disordered across the mirror plane and was refined in a general position with an occupancy factor of 0.5. An investigation of the acentric space group $Pn2_1a$ revealed the continued presence of disorder, high correlation values, and a higher R value. Due to the high thermal motion of the carbon atoms, hydrogen atoms could not be located. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.041$ and $R_w = 0.054$. A final difference Fourier showed no feature greater than 0.5 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table IV.[28]

X-ray Data Collection, Structure Determination, and Refinement for *trans*-[W(C_2H_4)$_2$(PMe$_3$)$_4$] (3). Single crystals of **3**, red parallelepipeds, were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($\theta > 18°$) accurately centered on the diffractometer are given in Table III. Systematic absences defined the space group as $P2_1/n$.

Data were collected as described for the previous compound. The intensities were corrected for Lorentz and polarization effects and for absorption. Neutral-atom scattering factors were obtained as noted above. The scattering was corrected for the real and imaginary components of anomalous dispersion.[27]

The positional parameters of the isostructural Mo analogue, *trans*-[Mo(C_2H_4)$_2$(PMe$_3$)$_4$],[7] were used as a starting point in the refinement of this compound. Least-squares refinement with isotropic thermal parameters led to $R = 0.048$. The hydrogen atoms were located with the aid of a difference Fourier map and included in the refinement with fixed contributions. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.028$ and $R_w = 0.032$. A final difference Fourier showed no feature greater than 0.3 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table V.[28]

Acknowledgment. We are indebted to the Comisión Asesora de Investigación Científica y Técnica (E.C.) and Ministerio de Educación y Ciencia (A.G.) for supporting this work and to Professor Jerry L. Atwood for the use of his diffractometer. Partial support has come from the Research Corp. (R.D.R.)

Registry No. **1**, 84879-22-1; **2**, 84879-24-3; **3**, 84879-23-2; **4**, 98720-85-5; **5**, 98720-86-6; **6**, 98720-87-7; *trans*-[Mo(C_2H_4)$_2$(PMe$_3$)$_4$], 82044-79-9; *trans,mer*-[Mo(C_2H_4)$_2$(CO)(PMe$_3$)$_3$], 82044-81-3; WCl$_4$(PMe$_3$)$_2$, 86567-86-4; WCl$_3$(PMe$_3$)$_3$, 85798-78-3.

Supplementary Material Available: Listings of thermal parameters and observed and calculated structure factors for **2** and **3** (9 pages). Ordering information is given on any current masthead page.

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[28] See paragraph at end of paper regarding supplementary material.

Contribution from the Department of Chemistry and Molecular Structure Center,
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The Tungsten–Tungsten Triple Bond. 11.[1] Ligand Redistribution Reactions Involving Chloride and Dimethylamide Ligands at Dimolybdenum and Ditungsten ($M\equiv M$) Centers Induced by Added Tertiary Phosphines. Preparations and Characterizations of $W_2Cl_2(NMe_2)_4(Me_2PCH_2PMe_2)$, $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$, and $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$

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Tertiary phosphines react with $M_2Cl_2(NMe_2)_4$ ($M\equiv M$) compounds (M = Mo and W) in hydrocarbon solvents to give a variety of products depending upon the metal and the phosphine. The bidentate phosphines L-L (L-L = $Me_2PCH_2PMe_2$ and $Me_2PCH_2CH_2PMe_2$) give isolable and kinetically stable 1:1 adducts: $M_2Cl_2(NMe_2)_4$(L-L). The monodentate phosphines L (L = PMe$_3$ and PMe$_2$Ph) induce ligand redistribution reactions to give $M_2Cl_3(NMe_2)_3L_2$, $M_2Cl_4(NMe_2)_2L_2$, and $M_2(NMe_2)_6$ compounds. The compounds $M_2Cl_4(NMe_2)_2L_2$, where M = Mo and L = PMe$_3$ and PMe$_2$Ph but not where M = W, were found to undergo reductive elimination (by way of β-hydrogen elimination from a NMe$_2$ ligand) in the presence of added phosphine to give $Mo_2Cl_4L_4$ ($M\overset{4}{-}M$) compounds. The compounds $M_2Cl_2(NMe_2)_4$(L-L) and $M_2Cl_{4-n}(NMe_2)_{2+n}L_2$, where n = 0 or 1, are formulated as compounds containing four-coordinate metal atoms united by M–M triple bonds. This has been verified by single-crystal X-ray diffraction studies for the compounds $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ (at −160 °C, a = 11.909 (3) Å, b = 13.271 (4) Å, c = 11.551 (3) Å, α = 104.76 (1)°, β = 108.64 (1)°, γ = 71.09 (1)°, Z = 2, d_{calcd} = 1.916 g cm^{-3}, and the space group is $P\bar{1}$) and $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ (at −158 °C, a = 17.624 (8) Å, b = 11.995 (5) Å, c = 14.397 (6) Å, β = 114.29 (3)°, Z = 4, d_{calcd} = 2.093 g cm^{-3}, and the space group is $P2_1/c$). In both molecules the W–W distances, 2.33 (2) Å (averaged), and W–P distances, 2.53 (1) Å (averaged), are similar while the W–N distances are notably shorter when N is bonded to W atoms having two Cl ligands and one PMe$_2$Ph ligand, 1.93 (1) Å (averaged), relative to W–N distances, 1.99 (1) Å (averaged), involving W atoms bonded to two NMe$_2$, one Cl, and one PMe$_2$Ph. In both compounds, the NMe$_2$ ligands contain trigonal-planar nitrogen atoms and the W–NC$_2$ units are aligned along with the W–W axis such that the nitrogen lone pairs may interact with the W d_{xy} atomic orbital, the one d orbital not used in either the $M\equiv M$ bond or the four M—L σ bonds. In a formal sense the W–N distance of 1.93 Å corresponds to a W–N double bond and the W–N distance of 1.99 Å to a W–N bond order of $1^1/_2$.

Introduction

Previously it was shown that $M_2Cl_2(NMe_2)_4$ compounds (M = Mo and W) were formed according to the reaction shown in eq 1.[2] The reaction was shown to be catalyzed by the presence

$$M_2(NMe_2)_6 + 2Me_3SiCl \rightarrow M_2Cl_2(NMe_2)_4 + 2Me_3SiNMe_2 \quad (1)$$

of HNMe$_2$. Attempts to prepare $M_2Cl(NMe_2)_5$ failed, yielding only a mixture of $M_2Cl_2(NMe_2)_4$ and $M_2(NMe_2)_6$. Attempts to prepare $M_2Cl_x(NMe_2)_{6-x}$ where $x \geq 3$ yielded only pink insoluble polymeric materials. We show here that the dinuclear unit $(M\equiv M)^{6+}$ is preserved in $M_2Cl_x(NMe_2)_{6-x}$ compounds where x = 3 and 4, by the addition of phosphine ligands.

Results and Discussion

Synthesis. $M_2Cl_2(NMe_2)_4$ compounds react with the diphosphines (L-L), $Me_2PCH_2PMe_2$ and $Me_2PCH_2CH_2PMe_2$, to give kinetically inert 1:1 adducts $M_2Cl_2(NMe_2)_4$(L-L). The ^{1}H NMR spectra of these 1:1 adducts leave little doubt that they

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[1] Part 10: Chisholm, M. H.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 3214.

[2] Akiyama, A.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407.

0020-1669/85/1324-4039$01.50/0

contain a central $(M{\equiv}M)^{6+}$ unit spanned by the chelating phosphine. With monodentate phosphines the initially formed adducts $M_2Cl_2(NMe_2)_4L_2$, where L = PMe_3 and PMe_2Ph, are kinetically labile toward phosphine dissociation. Since the $M_2Cl_2(NMe_2)_4$ compounds are themselves labile toward Cl for NMe_2 exchange reactions,[2] a disproportionation is possible, and indeed this is promoted by the addition of the monodentate phosphine as shown in eq 2 and 3.

$$3M_2Cl_2(NMe_2)_4 + 4L \xrightarrow[\text{toluene}]{25\ °C} 2M_2Cl_3(NMe_2)_3L_2 + M_2(NMe_2)_6 \quad (2)$$

$$L = PMe_3;\ t_\infty \text{ ca. } 5\ h\ (M = Mo),\ 7\ h\ (M = W)$$

$$L = PMe_2Ph;\ t_\infty \text{ ca. } 3\ h\ (M = Mo),\ 4\ h\ (M = W)$$

$$2M_2Cl_2(NMe_2)_4 + 2PMe_2Ph \xrightarrow[\text{toluene}]{50\ °C} M_2Cl_4(NMe_2)_2(PMe_2Ph)_2 + M_2(NMe_2)_6 \quad (3)$$

$$t_\infty \text{ ca. } 1 \text{ day } (M = Mo),\ 2 \text{ days } (M = W)$$

The compounds $M_2Cl_3(NMe_2)_3L_2$ are obtained by precipitation in reaction 2 but when redissolved in hydrocarbon solvents readily disproportionate according to eq 4.

$$4M_2Cl_3(NMe_2)_3L_2 \xrightarrow[\text{toluene}]{60\ °C} 3M_2Cl_4(NMe_2)_2L_2 + M_2(NMe_2)_6 + 2L \quad (4)$$

The overall rate of these phosphine-promoted ligand redistribution reactions is dependent on the metal, Mo > W, and the phosphine, $PMe_2Ph > PMe_3$. We believe this order is inversely related to the strength of M–L binding and that phosphine dissociation is the key initial step in eq 4. Consistent with this suggestion is the finding that the addition of excess phosphine slows down the rate of disproportionation 4.

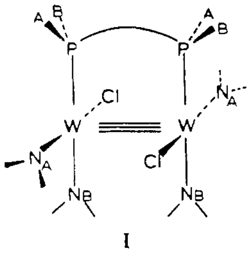
$Mo_2Cl_4(NMe_2)_2L_2$ compounds, but not $W_2Cl_4(NMe_2)_2L_2$ compounds, undergo a further reaction with added phosphine, leading, by reductive elimination, to the M–M quadruply bonded compounds $Mo_2Cl_4L_4$ as shown in eq 5.

$$Mo_2Cl_4(NMe_2)_2L_2 + 2L \xrightarrow[\text{toluene}]{60\ °C} Mo_2Cl_4L_4 + Me_2NH + HN(CH_2)_2 \quad (5)$$

The cyclic amine $HN(CH_2)_2$, which has been identified by ^1H NMR spectroscopy and GC/mass spectrometry, is the product of isomerization of $MeN{=}CH_2$. This suggests that, in addition to trace hydrolysis, a potential source of Me_2NH in all of the above reactions may involve β-hydrogen elimination[3] from a coordinated Me_2N ligand followed by reductive elimination of either HCl or $HNMe_2$. This process could be reversible and thus form the basis for amine/HCl-promoted ligand redistribution reactions.

NMR Spectroscopic Studies. All the compounds reported here have been characterized by ^1H and ^{31}P NMR spectroscopy, and data are recorded in the Experimental Section. Only the salient features are discussed below.

$M_2Cl_2(NMe_2)_4$(L-L) compounds show spectra consistent with the presence of a C_2 axis of symmetry and are fully consistent with the structure shown in I.



I

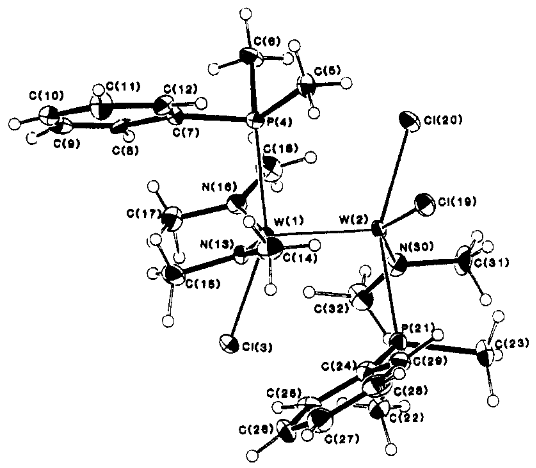


Figure 1. ORTEP view of the $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ molecule showing the number scheme used for the atoms.

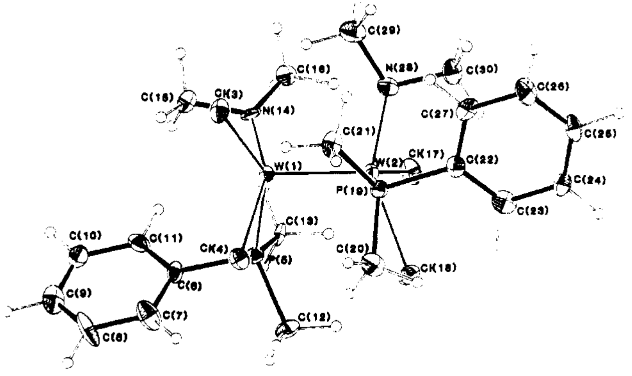
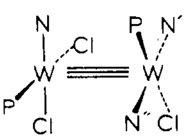


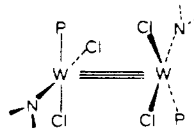
Figure 2. ORTEP view of the $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ molecule showing the number scheme used for the atoms.

There are two types of NMe_2 ligands, and at room temperature one type shows relatively rapid rotation about the M–N bonds while for the other rotation about the M–N bonds is slow on the NMR time scale.[4] The latter can reasonably be assigned to those NMe_2 groups trans to the M–P bonds that are most severely restricted by the cogging of the NC_2 blades, across the M–M bond. The alignment of the NC_2 blades along the M–M axis reflects Me_2N-to-M π bonding and is a characteristic of Me_2N units attached to the $(M{\equiv}M)^{6+}$ unit.[4] The magnitude of $J_{^{183}W-^{31}P}$ is rather small in these compounds, probably reflecting the high trans influence[5] of the W–NMe_2 bonds.

$M_2Cl_3(NMe_2)_3(PMe_3)_2$ and $M_2Cl_4(NMe_2)_2L_2$ compounds show well-separated proximal and distal NMe resonances consistent with frozen out rotations about the M–N bonds at room temperature. The NMR data are consistent with the schematic structures shown in II and III.



II



III

The NMe_2 ligands bonded to tungsten atoms bearing two Cl ligands show a small four-bond coupling to phosphorus: $^4J_{^{31}P-^1H} \simeq 4$ Hz. Presumably this reflects the increased W–N bond order in these W–NMe_2 groups.

The spectra of $M_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ must be recorded below −15 °C to suppress the facile dissociation of the PMe_2Ph ligands.

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(3) For other examples of β-H elimination from early-transition-metal dialkylamides accompanied by reductive elimination see: Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rideout, D. C. *Inorg. Chem.* **1978**, *17*, 3536. Meyer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651.

(4) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356.

(5) Appleton, T. G.; Clark, H. C.; Manzer, L. M. *Coord. Chem. Rev.* **1972**, *10*, 335.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2 \cdot {}^1/_2C_7H_8$ Molecule[a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	2695.5 (3)	2870.7 (2)	2778.8 (3)	10
W(2)	1480.4 (3)	1714.6 (3)	1559.0 (3)	11
Cl(3)	1414 (2)	4582 (2)	3634 (2)	16
P(4)	4663 (2)	1553 (2)	2415 (2)	13
C(5)	5025 (9)	135 (7)	2471 (9)	20
C(6)	5087 (9)	1550 (7)	1020 (8)	18
C(7)	5892 (8)	2012 (7)	3649 (8)	16
C(8)	6038 (7)	3042 (7)	3688 (8)	14
C(9)	6922 (9)	3418 (8)	4641 (8)	20
C(10)	7662 (8)	2846 (7)	5572 (9)	18
C(11)	7526 (9)	1840 (8)	5560 (9)	21
C(12)	6655 (8)	1419 (7)	4603 (8)	17
N(13)	3042 (6)	2495 (6)	4480 (7)	14
C(14)	3634 (9)	1569 (8)	5024 (9)	21
C(15)	3944 (9)	3311 (8)	5417 (9)	22
N(16)	2803 (7)	3665 (6)	1590 (7)	14
C(17)	3172 (8)	4661 (7)	2067 (9)	19
C(18)	2537 (9)	3462 (8)	251 (9)	22
Cl(19)	2089 (2)	43 (2)	2367 (2)	18
Cl(20)	2366 (2)	629 (2)	−111 (2)	18
P(21)	57 (2)	2212 (2)	2949 (2)	14
C(22)	−1035 (9)	3539 (8)	2916 (9)	20
C(23)	−981 (9)	1327 (8)	2329 (9)	22
C(24)	586 (8)	2110 (7)	4589 (8)	16
C(25)	793 (8)	3005 (7)	5473 (8)	18
C(26)	1147 (9)	2956 (8)	6729 (9)	20
C(27)	1328 (9)	1999 (8)	7092 (9)	23
C(28)	1154 (9)	1091 (9)	6231 (9)	25
C(29)	795 (8)	1152 (8)	5003 (8)	18
N(30)	176 (7)	2642 (6)	503 (7)	16
C(31)	−656 (9)	2072 (9)	−443 (9)	24
C(32)	−242 (9)	3782 (8)	419 (9)	21
C(33)	5823 (10)	5136 (10)	1182 (12)	39
C(34)	4074 (11)	5885 (10)	−424 (12)	37
C(35)	4905 (11)	6005 (10)	741 (11)	34
C(36)	4662 (19)	7231 (16)	1460 (19)	26

[a] C(31)–C(36) are for a toluene molecule of crystallization, which was found highly disordered.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	7576.6 (2)	570.0 (3)	5615.0	10
W(2)	7632.6 (2)	−1333.8 (3)	5356.1 (3)	10
Cl(3)	6984 (2)	874 (2)	6811 (2)	20
Cl(4)	6270 (1)	1312 (2)	4384 (2)	20
P(5)	7989 (1)	1198 (2)	4207 (2)	13
C(6)	8300 (6)	2652 (8)	4517 (7)	16
C(7)	7709 (6)	3469 (8)	4390 (8)	20
C(8)	7940 (6)	4554 (8)	4666 (7)	17
C(9)	8776 (6)	4853 (8)	5106 (7)	18
C(10)	9364 (7)	4053 (8)	5233 (8)	24
C(11)	9149 (6)	2953 (8)	4965 (7)	16
C(12)	8885 (6)	557 (8)	4102 (8)	18
C(13)	7224 (6)	1262 (9)	2904 (7)	23
N(14)	8706 (5)	902 (6)	6574 (6)	16
C(15)	8792 (6)	2033 (8)	7006 (7)	20
C(16)	9499 (6)	298 (8)	7029 (8)	24
Cl(17)	8888 (1)	−1888 (2)	5190 (2)	19
Cl(18)	6956 (1)	−1513 (2)	3513 (2)	16
P(19)	6180 (1)	−1840 (2)	5148 (2)	12
C(20)	5284 (6)	−1182 (9)	4184 (7)	19
C(21)	5993 (6)	−1716 (7)	6299 (7)	15
C(22)	6005 (6)	−3313 (7)	4791 (7)	15
C(23)	5699 (7)	−3607 (9)	3763 (8)	28
C(24)	5559 (7)	−4713 (9)	3477 (9)	31
C(25)	5723 (6)	−5530 (9)	4205 (9)	26
C(26)	6041 (6)	−5252 (8)	5205 (9)	25
C(27)	6174 (6)	−4151 (8)	5511 (7)	19
N(28)	8044 (4)	−1909 (7)	6729 (5)	15
C(29)	8263 (6)	−1454 (8)	7742 (7)	17
C(30)	8203 (6)	−3115 (8)	6811 (7)	18

Table III. Selected Bond Distances (Å) for the $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ Molecule

A	B	dist	A	B	dist
W(1)	W(2)	2.338 (1)	P(4)	C(7)	1.830 (9)
W(1)	Cl(3)	2.457 (2)	P(21)	C(22)	1.821 (10)
W(1)	P(4)	2.515 (2)	P(21)	C(23)	1.835 (11)
W(1)	N(13)	1.997 (7)	P(21)	C(24)	1.822 (9)
W(1)	N(16)	1.987 (7)	N(13)	C(14)	1.430 (12)
W(2)	Cl(19)	2.428 (2)	N(13)	C(15)	1.474 (12)
W(2)	Cl(20)	2.411 (2)	N(16)	C(17)	1.448 (12)
W(2)	P(21)	2.522 (2)	N(16)	C(18)	1.447 (12)
W(2)	N(30)	1.932 (7)	N(30)	C(31)	1.456 (12)
P(4)	C(5)	1.804 (10)	N(30)	C(32)	1.450 (12)
P(4)	C(6)	1.835 (9)	C–C(phenyl) (av)		1.386 (13)

Table IV. Selected Bond Distances (Å) for the $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ Molecule

A	B	dist	A	B	dist
W(1)	W(2)	2.322 (1)	P(5)	C(12)	1.817 (10)
W(1)	Cl(3)	2.380 (2)	P(5)	C(13)	1.806 (11)
W(1)	Cl(4)	2.424 (2)	P(19)	C(20)	1.800 (10)
W(1)	P(5)	2.534 (2)	P(19)	C(21)	1.823 (10)
W(1)	N(14)	1.940 (7)	P(19)	C(22)	1.830 (9)
W(2)	Cl(17)	2.415 (2)	N(14)	C(15)	1.474 (13)
W(2)	Cl(18)	2.430 (2)	N(14)	C(16)	1.468 (14)
W(2)	P(19)	2.526 (2)	N(28)	C(29)	1.452 (12)
W(2)	N(28)	1.931 (7)	N(28)	C(30)	1.469 (12)
P(5)	C(6)	1.828 (9)	C–C(phenyl) (av)		1.381 (14)

Solid-State and Molecular Structures. $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ (II) and $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ (III). Fractional coordinates and isotropic thermal parameters are given in Tables I and II. Selected bond distances and angles are given in Tables III–VI. Crystal data are summarized in Table VII, and ORTEP views of the two molecules are given in Figures 1 and 2.

The W–W distances, 2.338 (1) Å in II and 2.322 (1) Å in III, differ little from that seen in $W_2Cl_2(NMe_2)_4$, 2.301 (1) Å, and the subtle lengthenings probably reflect steric interactions across the dinuclear center. In both compounds the metal atoms are coordinated to four ligand atoms that lie roughly in a plane. Again the deviations of the W–W–L angles from 90° predominantly reflect steric repulsive interactions across the M–M bond. The compounds resemble the Lewis base adducts of $M_2(OR)_6$ compounds.[6]

The W–N distances in III and the W–N distance in II that involve the W atom bearing only one Me_2N ligand are ca. 1.93 Å, which represent the shortest W–NMe_2 distances thus far reported. The other W–N distances in II are quite notably longer, 1.99 (1) and 2.00 (1) Å. Since the four-coordinate W atom at the $(W{\equiv}W)^{6+}$ center has only one 5d orbital available for Me_2N-to-W π bonding, these distances represent formally M–N bonds of order 2 and 1.5 for the short and long distances, respectively.

The W–Cl and W–P bond distances are unexceptional.[7] For the $WCl_2(NMe_2)(PMe_2Ph)$ units in II and III, the W–Cl distances are ca. 0.02 Å longer for the bond trans to Me_2N ligands relative to those trans to PMe_2Ph ligands, indicating, for these molecules, the trans influence order[5] $Me_2N > PMe_2Ph$.

Concluding Remarks

The compounds $M_2Cl_x(NMe_2)_{6-x}L_2$, where $x = 3$ or 4 and L = PMe_3 or PMe_2Ph, provide excellent prospects as starting materials in the further studies of the chemistry of the $(W{\equiv}W)^{6+}$ center since the ligands Cl, NMe_2, and the phosphine are labile to substitution reactions. Their discovery as a result of phos-

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(6) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

(7) For typical W–Cl and W–P distances in dinuclear M–M multiply bonded compounds see: Cotton, F. A.; Walton, R. A. In "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; Chapter 3 and references therein.

Table V. Selected Bond Angles (deg) for the $W_2Cl_3(NMe_2)_3(PM_2Ph)_2$ Molecule

A	B	C	angle
W(2)	W(1)	Cl(3)	110.4 (1)
W(2)	W(1)	P(4)	93.8 (1)
W(2)	W(1)	N(13)	109.1 (2)
W(2)	W(1)	N(16)	104.5 (2)
Cl(3)	W(1)	P(4)	155.8 (1)
Cl(3)	W(1)	N(13)	89.1 (2)
Cl(3)	W(1)	N(16)	87.3 (2)
P(4)	W(1)	N(13)	82.9 (2)
P(4)	W(1)	N(16)	86.4 (2)
N(13)	W(1)	N(16)	145.3 (3)
W(1)	W(2)	Cl(19)	111.1 (1)
W(1)	W(2)	Cl(20)	109.3 (1)
W(1)	W(2)	P(21)	95.4 (1)
W(1)	W(2)	N(30)	102.5 (2)
Cl(19)	W(2)	Cl(20)	85.6 (1)
Cl(19)	W(2)	P(21)	80.0 (1)
Cl(19)	W(2)	N(30)	144.6 (2)
Cl(20)	W(2)	P(21)	154.6 (1)
Cl(20)	W(2)	N(30)	93.7 (2)
P(21)	W(2)	N(30)	86.3 (2)
W(1)	P(4)	C(5)	122.5 (3)
W(1)	P(4)	C(6)	117.6 (3)
W(1)	P(4)	C(7)	105.5 (3)
C(5)	P(4)	C(6)	103.1 (5)
C(5)	P(4)	C(7)	103.8 (5)
C(6)	P(4)	C(7)	101.8 (4)
W(2)	P(21)	C(22)	115.7 (3)
W(2)	P(21)	C(23)	107.6 (4)
W(2)	P(21)	C(24)	123.5 (3)
C(22)	P(21)	C(23)	101.2 (5)
C(22)	P(21)	C(24)	103.4 (4)
C(23)	P(21)	C(24)	102.6 (5)
W(1)	N(13)	C(14)	136.0 (6)
W(1)	N(13)	C(15)	114.5 (6)
C(14)	N(13)	C(15)	109.1 (8)
W(1)	N(16)	C(17)	118.8 (6)
W(1)	N(16)	C(18)	132.0 (6)
C(17)	N(16)	C(18)	109.2 (8)
W(2)	N(30)	C(31)	113.1 (7)
W(2)	N(30)	C(32)	137.1 (6)
C(31)	N(30)	C(32)	109.7 (8)
P(4)	C(7)	C(8)	118.3 (7)
P(4)	C(7)	C(12)	123.1 (7)
P(21)	C(24)	C(25)	120.1 (7)
P(21)	C(24)	C(29)	122.1 (7)
C–C–C(phenyl) (av)			120.0 (8)

phine-induced ligand redistribution reactions led us to seek a more direct, "one-pot" synthesis and this has been accomplished by the reaction shown in eq 6.

$$M_2(NMe_2)_6 + xMe_3SiCl + 2L \xrightarrow[\text{toluene}]{25\ °C} M_2Cl_x(NMe_2)_{6-x}L_2 + xMe_3SiNMe_2 \quad (6)$$

$$x = 3, 4;\ L = PMe_3, PMe_2Ph$$

Experimental Section

Materials and Preparations. All operations were carried out in dry and oxygen-free solvents and atmospheres (N_2). $Mo_2Cl_2(NMe_2)_4$ and $W_2Cl_2(NMe_2)_4$ were prepared according to literature methods.[2] Ligands (PMe_3, PMe_2Ph, $Me_2P(CH_2)_2PMe_2$, and $Me_2PCH_2PMe_2$) were purchased from Strem Chemicals and were used without any further purification. Nicolet 360-MHz and Varian XL-100 instruments were used to obtain ^1H and ^{31}P NMR spectra, respectively, while a Perkin-Elmer 283 infrared spectrometer was used to record IR spectra from Nujol mulls between CsI plates.

$W_2Cl_2(NMe_2)_4(Me_2PCH_2PMe_2)$. $W_2Cl_2(NMe_2)_4$ (1.5 g, 2.4 mmol) was suspended in toluene (5 mL), and $Me_2PCH_2PMe_2$ (1 equiv) was added via syringe with constant stirring. The color immediately changed to golden yellow. Stirring was continued for 10 min, after which the volatile components of the reaction mixture were removed under vacuum and the resulting solid was redissolved in a minimum volume of hot toluene. The solution was allowed to cool slowly to room temperature and let stand for 12 h after which bright yellow crystals, $W_2Cl_2(NMe_2)_4(Me_2PCH_2PMe_2)$ (1.5 g; yield 83%), were collected by filtration and dried in vacuum.

Table VI. Selected Bond Angles (deg) for the $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ Molecule

A	B	C	angle
W(2)	W(1)	Cl(3)	109.08 (6)
W(2)	W(1)	Cl(4)	109.51 (6)
W(2)	W(1)	P(5)	96.82 (6)
W(2)	W(1)	N(14)	102.55 (23)
Cl(3)	W(1)	Cl(4)	84.56 (9)
Cl(3)	W(1)	P(5)	152.74 (8)
Cl(3)	W(1)	N(14)	94.63 (23)
Cl(4)	W(1)	P(5)	78.75 (9)
Cl(4)	W(1)	N(14)	146.34 (24)
P(5)	W(1)	N(14)	87.71 (23)
W(1)	W(2)	Cl(17)	112.83 (6)
W(1)	W(2)	Cl(18)	103.18 (6)
W(1)	W(2)	P(19)	98.48 (6)
W(1)	W(2)	N(28)	102.11 (23)
Cl(17)	W(2)	Cl(18)	85.74 (9)
Cl(17)	W(2)	P(19)	147.91 (8)
Cl(17)	W(2)	N(28)	91.70 (22)
Cl(18)	W(2)	P(19)	80.26 (8)
Cl(18)	W(2)	N(28)	153.50 (24)
P(19)	W(2)	N(28)	88.34 (22)
W(1)	P(5)	C(6)	104.1 (3)
W(1)	P(5)	C(12)	119.0 (4)
W(1)	P(5)	C(13)	120.4 (4)
C(6)	P(5)	C(12)	104.0 (5)
C(6)	P(5)	C(13)	103.5 (5)
C(12)	P(5)	C(13)	103.6 (6)
W(2)	P(19)	C(20)	120.7 (4)
W(2)	P(19)	C(21)	115.2 (4)
W(2)	P(19)	C(22)	108.1 (3)
C(20)	P(19)	C(21)	103.6 (5)
C(20)	P(19)	C(22)	102.4 (5)
C(21)	P(19)	C(22)	105.2 (4)
W(1)	N(14)	C(15)	112.8 (6)
W(1)	N(14)	C(16)	136.5 (7)
C(15)	N(14)	C(16)	110.6 (8)
W(2)	N(28)	C(29)	136.6 (6)
W(2)	N(28)	C(30)	114.4 (6)
C(29)	N(28)	C(30)	109.0 (8)
P(5)	C(6)	C(7)	120.6 (7)
P(5)	C(6)	C(11)	120.7 (7)
P(19)	C(22)	C(23)	119.3 (8)
P(19)	C(22)	C(27)	122.1 (7)
C–C–C(phenyl) (av)			119.9 (10)

Anal. Calcd for $W_2Cl_2N_4P_2C_{13}H_{38}$: C, 20.79; H, 5.09; N, 7.45; Cl, 9.44. Found: C, 20.64; H, 4.98; N, 7.40; Cl, 9.42.

IR data (cm^{-1}): 2800 (s), 2760 (s), 1410 (w), 1285 (w), 1275 (w), 1255 (w, br), 1240 (m), 1145 (m), 1120 (w), 1042 (w, br), 950 (s), 940 (vs), 930 (s), 895 (w), 840 (w, d), 795 (w, br), 755 (w), 735 (w), 720 (w), 680 (vw), 660 (w), 540 (m, br).

^1H NMR data (obtained from toluene-d_8 solution at −50 °C; δ values reported relative to Me_4Si): 1.07 (t, J = 12.4 Hz, 6 H, PMe_2), 1.73 (t, J = 12.5 Hz, 6 H, PMe_2), 2.05 (s, 6 H, NMe_2), 2.69 (t, J = 14.4 Hz, 2 H, PCH_2P), 2.91 (br, 6 H, NMe_2), 4.41 (br, 6 H, NMe_2), 4.44 (s, 6 H, NMe_2).

$^{31}P\{^1H\}$ NMR spectral data (obtained from toluene-d_8; δ reported relative to H_3PO_4 as external standard): −2.27 (s, $^1J_{W-P}$ = 57 Hz, J_{P-P} = 21 Hz).

Similar reactions resulted in the formation of $Mo_2Cl_2(NMe_2)_4(Me_2PCH_2PMe_2)$ and $W_2Cl_2(NMe_2)_4(Me_2PCH_2CH_2PMe_2)$, which were obtained as microcrystalline yellow-brown solids and characterized by ^1H and ^{31}P NMR spectroscopy.

$Mo_2Cl_2(NMe_2)_4(Me_2PCH_2PMe_2)$. ^1H NMR spectral data (obtained from benzene-d_6 at 21 °C; δ reported relative to Me_4Si): 1.06 (virtual triplet, J = 7 Hz, 6 H, PMe_2), 1.69 (virtual triplet, J = 7 Hz, 6 H, PMe_2), 2.18 (s, 6 H, NMe_2), 2.20 (t, J = 10.8 Hz, 2 H, PCH_2P), 3.67 (br, 12 H, NMe_2), 4.51 (s, 6 H, NMe_2).

$^{31}P\{^1H\}$ NMR spectral data (from benzene-d_6; δ relative to H_3PO_4 as external standard): −3.96 (s).

$W_2Cl_2(NMe_2)_4(Me_2PCH_2CH_2PMe_2)$. ^1H NMR spectral data (from toluene-d_8 at 21 °C): 0.82 (virtual triplet, J = 7.2 Hz, 6 H, PMe_2), 1.50 (virtual triplet, J = 8.3 Hz, 6 H, PMe_2), 2.19 (s, 6 H, NMe_2), 2.27 (d,

Table VII. Summary of Crystallographic Data

	$W_2Cl_3(NMe_2)_3(PMe_2Ph)_2\cdot{}^1/_2C_7H_8$	$W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$
fw	935.67	873.96
space group	$P\bar{1}$	$P2_1/c$
a, Å	11.909 (3)	17.624 (8)
b, Å	13.271 (4)	11.995 (5)
c, Å	11.551 (3)	14.397 (6)
α, deg	104.76 (1)	
β, deg	108.64 (1)	114.29 (2)
γ, deg	71.09 (1)	
Z	2	4
V, Å^3	1613.02	2773.97
d(calcd), g/cm^{-3}	1.916	2.093
cryst size, mm	0.06 × 0.07 × 0.09	0.07 × 0.05 × 0.04
cryst color	dark red	brown-yellow
radiation	Mo Kα[a]	Mo Kα[a]
linear abs coeff, cm^{-1}	76.494	89.824
transmission factors	no abs cor	0.4620–0.5560
t, °C	−160	−158
diffractometer	Picker 4-circle[b]	Picker 4-circle
detector aperture, mm	3.0 × 4.0	3.0 × 4.0
sample to source dist, cm	23.5	23.6
takeoff angle, deg	2.0	2.0
scan speed, deg/min	4.0	4.0
scan width, deg	2.0 + dispersion	1.8 + dispersion
bkgd counts, s at each end of scan	10	8
2θ range, deg	6–50	6–45
total no. of data collcd	5807	4848
no. of unique data	5712	3630
no. of unique data with $F_o > 2.33\sigma(F_o)$	4780	3259
R(*F*)	0.036	0.030
$R_w(F)$	0.037	0.031
goodness of fit	0.884	0.868
largest Δ/δ	0.05	0.05

[a] λ = 0.71069 Å; graphite monochromator. [b] Locally modified and interfaced.

J = 10.8 Hz, part of CH_2 protons in $Me_2P(CH_2)_2PMe_2$), 3.63 (br, 12 H, NMe_2), 4.19 (s, 6 H, NMe_2).

$^{31}P\{^1H\}$ NMR spectral data (from toluene-d_8 solution): 3.16 (s, $^1J_{W-P}$ = 128 Hz, $^2J_{W-P}$ = 25 Hz).

$W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$. $W_2Cl_2(NMe_2)_4$ (0.9 g, 1.5 mmol) was suspended in toluene (4 mL), and PMe_2Ph (320 μL, 1.5 equiv) was added slowly via syringe with stirring of the solution. The color started to change to red, and after about 15 min, a red solid started to precipitate. Stirring was continued for 3$^1/_2$ h after which the red solid was filtered, washed with hexane (5 × 2 mL), and dried in vacuo. The compound was recrystallized from a minimum volume of hot toluene to yield dark red crystals of $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2\cdot{}^1/_2C_7H_8$ (0.75 g; 85% yield based on eq 2).

Anal. Calcd for $W_2Cl_3N_3P_2C_{25.5}H_{44}$: C, 32.06; H, 4.70; N, 4.48; Cl, 11.36. Found: C, 31.80; H, 4.62; N, 4.42; Cl, 11.82.

IR data (cm^{-1}): 3050 (w), 2810 (s), 2760 (s), 1490 (m), 1430 (s), 1415 (m), 1290 (w), 1280 (w), 1275 (w), 1260 (w), 1240 (w), 1140 (m), 1128 (w), 1100 (w), 1070 (w), 1040 (w), 1025 (w), 998 (w), 955 (m), 945 (vs), 935 (vs), 910 (vs), 865 (w), 835 (w), 800 (w, br), 750 (m), 740 (s), 725 (s), 709 (m), 695 (m), 690 (m), 685 (m), 670 (w), 550 (m, br), 540 (m), 490 (s), 465 (w), 425 (w), 405 (m), 380 (m), 345 (w), 310 (m), 295 (m), 270 (m), 259 (m), 245 (m).

^1H NMR spectral data (from a toluene-d_8 solution at −15 °C; δ relative to Me_4Si): 1.04 (s, 3 H, NMe_2), 1.24 (s, 3 H, NMe_2), 1.28 (d, J = 8 Hz, 3 H, PMe_2Ph), 1.69 (d, J = 9 Hz, 3 H, PMe_2Ph), 1.76 (d, J = 9 Hz, 3 H, PMe_2Ph), 2.18 (s, 3 H, NMe_2), 2.28 (d, J = 9 Hz, 3 H, PMe_2Ph), 2.77 (s, 3 H, NMe_2), 3.08 (s, 3 H, NMe_2), 4.55 (s, 3 H, NMe_2), 6.72–7.94 (m, 10 H, $PPhMe_2$).

$^{31}P\{^1H\}$ NMR spectral data (from a toluene-d_8 solution at −15 °C; δ relative to H_3PO_4 as external standard): 4.04 (d, J = 6.4 Hz), 0.75 (d, J = 6.4 Hz).

$W_2Cl_3(NMe_2)_3(PMe_3)_2$. $W_2Cl_2(NMe_2)_4$ (0.45 g, 0.75 mmol) was suspended in toluene (4 mL) and cooled to −196 °C. PMe_3 (1.5 equiv) was condensed onto the reaction mixture by the use of a calibrated vacuum manifold and the mixture then warmed to room temperature. The reaction mixture was stirred for 10 h, after which the volatile components of the reaction mixture were removed under vacuum and the resulting solid was redissolved in hexane (10 mL) and cooled to −15 °C. Dark red crystals of $W_2Cl_3(NMe_2)_3(PMe_3)_2$ were formed after 1 week, which were collected by filtration, washed with cold hexane (5 mL), and dried under vacuum. Yield: 0.18 g; 50% based on eq 2.

Anal. Calcd for $W_2Cl_3N_3P_2C_{12}H_{36}$: C, 19.1; H, 4.8; N, 5.5; Cl, 14.0. Found: C, 19.3; H, 4.9; N, 5.5; Cl, 12.8.

IR data (cm^{-1}): 2745 (s), 1410 (m), 1360 (m), 1295 (m), 1275 (s), 1230 (m), 1140 (m), 955 (vs), 935 (vs), 925 (vs), 725 (m).

^1H NMR spectral data (from a toluene-d_8 solution at 22 °C; δ relative to Me_4Si): 1.23 (d, J = 9 Hz, 9 H, PMe_3), 1.36 (d, J = 9.7 Hz, 9 H, PMe_3), 2.06 (d, J = 3.2 Hz, 3 H, NMe_2), 2.30 (s, 3 H, NMe_2), 2.41 (s, 3 H, NMe_2), 4.18 (s, 3 H, NMe_2), 4.35 (s, 3 H, NMe_2), 4.39 (d, J = 3.6 Hz, 3 H, NMe_2).

$^{31}P\{^1H\}$ NMR spectral data (from a toluene-d_8 solution at 23 °C; δ relative to H_3PO_4 as external standard): −1.66 (d, $^3J_{P-P}$ = 7.0 Hz, $^1J_{W-P}$ = 220 Hz), −4.77 (d, $^1J_{W-P}$ = 230 Hz).

$Mo_2Cl_3(NMe_3)_3(PMe_3)_2$ was prepared in a similar manner and characterized by ^1H NMR and ^{31}P NMR spectroscopy.

^1H NMR spectral data (from a toluene-d_8 solution at 22 °C): 1.15 (d, J = 8 Hz, 9 H, PMe_3), 1.27 (d, J = 8.5 Hz, 9 H, PMe_3), 2.5 (d, J = 2.1 Hz, 3 H, NMe_2), 2.25 (s, 3 H, NMe_2), 2.39 (s, 3 H, NMe_2), 4.13 (s, 3 H, NMe_2), 4.25 (s, 3 H, NMe_2), 4.31 (d, J = 2.0 Hz, 3 H, NMe_2).

$^{31}P\{^1H\}$ NMR spectral data (from a toluene-d_8 solution at 22 °C): −3.50 (d, J_{P-P} = 5.0 Hz), −6.71 (d).

$W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$. $W_2Cl_2(NMe_2)_4$ (0.6 g, 0.98 mmol) was dissolved in toluene (4 mL), and PMe_2Ph (140 μL, 1 equiv) was added by syringe. The solution was then stirred for 48 h at 60 °C, resulting in the precipitation of a reddish-brown solid, which was filtered, washed with hexane (2 × 5 mL), and dried in vacuo. Red-brown crystals of $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ were obtained upon cooling a concentrated toluene solution to ca. −15 °C for 2 weeks. Yield: 0.36 g; 48% based on eq 3.

Anal. Calcd for $W_2Cl_4N_2P_2C_{20}H_{34}$: C, 27.47; H, 3.89; N, 3.20; Cl, 16.23. Found: C, 27.53; H, 4.01; N, 3.14; Cl, 15.98.

IR data (cm^{-1}): 3050 (w), 1298 (w), 938 (s), 912 (s), 740 (m), 719 (m), 690 (m), 565 (w), 485 (m), 395 (m), 308 (sh, m), 255 (m), 245 (s), 225–200 (vs).

^1H NMR spectral data (obtained from a CD_2Cl_2 solution at 22 °C; δ reported downfield from Me_4Si): 2.08 (d, J = 3 Hz, 6 H, NMe_2), 2.24 (d, J = 10 Hz, 6 H, PMe_2Ph), 2.38 (d, J = 11 Hz, 6 H, PMe_2Ph), 4.57 (d, J = 3 Hz, 6 H, NMe_2), 7.35 (m, 6 H, PMe_2Ph), 7.48 (m, 4 H, PMe_2Ph).

$^{31}P\{^1H\}$ NMR spectral data (CD_2Cl_2 solvent; δ relative to H_3PO_4 as external standard): 5.09 (s, $^1J_{W-P}$ = 309 Hz).

$Mo_2Cl_4(NMe_2)_2(PMe_2Ph)_2$. Similar procedures were followed to prepare $Mo_2Cl_4(NMe_2)_2(PMe_2Ph)_2$, which was obtained as a red-brown microcrystalline solid and characterized by ^1H and ^{31}P NMR spectroscopy.

^1H NMR spectral data (from a CD_2Cl_2 solution): 2.09 (d, J = 3.4 Hz, 6 H, NMe_2), 2.15 (d, J = 7.2 Hz, 6 H, PMe_2Ph), 2.28 (d, J = 7.5 Hz, 6 H, PMe_2Ph), 4.45 (d, J = 3.1 Hz, 6 H, NMe_2).

$^{31}P\{^1H\}$ NMR spectral data (from a CD_2Cl_2 solution): 2.31 (s).

Alternate Syntheses. $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$. $W_2(NMe_2)_6$ (0.6 g, 0.95 mmol) was dissolved in toluene (4 mL), and Me_3SiCl (3 equiv) was added by syringe. The mixture was stirred for 2 days during which the color changed from yellow to orange. PMe_2Ph (270 μL, 2 equiv) was added by syringe, resulting in an immediate color change to dark red. The reaction mixture was stirred for 15 min after which the solvents and other volatile components were removed under vacuum. The residual red solid was redissolved in a minimum amount of hot toluene, and the solution was slowly cooled. When the solution was allowed to stand for 12 h, dark red crystals, $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ (0.82 g, 89% yield), were formed and collected by filtration.

$W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$. $W_2(NMe_2)_6$ (0.8 g, 1.26 mmol) was dissolved in toluene (4 mL), and Me_3SiCl (4 equiv) was added by syringe. The reaction mixture was stirred for 2$^1/_2$ days after which PMe_2Ph (360 μL, 2 equiv) was added. The color immediately changed to reddish brown with the formation of a precipitate, which was filtered, washed with hexane (2 × 5 mL), and dried under vacuum. The solid was then redissolved in hot toluene (4 mL) and, upon cooling, yielded brown crystals, $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ (0.96 g; 87% yield), which were collected by filtration.

Reaction of $Mo_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ with Excess PMe_2Ph (>2 Equiv). A solution of $Mo_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ (30 mg) was made in benzene-d_6 (0.5 mL) in an NMR tube, and PMe_2Ph (3 equiv) was added via a syringe. The tube was sealed and heated at 50 °C for 10 h. The original red-brown color of the solution turned blue after heating, and the volatile components of the reaction mixture were transferred into another NMR tube. ^{31}P and ^1H NMR spectra of the residual blue solid in benzene-d_6 suggested the formation of $Mo_2Cl_4(PMe_2Ph)_4$ (one virtual triplet in the ^1H NMR spectrum for the Me groups of the phosphine ligands at 1.81 ppm, $J = 9.8$ Hz, no resonances for NMe_2 protons; one single resonance was observed in the $^{31}P\{^1H\}$ NMR spectrum at −1.91 ppm).

The volatile components were identified (by ^1H NMR and GC/mass spectroscopy) to contain, other than benzene-d_6 and PMe_2Ph, Me_2NH and $\overline{CH_2CH_2N}H$.[8]

X-ray Structural Determinations. General operating facilities and listings of programs have been described previously.[9] Crystal data for the two compounds studied in this work are given in Table VII.

$W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$. A suitable sample was cleaved under an inert atmosphere from a larger crystal and transferred to the goniostat. A systematic search of a limited hemisphere of reciprocal space revealed no systematic absences or symmetry, leading to the assignment of a triclinic space group.

The structure was solved by a combination of Patterson and Fourier techniques and refined by full-matrix least squares. All hydrogen atoms were located and refined isotropically. Examination of ψ scans revealed only a 4% fluctuation in intensities, so no absorption correction was performed.

A final difference Fourier was featureless, the largest peak (of intensity 1.1 e/Å^3) lying at the site of W(2).

$W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$. A suitable, well-formed small crystal was selected and transferred to the goniostat, where it was cooled to −158 °C and characterized in the usual manner. The crystal was observed to be monoclinic, and the systematic extinctions identified the space group as $P2_1/c$. A total of 3259 reflections having F_o greater than $3\sigma(F_o)$ were used in the least-squares refinement of the structure.

The W atoms were located by means of direct methods, and the remaining atoms were located by Fourier techniques. All hydrogen atoms were located in a difference Fourier map. All non-hydrogen atoms were refined by full-matrix least squares with anisotropic thermal parameters, while the hydrogen atoms were refined by using isotropic thermal parameters. An absorption correction was carried out, and the corrected data were used for the refinements. The final difference map was essentially featureless, the largest peaks being associated with the W atoms.

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Registry No. $W_2Cl_2(NMe_2)_4(Me_2PCH_2PMe_2)$, 98481-55-1; $Mo_2Cl_2(NMe_2)_4(Me_2PCH_2PMe_2)$, 98481-56-2; $W_2Cl_2(NMe_2)_4(Me_2PCH_2CH_2PMe_2)$, 98481-57-3; $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$, 97285-93-3; $W_2Cl_3(NMe_2)_3(PMe_3)_2$, 98481-58-4; $Mo_2Cl_3(NMe_2)_3(PMe_3)_2$, 98481-59-5; $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$, 98481-60-8; $Mo_2Cl_4(NMe_2)_2(PMe_2Ph)_2$, 98481-61-9; $W_2Cl_2(NMe_2)_4$, 63301-81-5; $Mo_2Cl_2(NMe_2)_4$, 63301-82-6; $W_2(NMe_2)_6$, 54935-70-5; W, 7440-33-7.

Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, complete bond distances and angles excluding those of H atoms, and F_o and F_c and VERSORT drawings showing the atom-numbering scheme (71 pages). Ordering information is given on any current masthead page. The complete structural reports are available from the Indiana University Chemistry Library in microfiche form only at a cost of $2.50 per copy. For $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ and $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ request IU MSC Report Nos. 83057 and 83104, respectively.

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Preparation, Characterization, and Electrochemistry of Novel, Air-Stable Nitrosyl Complexes of Molybdenum and Tungsten of the Type $\{M\text{–}NO\}^{6,5,4}$ Containing the Ligand *N,N′,N″*-Trimethyl-1,4,7-triazacyclononane

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The reaction of $LM(CO)_3$ (L = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane; M = Mo (**1a**), W (**1b**)) with nitric acid yields air- and water-stable complexes $[LM(CO)_2NO]PF_6$ (M = Mo ([**2a**]PF_6), W ([**2b**]PF_6)) that contain a $\{M\text{–}NO\}^6$ group. Halogenation reactions of [**2a**]$^+$ and [**2b**]$^+$ afford a series of cationic complexes $[LM(NO)X_2]^+$ with a $\{M\text{–}NO\}^4$ moiety (M = Mo, X = Cl, Br, I; M = W, X = Br, Cl) that were reduced electrochemically and chemically to give paramagnetic, neutral 17e species $[LM(NO)X_2]$ with a $\{M\text{–}NO\}^5$ structure (M = Mo, X = Br, Cl; M = W, X = Br). $[LMo(NO)Cl_2]PF_6$ reacts with ethanol to yield the air- and water-stable species $[LMo(NO)Cl(OEt)]PF_6$, which was obtained as green crystals. Recrystallization of these green crystals from acetonitrile in the presence of a small amount of water gave blue crystals of identical composition. The tungsten analogue $[LW(NO)Br(OEt)]^+$ has also been obtained as a green Br_3^- salt and a blue PF_6^- salt. Cyclic voltammograms of all complexes with the $\{M\text{–}NO\}^4$ structure exhibit a reversible one-electron reduction to yield the corresponding species with $\{M\text{–}NO\}^5$ structure. Formal redox potentials are reported.

Introduction

The chemistry of neutral nitrosyl complexes of the type $[ML''(CO)_2NO]$ where L″ is η^5-$C_5H_5^-$[1,2] or hydridotris(1-pyrazolyl)borate[3] and M is molybdenum and tungsten has been investigated in depth in the past. Halogenation reactions of these complexes have led to an extensive class of compounds $ML''(NO)X_2$ (X = Cl, Br, I);[3-5] mixed alkoxy halogeno complexes have also been obtained, $ML''(NO)X(OR)$.[5] Two aspects of this chemistry have been intriguing: (i) While the η^5-C_5H_5 complexes are in general extremely oxygen- and moisture-sensitive, the corresponding tris(1-pyrazolyl)borate derivatives have been found to be quite stable in air and many of them do not react with water. (ii) Interestingly and rather unexpectedly, even the alkoxy complexes $Mo[HB(3,5\text{-}Me_2pz)_3]X(NO)(OR)$ (X = Cl,Br,I) do not hydrolyze,[5] in contrast with the behavior of many simple alkoxy complexes of molybdenum in various oxidation states.

We have recently investigated the chemistry of the small macrocycle, 1,4,7-triazacyclononane ([9]aneN_3) with chromium, molybdenum, and tungsten in low oxidation states and reported the preparation of air- and moisture-stable carbonyl and cationic

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