathered by the ω–2θ scan technique in the range 4° ≤ 2θ ≤ 45°. During the data collection 3 intensity standards were collected every 100 reflections. Slow decay of the intensity of the standards was observed. When the intensity of the standards reached 60% of the initial values, the data collection was interrupted and azimuthal scans (ψ scans) of 9 reflections having an Eulerian angle χ near 90° were collected. The data collection was completed with another crystal of approximately the same dimensions. The data were corrected for Lorentz and polarization factors. Decay and semiempirical absorption corrections were also applied.[12] Both data sets were merged together

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Table I. Crystal Data for $Zr_2Cl_6(dppe)_2 \cdot 2C_2H_4Cl_2 \cdot 1.5C_6H_5CH_3$ (**1**), $Zr_2Cl_6(PMe_2Ph)_4$ (**2**), and $Zr_2Cl_6(PEt_3)_4$ (**3**)

	1	2	3
formula	$C_{66}H_{67}Cl_{10}P_4Zr_2$	$C_{32}H_{44}Cl_6P_4Zr_2$	$C_{24}H_{60}Cl_6P_4Zr_2$
fw	1521.1	947.8	867.8
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
systematic absences	none	none	$h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$
a, Å	15.905 (1)	10.982 (5)	10.570 (2)
b, Å	20.389 (2)	11.079 (4)	14.997 (3)
c, Å	11.859 (2)	9.838 (4)	13.227 (2)
α, deg	98.21 (1)	114.12 (3)	90.0
β, deg	110.59 (1)	108.33 (4)	108.54 (2)
γ, deg	97.33 (1)	86.41 (4)	90.0
V, Å^3	3497 (2)	1034 (2)	1987 (1)
Z	2	1	2
d_{calcd}, g/cm^3	1.445	1.522	1.450
cryst size, mm	0.35 × 0.20 × 0.15	0.50 × 0.45 × 0.45	0.40 × 0.35 × 0.20
μ(Mo Kα), cm^{-1}	8.062	10.616	10.972
data collecn instrument	CAD-4	Rigaku	CAD-4/Syntex P3
radiation (monochromated in incident beam)		Mo Kα (λ = 0.71073 Å)	
orientation rflns: range (2θ), deg	25; $12 < 2\theta < 25$	25; $20 < 2\theta < 30$	25; $12 < 2\theta < 25$
temp, °C	23	21	23
scan method		ω–2θ	
data collecn range, 2θ, deg		$4 \leq 2\theta \leq 45$	
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	4003, 3978	2299, 1880	2099, 1815
no. of params refined	669	199	157
transmission factors: max, min	1.00, 0.95	1.00, 0.94	
R^a	0.060	0.049	0.047
$R_w{}^b$	0.069	0.072	0.070
quality-of-fit indicator^c	1.629	1.529	1.571
largest shift/esd, final cycle	0.48	0.01	0.31
largest peak, e/Å^3	0.73	0.72	0.56

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

with the help of the SHELX-76 program,[13] giving the agreement factor R = 0.021.

The structure was refined in the triclinic space group $P\bar{1}$. The positions of the two Zr atoms were determined from a Patterson map. The subsequent development of the coordination spheres of the two separate dizirconium molecules was routine. All non-hydrogen atoms were located with an alternating sequence of least-squares refinement and difference Fourier maps. After the refinement of the two independent dimers located at centers of inversion was completed, there were still several high-intensity peaks in the difference Fourier map. They were successfully modeled as two dichloroethane molecules and one toluene molecule at general positions. The ring of another toluene molecule was located at a center of inversion. However, the carbon atom of the methyl group could not be found and was not included in the calculations. The atoms of the solvent molecules showed somewhat high thermal parameters. This may be due to high thermal motion and/or to some sort of disorder. Table I summarizes the data pertaining to the crystallographic procedures and refinement. The atomic positional parameters are given in Table II. Selected bond distances and angles are listed in Table V.

Crystal Structure of $Zr_2Cl_6(PMe_2Ph)_4$ (2). The general procedures were routine and have been already described.[11] Lorentz, polarization, decay, and empirical absorption corrections were applied to the data.[12] A small crystal was affixed with epoxy cement inside a thin-walled capillary and the capillary then mounted on the goniometer head of a Rigaku diffractometer. The data were collected as indicated in Table I. The solution and refinement of the structure proceeded straightforwardly in the triclinic space group $P\bar{1}$. The coordinates of the Zr atom were obtained from a Patterson map, and an alternating series of least-squares refinements and difference electron density maps revealed all the remaining atoms. Hydrogen atoms were not included in the refinement, and all other atoms were refined anisotropically. No disorder or other nonroutine problem arose. The atomic positional parameters are given in Table III. Important bond distances and angles are listed in Table VI.

Crystal Structure of $Zr_2Cl_6(PEt_3)_4$ (3). A small crystal of $Zr_2Cl_6(PEt_3)_4$ (**3**) was glued inside a thin-walled capillary with epoxy cement. The capillary was mounted on the goniometer head of a CAD-4 diffractometer. The data were collected as indicated in Table I by using the procedures already described.[11] However, due to instrument failure the data collection, with the same crystal, was completed on a Syntex P3 diffractometer. Lorentz, polarization, and decay corrections were applied to the data,[12c] and both data sets were merged together with the help of the SHELX-76 program.[13] The structure was solved in the monoclinic $P2_1/n$ space group. The initial coordinates of the Zr atom were derived from a three-dimensional Patterson map. The remaining non-hydrogen atoms were located through alternating series of least-squares refinements and difference electron density maps. All refined atoms were given anisotropic thermal parameters except for carbon atoms of a disordered PEt_3 ligand. The two sets of three ethyl groups were refined with isotropic thermal parameters at half-occupancy. Hydrogen atoms were not included in the calculations. The atomic positional parameters are given in Table IV. Important bond distances and angles are listed in Table VII.

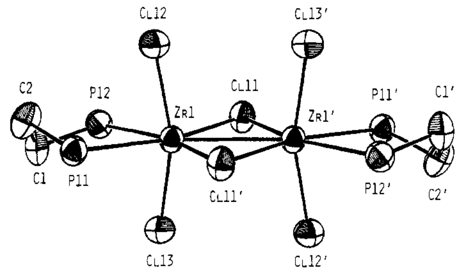

Figure 1. ORTEP drawing of the $Zr_2Cl_6P_4$ fragment of one of the $Zr_2Cl_6(dppe)_2$ molecules of $Zr_2Cl_6(dppe)_2 \cdot 2C_2H_4Cl_2 \cdot 1.5C_6H_5CH_3$ (**1**) with the atom-labeling scheme. Atoms are represented by their ellipsoids at the 50% probability level. Carbon atoms of the phenyl rings are omitted for clarity.

Results

Compound 1. There are two independent dinuclear molecules in the unit cell, each residing on a crystallographic inversion center. The two molecules are essentially identical, and one of them is depicted in Figure 1. While for each molecule the only rigorous symmetry is $\bar{1}$, each one has, effectively, the higher symmetry C_{2h}, where the C_2 axis coincides with the Zr–Zr bond and the plane of symmetry contains the two bridging chlorine atoms. The two five-membered chelate rings are puckered in the manner most frequently seen; in order to conform with the inversion center, they have enantiomorphous conformations,[14] one λ and the other δ,

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[13] Sheldrick, G. M. "SHELX-76, Program for Crystal Structure Determination"; University of Cambridge: Cambridge, England.

Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $Zr_2Cl_6(dppe)_2 \cdot 2C_2H_4Cl_2 \cdot 1.5C_6H_5CH_3$ (**1**)^a

atom	*x*	*y*	*z*	*B*	atom	*x*	*y*	*z*	*B*
Zr1	0.05198 (9)	0.06540 (6)	0.0977 (1)	3.22 (3)	C52	0.399 (1)	0.6953 (8)	0.206 (1)	6.4 (5)
Zr2	0.45149 (8)	0.56032 (6)	0.5155 (1)	3.35 (3)	C53	0.444 (1)	0.7411 (8)	0.158 (1)	8.1 (5)
Cl11	−0.0732 (2)	0.0546 (2)	−0.1113 (3)	4.10 (9)	C54	0.496 (1)	0.8026 (7)	0.225 (1)	7.3 (5)
Cl12	0.1741 (2)	0.0939 (2)	0.0250 (3)	4.45 (9)	C55	0.512 (1)	0.8201 (8)	0.351 (2)	9.0 (6)
Cl13	−0.0465 (2)	0.0712 (2)	0.2135 (3)	4.70 (9)	C56	0.467 (1)	0.7725 (7)	0.402 (1)	6.4 (5)
Cl21	0.4640 (2)	0.5007 (2)	0.3199 (3)	4.14 (9)	C61	0.2437 (9)	0.6245 (7)	0.268 (1)	5.2 (4)
Cl22	0.5782 (2)	0.6526 (2)	0.5620 (3)	4.76 (9)	C62	0.223 (1)	0.5567 (8)	0.203 (1)	6.9 (5)
Cl23	0.3010 (2)	0.4937 (2)	0.4677 (3)	5.3 (1)	C63	0.139 (1)	0.536 (1)	0.091 (2)	10.1 (7)
P11	0.1989 (2)	0.1085 (2)	0.3205 (3)	3.79 (9)	C64	0.078 (1)	0.5798 (9)	0.061 (2)	11.0 (7)
P12	0.0630 (3)	0.2048 (2)	0.1497 (3)	3.91 (9)	C65	0.101 (1)	0.6456 (9)	0.131 (2)	10.4 (7)
P21	0.3542 (3)	0.6517 (2)	0.3936 (3)	4.4 (1)	C66	0.183 (1)	0.6694 (8)	0.238 (1)	7.5 (5)
P22	0.3996 (2)	0.6312 (2)	0.6886 (3)	3.98 (9)	C71	0.4792 (9)	0.7051 (6)	0.797 (1)	4.2 (3)
C1	0.1404 (9)	0.2311 (6)	0.314 (1)	4.7 (4)	C72	0.4451 (9)	0.7626 (6)	0.836 (1)	4.9 (4)
C2	0.2289 (9)	0.2022 (6)	0.334 (1)	4.7 (4)	C73	0.511 (1)	0.8191 (7)	0.921 (1)	6.2 (5)
C3	0.332 (1)	0.7077 (6)	0.514 (1)	5.7 (4)	C74	0.605 (1)	0.8159 (7)	0.964 (1)	6.5 (5)
C4	0.3004 (8)	0.6633 (6)	0.597 (1)	4.2 (3)	C75	0.637 (1)	0.7600 (7)	0.925 (1)	6.0 (4)
C11	0.1158 (9)	0.2589 (6)	0.071 (1)	4.2 (3)	C76	0.5714 (9)	0.7037 (7)	0.839 (1)	4.9 (4)
C12	0.089 (1)	0.2372 (7)	−0.053 (1)	5.6 (4)	C81	0.3576 (8)	0.5859 (6)	0.786 (1)	4.3 (3)
C13	0.124 (1)	0.2814 (7)	−0.119 (1)	6.6 (5)	C82	0.266 (1)	0.5596 (7)	0.751 (1)	6.8 (4)
C14	0.181 (1)	0.3430 (7)	−0.060 (1)	7.1 (5)	C83	0.237 (1)	0.5220 (8)	0.833 (1)	7.9 (5)
C15	0.208 (1)	0.3623 (7)	0.067 (1)	6.8 (5)	C84	0.304 (1)	0.5157 (7)	0.945 (1)	7.1 (5)
C16	0.174 (1)	0.3210 (6)	0.134 (1)	5.8 (4)	C85	0.391 (1)	0.5429 (8)	0.975 (1)	9.0 (6)
C21	−0.0398 (9)	0.2402 (6)	0.140 (1)	4.8 (4)	C86	0.422 (1)	0.5773 (7)	0.895 (1)	6.4 (5)
C22	−0.119 (1)	0.2120 (8)	0.044 (2)	7.8 (6)	Cl50	0.8071 (4)	0.6685 (3)	0.3863 (4)	12.0 (2)
C23	−0.199 (1)	0.2398 (9)	0.025 (2)	10.1 (7)	Cl60	0.6291 (4)	0.6697 (3)	0.1446 (5)	11.9 (2)
C24	−0.193 (1)	0.2960 (8)	0.114 (2)	8.1 (6)	C5	0.686 (1)	0.621 (1)	0.337 (2)	13.8 (6)
C25	−0.113 (1)	0.3250 (9)	0.208 (2)	10.7 (6)	C6	0.622 (1)	0.645 (1)	0.273 (2)	13.2 (8)
C26	−0.032 (1)	0.2984 (9)	0.223 (1)	8.3 (5)	Cl70	0.6378 (7)	0.0937 (5)	−0.0464 (9)	22.5 (4)*
C31	0.3039 (9)	0.0780 (7)	0.335 (1)	4.7 (4)	Cl80	0.6180 (7)	−0.0000 (5)	0.1487 (9)	24.4 (4)*
C32	0.3715 (9)	0.1148 (8)	0.303 (1)	5.7 (4)	C7	0.690 (2)	0.022 (1)	−0.009 (2)	15.7 (9)*
C33	0.454 (1)	0.0890 (9)	0.309 (1)	7.9 (6)	C8	0.714 (2)	0.031 (1)	0.111 (2)	17 (1)*
C34	0.463 (1)	0.0267 (9)	0.339 (1)	8.9 (6)	C91	0.087 (2)	0.847 (1)	0.388 (2)	17 (1)*
C35	0.396 (1)	−0.0069 (9)	0.373 (2)	9.4 (6)	C92	0.161 (1)	0.847 (1)	0.373 (2)	10.9 (6)*
C36	0.311 (1)	0.0141 (8)	0.366 (1)	7.7 (5)	C93	0.238 (2)	0.863 (1)	0.467 (2)	15.9 (9)*
C41	0.1851 (9)	0.0993 (6)	0.465 (1)	4.0 (3)	C94	0.245 (2)	0.857 (2)	0.607 (3)	25 (2)*
C42	0.232 (1)	0.1490 (8)	0.570 (1)	8.3 (6)	C95	0.128 (2)	0.811 (2)	0.575 (3)	20 (1)*
C43	0.222 (1)	0.1423 (8)	0.681 (1)	9.7 (7)	C96	0.051 (2)	0.817 (2)	0.484 (3)	23 (1)*
C44	0.164 (1)	0.0848 (9)	0.683 (1)	9.3 (6)	C97	0.068 (1)	0.733 (1)	0.473 (2)	11.3 (7)*
C45	0.121 (1)	0.037 (1)	0.582 (1)	9.7 (6)	C101	0.050 (2)	0.466 (1)	0.475 (2)	15.2 (9)*
C46	0.128 (1)	0.0419 (8)	0.463 (1)	7.2 (5)	C102	0.055 (2)	0.516 (1)	0.395 (2)	18 (1)*
C51	0.4108 (9)	0.7130 (6)	0.329 (1)	4.6 (4)	C103	−0.012 (2)	0.558 (1)	0.449 (3)	19 (1)*

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

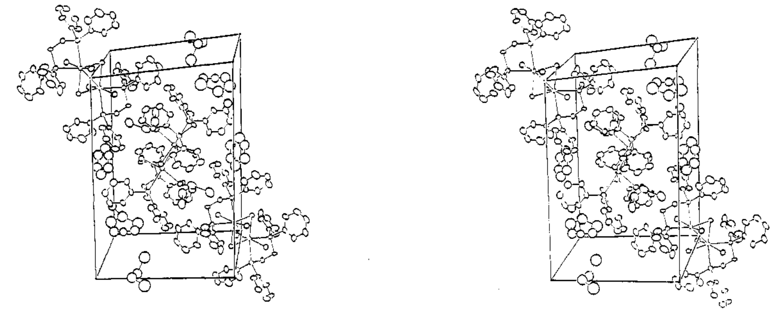

Figure 2. ORTEP stereodiagram for $Zr_2Cl_6(dppe)_2 \cdot 2C_2H_4Cl_2 \cdot 1.5C_6H_5CH_3$ (**1**). The axes are oriented as follows: *a*, across; *b*, down; *c*, toward viewer.

and the molecule is a meso form. In $M_2Cl_6(chelate)_2$ molecules generally, there appears to be no particular preference for meso ($\delta\lambda$) as opposed to $\delta\delta$ or $\lambda\lambda$ forms.[15-17] One compound, $Ta_2Cl_6(depe)_2$, has been obtained in both meso and optically active forms,[16] and no significant differences in molecular dimensions apart from those intrinsic to the ring conformation were found. In the only other exact stoichiometric analogue to **1**, namely $W_2Cl_6(dppe)_2$, the meso form was found.[17] Very probably, crystal-packing forces play a major role in determining the ring conformations and in solution it is possible that there could be a mixture of the meso and equimolar amounts of $\delta\delta$ and $\lambda\lambda$ isomers.

The requirements of the chelate rings lead to relatively small P–Zr–P angles of ca. 76°, whereas in the other $Zr_2Cl_6(PR_3)_4$ compounds the corresponding angles are ca. 96°. The internal Cl_b–Zr–Cl_b angles are ca. 104.5°, which indicates a drawing together of the Zr atoms as a result of Zr–Zr bond formation.

Compounds 2 and 3. In each of these compounds the molecules are packed without solvent of crystallization and they reside on inversion centers. They have the same type structure as the previously reported[10] $Zr_2Cl_6(P\text{-}n\text{-}Bu_3)_4$, namely, one in which all four of the phosphine ligands lie in the central or equatorial plane. Thus, all three $Zr_2Cl_6(PR_3)_4$ compounds differ from the other

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Table III. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $Zr_2Cl_6(PMe_2Ph)_4$ (**2**)[a]

atom	x	y	z	B
Zr	0.10936 (9)	0.41650 (8)	0.05434 (8)	2.47 (2)
Cl(1)	−0.0426 (2)	0.5522 (2)	0.2001 (2)	3.34 (6)
Cl(2)	0.2853 (3)	0.5883 (2)	0.1983 (3)	4.21 (7)
Cl(3)	−0.0131 (3)	0.2064 (2)	−0.0616 (3)	4.10 (6)
P(1)	0.1811 (3)	0.3603 (2)	0.3162 (2)	3.31 (6)
P(2)	0.2993 (2)	0.2843 (2)	−0.0669 (2)	2.92 (6)
C(11)	0.2879 (9)	0.2296 (8)	0.3276 (9)	3.2 (2)
C(12)	0.411 (1)	0.2575 (9)	0.4320 (9)	3.9 (2)
C(13)	0.490 (1)	0.157 (1)	0.431 (1)	5.7 (3)
C(14)	0.447 (1)	0.024 (1)	0.325 (1)	5.3 (3)
C(15)	0.321 (1)	−0.0033 (9)	0.221 (1)	5.1 (3)
C(16)	0.242 (1)	0.0977 (9)	0.218 (1)	4.3 (3)
C(17)	0.256 (1)	0.509 (1)	0.499 (1)	5.8 (4)
C(18)	0.043 (1)	0.305 (1)	0.352 (1)	5.4 (3)
C(21)	0.2528 (9)	0.1182 (8)	−0.2234 (9)	3.1 (2)
C(22)	0.268 (1)	0.0082 (9)	−0.185 (1)	5.3 (3)
C(23)	0.226 (1)	−0.121 (1)	−0.306 (1)	6.1 (4)
C(24)	0.175 (1)	−0.137 (1)	−0.455 (1)	5.7 (4)
C(25)	0.160 (1)	−0.025 (1)	−0.494 (1)	6.5 (4)
C(26)	0.200 (1)	0.099 (1)	−0.379 (1)	5.0 (3)
C(27)	0.448 (1)	0.266 (1)	0.071 (1)	4.7 (3)
C(28)	0.362 (1)	0.3731 (9)	−0.158 (1)	4.5 (3)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement 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. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $Zr_2Cl_6(PEt_3)_4$ (**3**)[a]

atom	x	y	z	B
Zr	0.08238 (7)	0.41986 (4)	0.06791 (5)	3.24 (2)
Cl1	0.1607 (2)	0.5771 (1)	0.0490 (2)	4.48 (5)
Cl2	0.0365 (2)	0.4457 (2)	0.2342 (2)	4.96 (5)
Cl3	0.1688 (2)	0.3619 (1)	−0.0677 (2)	4.75 (5)
P1	0.0131 (2)	0.2401 (1)	0.0844 (2)	3.57 (5)
P2	0.3457 (3)	0.4055 (2)	0.2053 (2)	5.52 (6)
C1	−0.0768 (9)	0.2178 (6)	0.1793 (6)	4.9 (2)
C2	−0.2114 (9)	0.2693 (7)	0.1546 (8)	6.5 (3)
C3	0.1404 (9)	0.1517 (5)	0.1276 (7)	4.9 (2)
C4	0.2214 (9)	0.1374 (6)	0.0510 (8)	6.4 (3)
C5	−0.0967 (9)	0.1992 (5)	−0.0448 (6)	4.6 (2)
C6	−0.149 (1)	0.1014 (6)	−0.0451 (8)	6.5 (3)
C7	0.472 (2)	0.359 (2)	0.153 (2)	7.8 (6)*
C8	0.507 (3)	0.582 (2)	0.926 (2)	8.6 (6)*
C9	0.341 (2)	0.312 (1)	0.312 (1)	5.3 (4)*
C10	0.486 (2)	0.293 (2)	0.391 (2)	7.2 (5)*
C11	0.427 (2)	0.494 (1)	0.281 (1)	6.1 (4)*
C12	0.383 (2)	0.582 (2)	0.302 (2)	7.4 (5)*
C13	0.396 (2)	0.480 (1)	0.326 (2)	6.2 (4)*
C14	0.356 (2)	0.545 (2)	0.344 (2)	8.4 (6)*
C15	0.531 (2)	0.544 (1)	0.878 (2)	6.5 (5)*
C16	0.397 (2)	0.524 (2)	0.823 (2)	8.1 (6)*
C17	0.444 (3)	0.306 (2)	0.254 (2)	10.1 (7)*
C18	0.416 (3)	0.229 (2)	0.838 (2)	11.6 (9)*

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

structurally characterized $M_2C_6L_4$ compounds, namely, $Ta_2Cl_6(PMe_3)_4$[18] and $W_2Cl_6(py)_4$,[19] which have structures with two axial L ligands on one metal atom and two equatorial L ligands on the other metal atom. The factors favoring one of these structure types rather than the other have not been identified.

The principal bond lengths and angles (or the appropriate average values) for compounds **1**, **2**, and **3**, as well as for $Zr_2Cl_6(P\text{-}n\text{-}Bu_3)_4$, are listed for comparison in Table VIII.

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for $Zr_2Cl_6(dppe)_2{\cdot}2C_2H_4Cl_2{\cdot}1.5C_6H_5CH_3$ (**1**)[a]

Zr1–Zr1′	3.099 (2)	Zr2–Zr2′	3.109 (2)
Zr1–Cl11	2.534 (3)	Zr2–Cl21	2.547 (3)
Zr1–Cl11′	2.528 (3)	Zr2–Cl21′	2.538 (3)
Zr1–Cl12	2.424 (3)	Zr2–Cl22	2.414 (3)
Zr1–Cl13	2.421 (3)	Zr2–Cl23	2.421 (3)
Zr1–P11	2.771 (3)	Zr2–P21	2.808 (3)
Zr1–P12	2.785 (3)	Zr2–P22	2.762 (3)
P11–C2	1.874 (10)	P21–C3	1.863 (11)
P12–C1	1.857 (11)	P22–C4	1.834 (11)
C1–C2	1.548 (15)	C3–C4	1.583 (15)

Zr1–Zr1–Cl12	97.75 (8)	Zr2–Zr2–Cl22	99.11 (9)
Zr1–Zr1–Cl13	100.32 (9)	Zr2–Zr2–Cl23	96.94 (9)
Zr1–Cl11–Zr1	75.48 (8)	Zr2–Cl21–Zr2	75.38 (8)
Cl11–Zr1–Cl11′	104.52 (8)	Cl21–Zr2–Cl21′	104.62 (8)
Cl12–Zr1–Cl13	161.8 (1)	Cl22–Zr2–Cl23	163.8 (1)
P11–Zr1–P12	76.25 (9)	P21–Zr2–P22	75.64 (9)
Zr1–P11–C2	104.2 (4)	Zr2–P21–C3	105.1 (4)
Zr1–P12–C1	104.0 (4)	Zr2–P22–C4	104.0 (4)
P11–C2–C1	108.0 (8)	P21–C3–C4	109.5 (8)
P12–C1–C2	109.5 (8)	P22–C4–C3	107.9 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

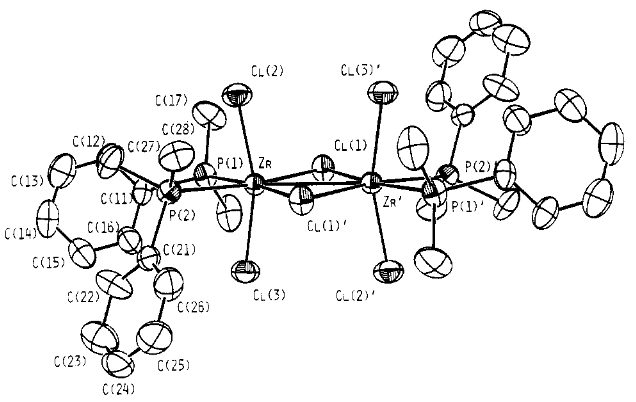

Figure 3. ORTEP drawing of $Zr_2Cl_6(PMe_2Ph)_4$ (**2**) with the atom-labeling scheme. Atoms are represented by their ellipsoids at the 50% probability level.

Discussion

The work reported here was undertaken for two reasons: (1) We are interested in having more detailed knowledge of (μ-Cl)$_2$-bridged dizirconium(III) compounds for comparison with the similar compounds of the metals of groups V–VIII, where M–M bonds of various orders exist.[1,5,20] (2) We wish to explore further the chemistry whereby $Zr_2X_6(PR_3)_4$ compounds give rise to the olefin-bridged compounds $X_3(PR_3)Zr(\mu_2,\eta^4\text{-}C_2R_4)Zr(PR_3)X_3$, which we have recently reported.[21] We shall deal with these two aspects of the work in the order they have just been mentioned and then with a few other points.

The Zr–Zr distances in all four compounds listed in Table VIII are similar, ranging from 3.10 to 3.18 Å. In all cases the Cl_b–Zr–Cl_b angles (102.6–104.6°) show that an attractive force exists between the metal atoms and we therefore associate Zr–Zr distances of 3.14 ± 0.04 Å with the presence of Zr–Zr single bonds formed by overlap of dσ orbitals (a σ^2 configuration).

The two compounds with which $Zr_2Cl_6(dppe)_2$ can most informatively be compared are the stoichiometric analogues containing Nb[22] and Mo.[17] Figure 6 shows a comparison of the M–M distances in these three compounds with one another in a way that takes account of the trend in atomic radii as the latter are reflected in the R_1 values of Pauling.[23] By plotting the differences between

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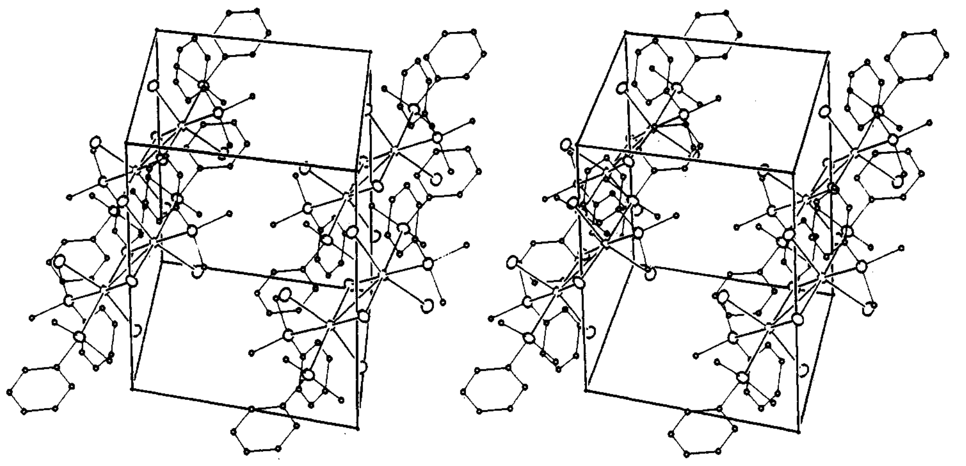


Figure 4. ORTEP stereodiagram for $Zr_2Cl_6(PMe_2Ph)_4$ (**2**). The axes are oriented as follows: *a*, across; *b*, down; *c*, toward viewer.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $Zr_2Cl_6(PMe_2Ph)_4$ (**2**)[a]

Zr–Zr	3.127 (1)	Zr–P(1)	2.760 (3)	P(1)–C(18)	1.85 (1)
Zr–Cl(1)	2.555 (3)	Zr–P(2)	2.770 (3)	P(2)–C(21)	1.824 (7)
Zr–Cl(1)′	2.539 (2)	P(1)–C(11)	1.823 (9)	P(2)–C(27)	1.83 (1)
Zr–Cl(2)	2.429 (3)	P(1)–C(17)	1.853 (8)	P(2)–C(28)	1.85 (1)
Zr–Cl(3)	2.405 (3)				
Zr–Zr–Cl(2)	99.22 (7)	Cl(1)′–Zr–P(2)	81.03 (8)	Zr–P(1)–C(18)	112.9 (3)
Zr–Zr–Cl(3)	98.64 (7)	Cl(2)–Zr–Cl(3)	162.1 (1)	Zr–P(2)–C(21)	116.8 (3)
Cl(1)–Zr–Cl(1)′	104.26 (8)	Cl(2)–Zr–P(1)	86.19 (9)	Zr–P(2)–C(27)	117.7 (4)
Cl(1)–Zr–Cl(2)	94.28 (8)	Cl(2)–Zr–P(2)	79.76 (8)	Zr–P(2)–C(28)	111.9 (3)
Cl(1)–Zr–Cl(3)	96.54 (9)	Cl(3)–Zr–P(1)	82.02 (9)	C(11)–P(1)–C(17)	104.9 (5)
Cl(1)–Zr–P(1)	78.87 (8)	Cl(3)–Zr–P(2)	88.19 (9)	C(11)–P(1)–C(18)	100.4 (5)
Cl(1)–Zr–P(2)	172.57 (6)	P(1)–Zr–P(2)	96.19 (8)	C(17)–P(1)–C(18)	104.0 (6)
Cl(1)′–Zr–Cl(2)	97.02 (9)	Zr–Cl(1)–Zr	75.74 (7)	C(21)–P(2)–C(27)	104.4 (4)
Cl(1)′–Zr–Cl(3)	94.04 (8)	Zr–P(1)–C(11)	120.8 (3)	C(21)–P(2)–C(28)	103.0 (4)
Cl(1)′–Zr–P(1)	175.27 (7)	Zr–P(1)–C(17)	112.0 (4)	C(27)–P(2)–C(28)	101.0 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Selected Bond Distances (Å) and Bond Angles (deg) for $Zr_2Cl_6(PEt_3)_4$ (**3**)[a]

Zr1–Zr1′	3.169 (1)	Zr1–Cl1	2.538 (2)
Zr1–Cl1′	2.542 (2)	Zr1–Cl2	2.430 (2)
Zr1–Cl3	2.419 (2)	Zr1–P1	2.820 (2)
Zr1–P2	2.806 (2)		
Zr1–Zr1′–Cl2	99.20 (5)	Zr1–Zr1′–Cl3	96.96 (5)
Zr1–Cl11–Zr1	77.19 (5)	Cl1–Zr1–Cl1′	102.81 (5)
P1–Zr1–P2	96.02 (6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

the actual M-M distances and $2\Delta_M$, where $\Delta_M = R_1^{Nb} - R_1^{M}$, we obtain a direct indication of how the actual M-M bond strengths differ from the bond strength in the niobium compound, and from this we may make inferences regarding electronic configurations and bond orders.

It is clear from Figure 6 that both the Zr–Zr and Mo–Mo bonds are weaker than the Nb–Nb bond. This is consistent with the presumed existence of a $\sigma^2\pi^2$ bonding configuration in the niobium compound and only a σ^2 configuration for the zirconium compound. The fact that the Mo–Mo bond length is also appreciably greater than the Nb–Nb distance after allowance for the inherent decrease in atomic size is indicative of a $\sigma^2\pi^2\delta^{*2}$ configuration in the molybdenum case, in accord with results previously reported for $Mo_2Cl_6(dppm)_2$ and $Mo_2Cl_6(dmpm)_2$ compounds.[1,5,20]

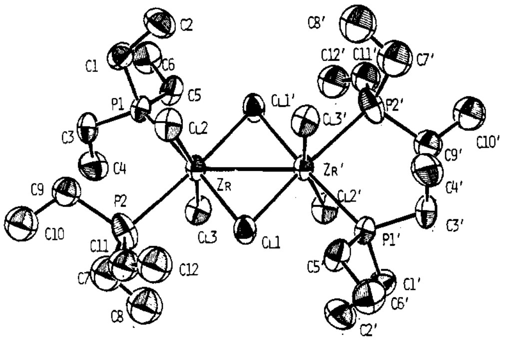


Figure 5. ORTEP drawing of $Zr_2Cl_6(PEt_3)_4$ (**3**) with the atom-labeling scheme. Atoms are represented by their ellipsoids at the 50% probability level.

Turning now to the reactivity of the zirconium compounds with 1,2-dichloroethane to give μ_2,η^4-C_2H_4-bridged species,[21] we note the remarkable fact that the $Zr_2Cl_6(dppe)_2$ compound does not react. On the contrary, it can be recrystallized from 1,2-$C_2H_4Cl_2$ to give the solvated crystals that we used in the structure determination. The fact that an ethylene-bridged product is not ob-

Table VIII. Selected Bond Distances (Å) and Angles (deg) for $Zr_2Cl_6(LL)_2$ and $Zr_2Cl_6L_4$ Type Compounds

	Zr–Zr	Zr–P	P–Zr–P	Zr–Cl_b	Cl_b–Zr–Cl_b	Zr–Cl_t	Cl_t–Zr–Cl_t	source
$Zr_2Cl_6(dppe)_2$[a]	3.099 (2)	2.778 [7]	76.25 (9)	2.531 [3]	104.52 (8)	2.422 [2]	161.8 (1)	this work
	3.109 (2)	2.785 [23]	75.64 (9)	2.542 [4]	104.62 (8)	2.418 [4]	163.8 (1)	
$Zr_2Cl_6(PMe_2Ph)_4$	3.127 (1)	2.765 [5]	96.19 (8)	2.547 [8]	104.26 (8)	2.417 [12]	162.1 (1)	this work
$Zr_2Cl_6(PEt_3)_4$	3.169 (1)	2.813 [7]	96.02 (6)	2.540 [2]	102.81 (5)	2.424 [5]	163.77 (6)	this work
$Zr_2Cl_6(PBu_3)_4$	3.182 (1)	2.834 [5]	96.25 (5)	2.544 [2]	102.57 (5)	2.431 [2]	165.11 (6)	ref 10

[a] There are two independent dimers in the unit cell.

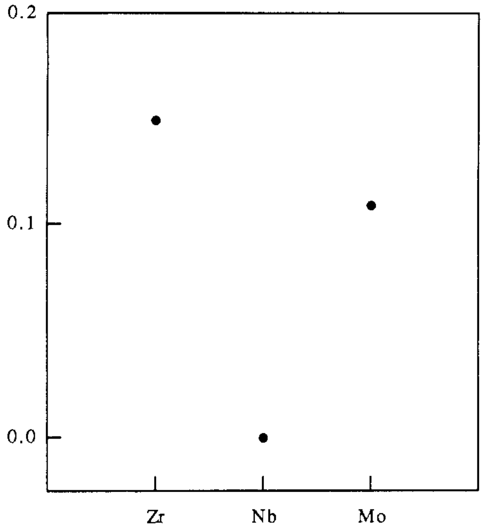
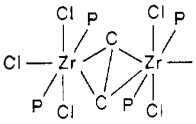


Figure 6. Plot of M-M distances in the three $M_2Cl_6(dppe)_2$ compounds corrected for the relative radii of the metal atoms (see text).

tained might well be attributed to the fact that the disposition of ligands found in the $Zr_2Cl_6(PEt_3)_4(C_2H_4)$ molecule, shown schematically as I, cannot be obtained when the pairs of phosphorus atoms are tied together by the dimethylene bridge. This, however, does not provide a wholly satisfactory explanation for the lack of reactivity of $Zr_2Cl_6(dppe)_2$ toward 1,2-$C_2H_4Cl_2$. We have previously suggested that the reaction of 1,2-$C_2H_4Cl_2$ with $Zr_2Cl_6(PR_3)_4$ compounds proceeds according to eq 1, although

$$2Zr_2Cl_6(PR_3)_4 + C_2H_4Cl_2 \rightarrow Zr_2Cl_6(PEt_3)_4(C_2H_4) + 2ZrCl_4(PEt_3)_2 \quad (1)$$

we have not conclusively demonstrated the formation of $ZrCl_4(PEt_3)_2$. It is not obvious why $Zr_2Cl_6(dppe)_2$ could not react with 1,2-$C_2H_4Cl_2$ according to eq 2. Clearly, the chemistry of these dinuclear zirconium(III) compounds requires further study.



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$$Zr_2Cl_6(dppe)_2 + C_2H_4Cl_2 \rightarrow 2ZrCl_4(dppe)_2 + C_2H_4 \quad (2)$$

A formal point to be noted here in comparing the structural parameters collected in Table VIII is that the Zr-P distances in the three $Zr_2Cl_6(PR_3)_4$ compounds show a variation, whereas all the Zr-Cl distances are essentially identical. We shall not attempt to reconcile the Zr-P distances in $Zr_2Cl_6(dppe)_2$ with those in the other compounds since the P-Zr-P angle is so very different and this might have a serious but unpredictable effect on the Zr-P bond strengths. We therefore compare only the last three compounds in Table VIII. We first note that statistically there is little significance to the apparent difference between the Zr-P distances in the PEt_3 and PBu_3 cases. It is not significant at the commonly used 3σ level since it and its esd are 0.021 [8] Å. However, between the value in the PMe_2Ph compound and the average of those in the other two compounds, there is a significant difference of 0.068 [8] Å. The shorter Zr-P bond in the PMe_2Ph compound indicates that this phosphine is a better donor (stronger Lewis base) than the trialkylphosphines. This order of basicity is in accord with the results of previous studies,[24,25] which have shown that, contrary to expectation from simple inductive arguments, phosphine basicity increases in the order $PMe_3 < PMe_2Ph < PMePh_2$.

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Registry No. **1**, 112571-00-3; **2**, 112421-71-3; **3**, 77061-31-5; $ZrCl_4$, 10026-11-6; Zr, 7440-67-7.

Supplementary Material Available: Full listings of bond distances, bond angles, and isotropic equivalent displacement parameters for $Zr_2Cl_6(dppe)_2 \cdot 2C_2H_4Cl_2 \cdot 1.5C_6H_5CH_3$ (**1**), $Zr_2Cl_6(PMe_2Ph)_4$ (**2**), and $Zr_2Cl_6(PEt_3)_4$ (**3**) (13 pages); listings of observed and calculated structure factors for **1**-**3** (46 pages). Ordering information is given on any current masthead page.

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Oxidative-Addition Reactions of S-S and Se-Se Bonds to Mo_2 and W_2 Quadruple Bonds

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Oxidative-addition chemistry of the quadruply bonded molybdenum and tungsten $M_2Cl_4(dppm)_2$ dimers (dppm = bis(diphenylphosphino)methane) has been investigated by using diphenyl disulfide, diphenyl diselenide, dichloromethane, and chlorine as the oxidizing agents. The products to be discussed here are the following: $W_2(\mu\text{-SPh})_2Cl_4(dppm)_2$ (**1**), $W_2(\mu\text{-SPh})(\mu\text{-Cl})Cl_4(dppm)_2$ (**2**), $W_2(\mu\text{-SePh})_2Cl_4(dppm)_2$ (**3**), $W_2(\mu\text{-SePh})(\mu\text{-Cl})Cl_4(dppm)_2$ (**4**), $W_2(\mu\text{-Cl})_2Cl_4(dppm)_2$ (**5**), $Mo_2(\mu\text{-SPh})(\mu\text{-Cl})Cl_4(dppm)_2$ (**6**), and $Mo_2(\mu\text{-Cl})_2Cl_4(dppm)_2$ (**7**). The structural characterization of compounds **1**, **4**, and **6** is reported here. Pertinent crystal data are as follows: **1**, $P\bar{1}$, a = 12.991 (2) Å, b = 13.851 (3) Å, c = 11.693 (2) Å, α = 111.28 (2)°, β = 103.43 (2)°, γ = 89.03 (2)°, V = 1903 (1) Å^3, W-W = 2.787 (1) Å; **4**, $Pna2_1$, a = 39.335 (10) Å, b = 15.371 (4) Å, c = 11.774 (3) Å, V = 7119 (5) Å^3, W-W = 2.708 (2) Å; **6**, $P2_1/n$, a = 12.096 (4) Å, b = 24.474 (6) Å, c = 23.329 (5) Å, β = 100.73 (2)°, V = 6786 (3) Å^3, Mo-Mo = 2.788 (1) Å.

Introduction

Previous reports from this laboratory have established the synthetic utility of oxidative-addition reactions in which reagents such as halogens, X_2, or disulfides, RSSR, react with M-M multiple bonds to give products in which the M-M bond order is reduced and X or RS groups serve as bridging ligands. The first examples were those in which $M_2Cl_4(dto)_2$ and $Mo_2Cl_4(dmpe)_2$ [dto = 3,6-dithiaoctane and dmpe = 1,2-bis(dimethylphosphino)ethane] reacted with diethyl disulfide to form $Mo_2(\mu\text{-SEt})_2Cl_4(dto)_2$ and $Mo_2(\mu\text{-SEt})_2Cl_4(dppe)_2$, respectively.[1] The formation of small amounts of $Mo_2(\mu\text{-Cl})_2Cl_4(dto)_2$ from $Mo_2Cl_4(dto)_2$ dissolved in dichloromethane[2] probably represents

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(1) (a) Cotton, F. A.; Powell, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3372. (b) Cotton, F. A.; Diebold, M. P.; O'Connor, C. J.; Powell, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7438.