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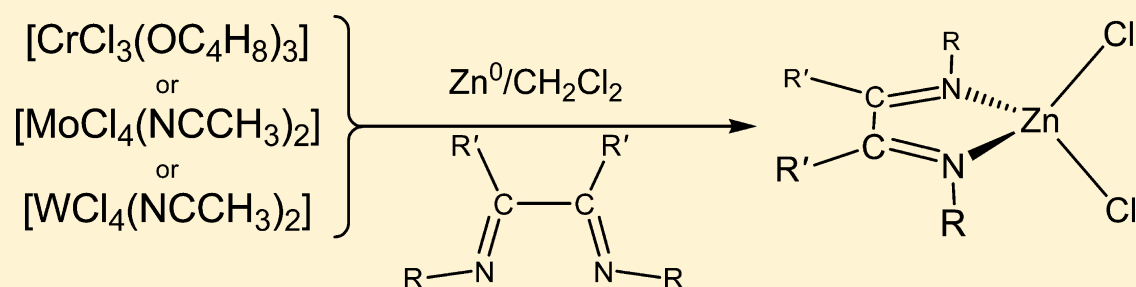
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Element Misidentification in X-ray Crystallography: A Reassessment of the $[\text{MCl}_2(\text{diazadiene})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) SeriesAngelique F. Greene,[†] P. Chandrasekaran,[‡] Yong Yan,^{†,‡} Joel T. Mague,[†] and James P. Donahue^{*,†}[†]Department of Chemistry, Tulane University, 6400 Freret Street, New Orleans, Louisiana 70118-5698, United States[‡]Department of Chemistry and Biochemistry, Lamar University, Beaumont, Texas 77710, United States

S Supporting Information



ABSTRACT: A series of reports describing the syntheses and structures of $[\text{MCl}_2(\text{diazadiene})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) complexes is reassessed in the context of known chemistry of low-valent Group VI metal complexes, crystallographic trends such as $\text{M}-\text{Cl}$ bond lengths and unit cell volumes, and calculated metal–ligand bond lengths. Crystallographic data and computational results are inconsistent with any of these species being second or third row transition metal complexes. A review of the crystallographic information files accompanying the $[\text{MCl}_2(\text{diazadiene})]$ ($\text{M} = \text{Mo}, \text{W}$) published structures reveals that the metal atoms were inappropriately treated with partial site occupancy factors (0.775 for Mo; 0.4005 and 0.417 for W), the effect of which was to manifest lighter-element behavior and better refinement in accord with the metal atoms' correct identity. A deliberate synthesis and characterization by X-ray diffraction of $[\text{ZnCl}_2(\text{Mes}^{\text{dad}}\text{Me})]$ ($\text{Mes}^{\text{dad}}\text{Me} = 1,4\text{-bis}(2,4,6\text{-trimethylphenyl})\text{-}2,3\text{-dimethyl-}1,4\text{-diaz-}1,3\text{-butadiene}$) are reported. Refinement of this structure with the same combination of second or third row metal and offsetting partial site occupancy is shown to provide final refinement statistics essentially the same as with the correct model employing $\text{M} = \text{Zn}$ at site occupancy 1.00. Use of the published method for synthesis of $[\text{WCl}_2(\text{diazadiene})]$ with $\text{Mes}^{\text{dad}}\text{Me}$ and $[\text{WBr}_4(\text{MeCN})_2]$ in lieu of $[\text{WCl}_4(\text{MeCN})_2]$ is shown to produce $[\text{ZnBr}_2(\text{Mes}^{\text{dad}}\text{Me})]$, which has also been characterized by X-ray diffraction. It is concluded that the unusual putative 12-electron $[\text{MCl}_2(\text{diazadiene})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) complexes are in all cases the corresponding $[\text{ZnCl}_2(\text{diazadiene})]$ complexes, Zn having been commonly employed as reducing agent in their synthesis.

■ INTRODUCTION

The synthesis, structures, and reactivity of low and middle valent coordination complexes of tungsten have been of ongoing interest to our group, in part because of the promise such compounds have to effect multielectron, small molecule transformations.¹ A series of reports by Bouachir and co-workers in 2006^{2–4} describing the syntheses and structures of diazadiene (dad) complexes of the type of $[\text{MCl}_2(\text{dad})]$ (Figure 1) drew our attention because the combination of this low coordination number and formal oxidation state requires the formulation of these compounds as highly unusual, if not unprecedented, 12-electron species. We are unaware of any comparable compounds for any of the Group VI metals.

The structures of four of these compounds (Figure 1, 1a, 2c, 3a, 3c), determined by room temperature X-ray crystallography, were described. Although neither the refinement statistics (as-presented R -factors, goodness-of-fit, and magnitude of residual peaks and holes) nor the shapes of the thermal ellipsoids for any of the atoms appear obviously anomalous for

these room-temperature structures, other aspects of the chemical crystallography within the larger context of many other structurally identified chromium, molybdenum, and tungsten complexes, cast considerable doubt upon the formulation of these compounds as Group VI species and suggest that they are in all cases the corresponding $[\text{ZnCl}_2(\text{dad})]$ complexes. We note that Theopold has expressed skepticism regarding the identity of the chromium complexes on the basis that the observed diamagnetism is inconsistent with a first row d^4 ion in a tetrahedral environment,⁵ while Konchenko and co-workers have very recently reported that, in their hands, the synthetic procedure described for the chromium complexes yields the zinc species.⁶

In the following,⁷ we present a series of general observations about the chemistry of low-valent Group VI metals, particularly tungsten, that are incompatible with the compounds reported

Received: September 3, 2013



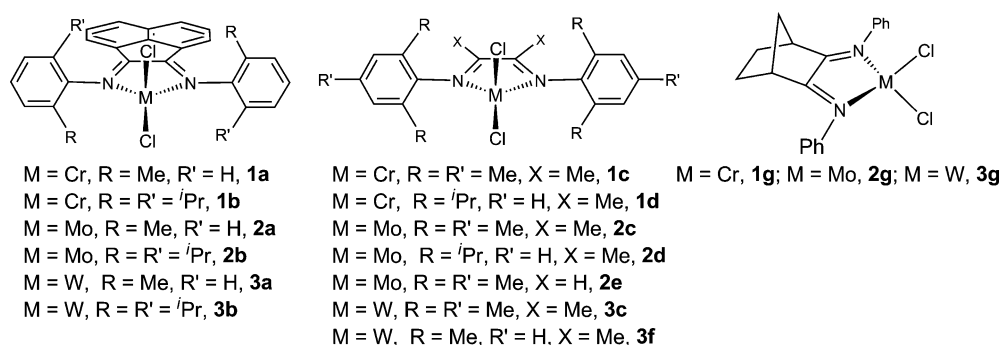


Figure 1. $[\text{MCl}_2(\text{dad})]$ compounds (dad = diazadiene, M reportedly Cr (1), Mo (2), or W (3)) described by Bouachir and co-workers.^{2–4} The letter notation in the compound name refers to a specific diazadiene ligand; for example, **1c** and **2c** share in common the ligand with Me groups on the chelate backbone and *N*-mesityl substituents. Not all combinations of metal (1, 2, or 3) with ligand were reported.

Table 1. Summary of Structural and Crystallographic Data for $[\text{MCl}_2(\text{diazadiene})]$ Compounds

	1a	2c ·CH ₂ Cl ₂	3a	3c ·CH ₂ Cl ₂	4 ·THF
M–N, Å	2.070(8) 2.074(8)	2.087(5) 2.089(5)	2.063(14) 2.099(13)	2.038(4) 2.066(4)	2.0647(12) 2.0699(12)
M–Cl, Å	2.190(3) 2.197(4)	2.204(2) 2.220(2)	2.173(7) 2.178(6)	2.2139(19) 2.227(2)	2.2055(4) 2.2130(4)
N–C _{chelator} , Å	1.283(12) 1.287(11)	1.267(8) 1.258(8)	1.227(19) 1.27(2)	1.255(7) 1.264(7)	^c
C–C _{chelator} , Å	1.502(12)	1.523(9)	1.59(2)	1.512(7)	^c
N–M–N, deg	81.2(3)	78.17(19)	81.3(6)	78.57(17)	78.89(5)
Cl–M–Cl, deg	120.65(18)	115.96(9)	120.5(3)	117.44(8)	116.568(16)
temp, K	293(2)	293(2)	293(2)	293(2)	91.0(2)
xtl system	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic
space grp	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	11.825(5)	12.8712(8)	11.733(3)	12.810(3)	12.9137(4)
<i>b</i> , Å	12.034(4)	14.6594(9)	12.003(3)	14.552(4)	14.2762(4)
<i>c</i> , Å	16.393(8)	14.4046(9)	16.332(5)	14.349(3)	14.3954(5)
β , deg	90	90.662(7)	90	90.68(3)	90.766(1)
<i>V</i> , Å ³	2332.8(17)	2717.8(3)	2300.1(11)	2674.6(11)	2653.68(14)
indep data	5028	5680	3446	5249	7164
parmtrs refined	280	268	215	272	^c
<i>R</i> ₁ , <i>wR</i> ₂ ^a	0.0735, 0.1921	0.0808, 0.2265	0.0881, 0.2403	0.0697, 0.2110	0.029, 0.068
<i>R</i> ₁ , <i>wR</i> ₂ ^b	0.2420, 0.2487	0.1876, 0.2884	0.2698, 0.3313	0.1219, 0.2518	^c
GOF	0.972	0.996	1.004	1.021	1.02
resid density	0.466, –0.461	1.112, –1.128	0.633, –0.504	1.308, –0.823	0.44, –0.39

^aData cut at $I < 2\sigma I$. ^bAll data used. ^cData unavailable.

and note points in the published work wherein room for doubt has been admitted. The similarity of metal ligand lengths within the set of $[\text{MCl}_2(\text{dad})]$ crystal structures is noted, as is their conformity with the set of known $[\text{ZnCl}_2(\text{dad})]$ complexes. A survey of M–Cl (M = Cr, Mo, W) ligand bond lengths and of unit cell volumes for isostructural, isomorphous chromium and tungsten compounds shows consistent and significant differences between the two elements that are not reflected in the set of compounds posited as being as $[\text{MCl}_2(\text{dad})]$ (M = Cr, W) species. Although we do not believe that diamagnetic tetrahedral $[\text{MCl}_2(\text{dad})]$ (M = Cr, Mo, W) species would be stable and amenable to characterization in the fashion reported, calculated gas phase structures do reflect bond length differences between the Cr and W species that should be — and are not — manifested experimentally. Examination of the Supporting Information accompanying the structures of **2c**·CH₂Cl₂, **3a**, and **3c**·CH₂Cl₂ shows the metal atoms were refined with partial occupancies. We report a deliberate preparation and crystallographic characterization of

$\text{ZnCl}_2(\text{Mes}^{\text{dad}}\text{Me})\cdot\text{CH}_2\text{Cl}_2$ (Mes^{dad}Me = 1,4-bis(2,4,6-trimethylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene) and show the results of refinement as the identity of M is varied as Cr, Mo, and W with full and partial site occupancy factors. Finally, we show that the procedure reported to produce $[\text{WCl}_2(\text{diazadiene})]$ complexes, when implemented with Mes^{dad}Me and $[\text{WBr}_4(\text{MeCN})_2]$ in lieu of the corresponding chloride complex, produces in our hands crystalline $\text{ZnBr}_2(\text{Mes}^{\text{dad}}\text{Me})\cdot\text{CH}_2\text{Cl}_2$.

DISCUSSION

Figure 1 illustrates the family of complexes (**1**–**3**) that are the subject of this reexamination, while Table 1 summarizes the key structural parameters, unit cell information, and refinement data associated with the compounds that were characterized by X-ray crystallography. The reported syntheses proceed from $[\text{CrCl}_3(\text{thf})_3]$ or $[\text{MCl}_4(\text{solv})_2]$ (M = Mo, solv = thf; M = W, solv = MeCN) by reduction with elemental zinc in the presence of the diazadiene ligand. We note that the method of synthesis

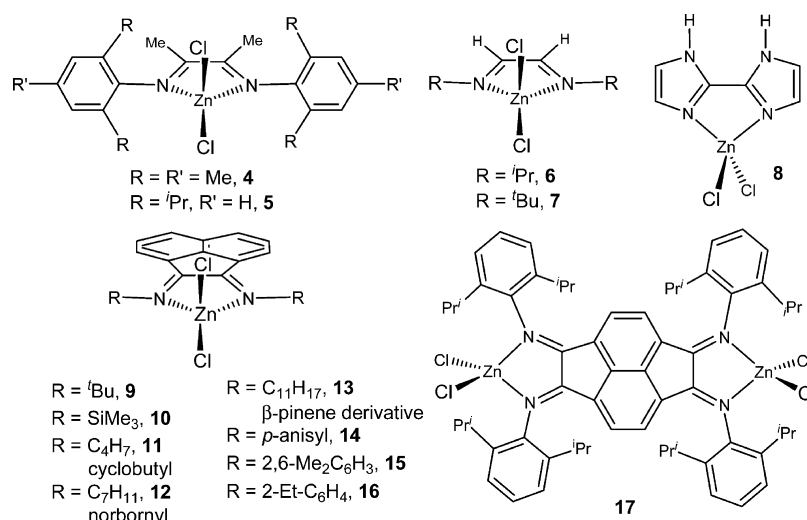


Figure 2. Crystallographically characterized $[\text{ZnCl}_2(\text{dad})]$ complexes.

does not obviate the formation of the $[\text{ZnCl}_2(\text{dad})]$ complexes by separating the Zn(II) byproduct prior to the introduction of the diazadiene ligand and further observe that the adulteration of minor amounts of impurities into a lightly colored, crystalline Zn(II) compound can readily present virtually any color, even black. An elemental analysis (C, H, N) for **1d** was reported that was consistent with its formulation, although the calculated mass percentages change relatively little if the compound is assumed to contain Zn rather than Cr. The Mo and W compounds were characterized only spectroscopically by IR and ^1H and ^{13}C NMR. Physical techniques such as mass spectrometry or analytical methods such as elemental analysis that would have been more decisive in corroborating their identity were not employed.

The chemistry of divalent molybdenum and tungsten is comprised largely of quadruply bonded species,^{8,9} the formation of the metal–metal multiple bond being an avenue by which the low electron count, noted at the outset as implausible, is alleviated. Noncarbonyl mononuclear Cr^{II} , Mo^{II} , and W^{II} compounds, while known,^{10–19} are generally six-coordinate species and still prone to the formation of metal–metal multiple bonds.^{20–22} The divalent state, for tungsten at least, is typically achieved by reduction of WCl_4 with strong reducing agents such as Mg ,¹⁷ Na/Hg amalgam,^{16,18–20,22} $\text{Na}[\text{HBEt}_3]$,⁸ or KC_8 ²³ in the presence of the desired supporting ligand. To the best of our knowledge, potentials for reduction of $[\text{WCl}_4(\text{MeCN})_2]$, the starting material employed for the synthesis of $[\text{WCl}_2(\text{dad})]$, have not been reported, but we view it as unlikely that Zn^0 would have reducing power sufficient to prepare divalent tungsten from a tetravalent precursor.

Compounds **1a** and **3a** are isostructural and isomorphous in orthorhombic space group $P2_12_12_1$ (Table 1), while **2c** and **3c** are similarly related but occur in monoclinic space group 14. An immediately apparent anomaly is a set of M–Cl and M–N bond lengths for **1a** and **3a** that are the same within the resolution of the data despite the former being a first row metal and the latter a third row metal with significantly greater ionic radius that should manifest itself with significantly longer metal–ligand bond lengths. The atomic radius of W is $\sim 9\%$ larger than that of Cr, and the difference, while variable depending on redox state, is generally more pronounced for ionic radii.²⁴ We note also the generally high *R*-factors that are

reported, particularly those obtained when all data are included (Table 1). Even for diffraction data collected at room temperature, convergence with wR_2 values well below 0.200 would be generally expected.

Shown in the rightmost column of Table 1 are selected structural and crystallographic data from a recently reported structural study⁶ of $[\text{ZnCl}_2(\text{Mes}^{\text{dad}}\text{Me})]\cdot\text{THF}$, **4**·THF, the zinc compound that is isostructural to compounds **2c** and **3c**, which is consistent with the latter species being incorrectly formulated. The Zn–Cl and Zn–N bond lengths shown for **4**, which show lower uncertainties reflecting the higher quality of the data, are indistinguishable from the M–Cl and M–N bond lengths reported for **2c** and **3c**.

A moderate number of $[\text{ZnCl}_2(\text{dad})]$ compounds have been deliberately prepared and structurally identified by X-ray crystallography. Figure 2 illustrates this set of compounds, while Table 2 summarizes selected structural data. Table 2 reveals a range of 2.173(2)–2.252(7) Å for Zn–Cl bond lengths, the average value being 2.207 Å, and a range for Zn–N bond distances of 2.0647(12)–2.147(4) Å, the average being 2.091 Å. The imine $\text{N}=\text{C}$ bond lengths and $\text{C}-\text{C}_{\text{cholate}}$ bonds lengths are in all cases typical at ~ 1.27 and ~ 1.54 Å, respectively. The metal ligand bond lengths reported for compounds **1a** and **2c** (Table 1) occur within the ranges noted above and near the average values. However, bond lengths for the compounds formulated as tungsten species are noticeably more irregular and do not compare simply to the values collected in Table 2. For example, metal–chloride bond lengths for **3a** (2.173(7), 2.178(6) Å) occur at the low end of the range of Zn–Cl values, while metal–nitrogen bond lengths for **3c** (2.066(4), 2.038(4) Å) occur at and below the low end of the range of Zn–N values in Table 2.

A survey of M–Cl bond lengths is presented in Table 3 for chromium, molybdenum, and tungsten complexes across a range of formal oxidation states (0–6), coordination numbers, and geometries. While not an exhaustive listing of Group VI M–Cl bond lengths, Table 3 is nonetheless extensive and supports the identification of an unambiguous structural trend. At parity of ligand environment and redox state, Mo–Cl and W–Cl bond lengths are typically ~ 0.1 Å longer than analogous Cr–Cl values. While certain specific comparisons in Table 3 admit of smaller differences, we emphasize that Table 3 shows

Table 2. Summary of Crystallographically Identified [ZnCl₂(dad)] Complexes

compd #	Zn–Cl, Å	Zn–N, Å	Cl–Zn–Cl, deg	ref
4	2.2055(4), 2.2130(4)	2.0647(12), 2.0699(12)	116.568(16)	6
5 ^a	2.2085(7), 2.2026(8)	2.0873(15)	116.73(3)	6
6 ^b	2.2095(4)	2.0754(10)	121.47(3)	6
7	2.2163(3), 2.2110(3)	2.0754(8), 2.0825(9)	115.254(10)	6
8 ^b	2.252(7)	2.064(3)	109.8(2)	25
9	2.219(1), 2.225(1)	2.083(3), 2.078(3)	118.44(4)	26
10 ^b	2.2173(7)	2.076(2)	122.67(4)	27
11	2.214(8), 2.218(7)	2.081(2), 2.085(2)	119.61(3)	28
12	2.194(2), 2.224(2)	2.093(5), 2.096(5)	116.27(8)	28
13	2.204(2), 2.2035(9)	2.079(7), 2.079(1)	114.51(9)	29
14	2.2013(6), 2.2180(6)	2.085(2), 2.071(2)	116.80(2)	30
15 ^a	2.1967(15), 2.1979(15)	2.114(2)	117.67(6)	31
16	2.1863(15), 2.2138(14)	2.113(3), 2.125(3)	118.03(6)	31
17 ^c	2.173(2), 2.187(2), 2.188(2), 2.195(2)	2.109(4), 2.121(4), 2.128(5), 2.147(4)	120.26(6), 121.17(6)	32

^aCompound resides on mirror plane coincident with ZnCl₂ plane and bisecting the diazadiene ligand. ^bCompound resides on a crystallographic 2-fold axis bisecting the Cl–Zn–Cl angle. ^cTwo half-molecules occur in the asymmetric unit.

no W–Cl or Mo–Cl bond lengths that are shorter than the corresponding values in related Cr complexes. This observation is at stark variance with the data in Table 2, where **3a** is seen to have nominally shorter M–Cl bond lengths (2.173(7), 2.178(6) Å) than **1a** (2.190(3), 2.197(4) Å). That the M–Cl bond lengths listed for **2c**, **3a**, and **3c** are all significantly shorter by ~0.1 Å than even the shortest Mo–Cl and W–Cl values catalogued in Table 3 is a compelling indication that M is a first row element in all these compounds. This point regarding metal–ligand bond length differences for first row versus second and third row transition metals is obviously pertinent to the M–N_{imine} bond lengths as well. Although a broad survey of M–N_{imine} (M = Cr, Mo, W) bond lengths has not been undertaken, arbitrarily selected comparisons, such as the M–N bonds in [M(CO)₅(pyridine)] (M = Cr: 2.165(4) Å;⁸⁹ M = W: 2.258(7), 2.272(6) Å⁹⁰) and [M(2,2':6',2''-terpyridine)₂] (M = Cr: 1.949(1), 2.018(1) Å;⁹¹ M = W: 2.050(2), 2.077(2) Å⁹¹) corroborate the expectation.

The occurrence of isostructural, isomorphous species for transition metals within the same triad is relatively common, even for the first and third row metals. The generally longer metal–ligand bond lengths for complexes with the third row elements versus first row metals, noted above, are typically reflected in unit cell volumes that are appreciably larger, within the derived uncertainties, for the third row species over their first row counterparts. Table S1, Supporting Information presents a compilation of the unit cell volumes for isostructural, isomorphous chromium and tungsten complexes taken from a survey of the Cambridge Structural Database. The entries in Table S1 are restricted to data sets measured at the same or similar temperature (±30 K), as temperature has a direct and important effect upon the physical dimensions of the unit cell. Although not exhaustive, Table S1 includes all homologous Cr–W pairs of which we are aware and shows that it is

improbable⁹² that a tungsten complex would display a smaller unit cell volume than its chromium homologue. The smaller unit cell volume shown in Table 1 for **3a** (2300.1(11) Å³) is therefore implausible in view of the corresponding volume of 2332.8(17) Å³ given for isostructural **1a**.

Both hybrid and pure density functionals have been reported to be generally useful in replicating the structures and properties of transition metal complexes. Although calculated metal–ligand bond lengths using the B3LYP functional employed here are typically larger than experimentally determined values,⁹³ the “errors” associated with the series of compounds optimized here are likely systematic and therefore would not obscure an assessment of bond length differences between compounds. Starting with the crystallographic coordinates for the tetrahedral compound reported as [CrCl₂(^{Mes}dad^{Me})], we find that, with M = Cr, Mo, or W and an S = 0 spin state, convergence toward an energy minimum corresponding to a tetrahedral structure of C_{2v} symmetry is quickly achieved. Although we do not believe these gas phase energy-minimized structures correspond to isolable or observable species in solution or solid phase, it is noteworthy that the calculated metal–ligand bond lengths for this M = Cr, Mo, W series (Table 4) reflect a significant ~0.1 Å difference between the first row metal and its second and third row congeners that is comparable to the differences observed experimentally by X-ray diffraction, as summarized in Table 3. We find the nonadherence to this general trend by the compounds identified as [MCl₂(dad)] (M = Cr, Mo, W) species to be a further basis for our contention that these molecules are misidentified.

To directly assess the effect of variation of the identity of the metal atom upon the refinement behavior of diffraction data for the type of zinc compound in question, we have deliberately prepared, crystallized, and obtained our own X-ray diffraction data for [ZnCl₂(^{Mes}dad^{Me})]·CH₂Cl₂ (^{Mes}dad^{Me} = 1,4-bis(2,4,6-trimethylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene). It is this compound that we assert is the true identity of both **2c**·CH₂Cl₂ and **3c**·CH₂Cl₂ in Table 1. Crystallographic data for [ZnCl₂(^{Mes}dad^{Me})]·CH₂Cl₂ are collected in Table 5, where the highly similar unit cell dimensions between [ZnCl₂(^{Mes}dad^{Me})]·CH₂Cl₂ and **2c**·CH₂Cl₂ and **3c**·CH₂Cl₂ are easily seen. As gauged by R₁ and wR₂ values, overall refinement for [ZnCl₂(^{Mes}dad^{Me})]·CH₂Cl₂ is better than given for **2c**·CH₂Cl₂ and **3c**·CH₂Cl₂, which may be attributed at least in part to correct identification of the metal atom. A greater amount of data collected at lower temperature also contributes to these lower values. The results of refining Zn as Cr, Mo, and W instead are summarized in Table 6. When M = Cr, final R₁ and wR₂ values for data cut at I < 2σI (0.0926, 0.2712) are roughly comparable to the values presented by Bouachir et al. (0.0735, 0.1921). Unsurprisingly, we find that while prompted to refine an extinction parameter because the metal atom is now too light, all non-hydrogen atoms can be refined anisotropically and produce thermal ellipsoids that are not untoward in appearance. Notably, if the metal atom is identified as Mo, we find final R₁ and wR₂ values (0.0730, 0.2308) that are quite similar to those reported for **2c**·CH₂Cl₂ (0.0808, 0.2265). Again, no obviously anomalous-looking thermal ellipsoids result for any atoms when anisotropic refinement is implemented. With M = W, the refinement behavior dramatically worsens, as expected, with R₁ and wR₂ ballooning to 0.1893 and 0.5145, respectively (cf. 0.0697, 0.2110 for **3c**·CH₂Cl₂) and nonpositive definite

Table 3. Representative Cr–Cl (red), Mo–Cl (green), and W–Cl (blue) Bond Lengths

Metal Complex	M–Cl Bond length(s), Å	Ref.
M⁰		
[K ⁺ ·18-crown-6][Cr(CO) ₅ Cl]	2.534(7)	33
[H ₃ O ⁺ ·18-crown-6][W(CO) ₅ Cl]	2.68(1)	33
[ⁿ Bu ₄ N][W(CO) ₅ Cl]	2.5602(8)	34
[Ph ₃ PNPPh ₃][W(CO) ₅ Cl]	2.560(3)	35
[Et ₄ N][W(CO) ₅ Cl]	2.6406(12)	<i>a</i>
M¹⁺		
<i>trans</i> -[MoCl(N ₂)(PMe ₃) ₄]	2.415(8)	36
<i>trans</i> -[WCl(N ₂)(PMe ₃) ₄]	2.46(1)	36
M²⁺		
[CrCl ₂ (dmpe) ₂] ^b	2.351(3), 2.345(3)	10
[CrCl ₂ (depe) ₂] ^c	2.3414(7)	11
[CrCl ₂ ((PH ⁱ Pr) ₂ C ₆ H ₄) ₂]	2.336(4), 2.334(4)	12
[MoCl ₂ (dmpe) ₂] ^b	2.435(1)	37
[MoCl ₂ (dppe) ₂]·0.5C ₅ H ₁₂ ^d	2.424(3), 2.444(3)	38
[MoCl ₂ (dppe) ₂]·2THF ^d	2.4346(5)	38
[MoCl ₂ (dppb) ₂] ^e	2.410(1)	14
[MoCl ₂ (PMe ₃) ₄]	2.4662(7)	39
[WCl ₂ (PMe ₃) ₄]	2.4572(9)	39
[WCl ₂ (PMePh ₂) ₄]	2.4270(4), 2.4289(4)	1
M³⁺		
Cs ₃ [Cl ₃ Cr(μ-Cl ₃)CrCl ₃]	2.34 ^f	40
[Et ₃ NH] ₃ [Cl ₃ Cr(μ-Cl ₃)CrCl ₃]	2.286(2), 2.305(2), 2.310(2) ^f	41
Cs ₃ [Cl ₃ Mo(μ-Cl ₃)MoCl ₃]	2.384(6) ^f	42
[MeNH ₃] ₃ [Cl ₃ Mo(μ-Cl ₃)MoCl ₃]	2.361(5), 2.405(6) ^f	43
Cs ₃ [Cl ₃ W(μ-Cl ₃)WCl ₃]	2.407(9) ^f	44
[HP(C ₆ H ₂ -2,4,6-(OMe) ₃) ₃] ₃ [Cl ₃ W(μ-Cl ₃)WCl ₃]	2.409(3), 2.412(3), 2.425(3), 2.411(3), 2.410(3), 2.419(3) ^f	45
[CrCl ₂ (dmpe) ₂][BPh ₄] ^b	2.293(4)	46
[MoCl ₂ (dippe) ₂][BF ₄] ^g	2.392(2), 2.397(2)	47
[WCl ₂ (dppe) ₂][BF ₄] ¹ · ¹ / ₃ CH ₂ Cl ₂ ^d	2.312(5)	48
[WCl ₂ (dppe) ₂][PF ₆] ^d	2.3218(16), 2.3188(11), 2.3190(10), 2.3232(13)	49
[Ph ₄ P][{HB(pyz) ₃ }CrCl ₃] ^h	2.3355(11), 2.3405(11), 2.3445(11)	50
[Et ₄ N][{HB(3,5-Me ₂ pyz) ₃ }MoCl ₃]·MeCN ⁱ	2.4304(5), 2.4331(2)	51
[NH ₄] _{0.5} [Et ₄ N] _{0.5} [{HB(pyz) ₃ }WCl ₃] ^h	2.4391(2)	51
[<i>mer</i> -CrCl ₃ (PMe ₂ Ph) ₂ (OPMe ₂ Ph)]	2.346(3), 2.319(3), 2.330(3)	52
[<i>mer</i> -{P(CH ₂ CH ₂ PPh ₂) ₃ }CrCl ₃]	2.292(6), 2.306(4), 2.320(5)	53
[<i>fac</i> -{CH ₃ C(CH ₂ PMe ₂) ₃ }CrCl ₃]·CH ₂ Cl ₂	2.328(2), 2.333(2), 2.334(2)	54
[<i>mer</i> -{MeP(CH ₂ CH ₂ CH ₂ PMe ₂) ₂ }MoCl ₃]· ³ / ₄ THF	2.396(3), 2.419(3), 2.443(3)	55
[<i>mer</i> -{PhP(CH ₂ CH ₂ CH ₂ PPh ₂) ₂ }MoCl ₃]·CH ₂ Cl ₂	2.382(8), 2.396(9), 2.439(8)	55
[<i>mer</i> -MoCl ₃ (PMe ₂ Ph) ₃]	2.400(1), 2.420(1), 2.427(1)	56
[<i>fac</i> -WCl ₃ (PMe ₃) ₃]	2.450(3), 2.452(2), 2.458(2)	<i>a</i>
[<i>fac</i> -WCl ₃ (PMe ₂ Ph) ₃]	2.4416(16), 2.4475(16), 2.4545(15)	57
[Ph ₃ PNPPh ₃][CpCrCl ₃]	2.291(2), 2.300(2), 2.312(2)	58
[Cp* ₂ Cr][Cp*CrCl ₃]	2.3195(14), 2.3208(14), 2.3308(14)	59

Table 3. continued

Metal Complex	M–Cl Bond length(s), Å	Ref.
M³⁺		
[HpyNH ₂][Cr(bipy)Cl ₄]	2.3415(13), 2.3515(12), 2.3172(9)	60
[PPh ₄][Mo(bipy)Cl ₄]	2.428(1), 2.432(1), 2.433(1), 2.440(1)	61
[PHMe ₃][CrCl ₄ (PMe ₃) ₂]	2.327(1), 2.353(1)	52
[PPh ₄][MoCl ₄ (PMePh ₂) ₂]	2.434(1), 2.429(1)	62
[PPh ₄][MoCl ₄ (PEt ₃) ₂]	2.421(3), 2.434(2), 2.441(3), 2.452(2)	62
[PHEtPh ₂][MoCl ₄ (PEt ₂ Ph) ₂]· <i>n</i> -C ₆ H ₁₄	2.427(4), 2.433(4), 2.450(4), 2.455(4)	62
[Cp* ₂ Co][WCl ₄ (PMePh ₂) ₂]	2.4355(6), 2.4092(6) ^j	1
[NH ₂ Me ₂] ₄ [CrCl ₆]Cl	2.356(2), 2.350(3), 2.372(2)	63
[NH ₂ Me ₂] ₄ [WCl ₆]Cl	2.5605(10), 2.5704(11), 2.6008(10)	64
M⁴⁺		
<i>trans</i> -[CrCl(NEt)(dmpe) ₂][CF ₃ SO ₃]	2.425(4)	65
<i>trans</i> -[MoCl(NMe)(dppe) ₂][PF ₆]·CH ₂ Cl ₂	2.492(2)	66
<i>trans</i> -[WCl(NEt)(dppe) ₂][PF ₆]·CH ₂ Cl ₂	2.471(2)	67
[Cp* ₂ MoCl ₂]	2.462(2), 2.466(2)	68
[(Me ₂ C(C ₅ Me ₄) ₂ WCl ₂)]	2.452(2)	69
[(Me ₂ Si(C ₅ Me ₄) ₂ WCl ₂)]	2.440(2), 2.444(2)	70
[(Me ₂ Si(C ₅ H ₂ Me ₂) ₂ WCl ₂)]	2.439(1), 2.450(1)	71
[MoCl ₄ (4-Et-pyridine-N) ₂]	2.340(1)	72
[<i>cis</i> -MoCl ₄ (H ₂ N ⁱ Bu) ₂]	2.424(4), 2.428(5), 2.430(4), 2.445(4)	73
[<i>trans</i> -MoCl ₄ (H ₂ N ⁱ Bu) ₂]·4NH ₂ ⁱ Bu	2.401(4), 2.426(5), 2.457(5), 2.484(4)	
[WCl ₄ (PMe ₃) ₂]	2.3140(8), 2.3581(6)	1
[WCl ₄ PM ₂ Ph ₂]	2.3486(5), 2.3411(5)	1
[WCl ₄ (PMePh ₂) ₂]	2.3379(7), 2.3466(6)	1
[WCl ₄ (dppe)]	2.268(2), 2.330(2), 2.384(2), 2.331(2)	1
[PClPh ₃] ₂ [MoCl ₆]	2.3825(5)	74
[Me ₃ PhN] ₂ [WCl ₆]	2.365(1), 2.376(2), 2.385(1)	75
[PPh ₄] ₂ [WCl ₆]·4MeCN	2.339(2), 2.355(2), 2.372(2)	76
[K(18-crown-6)(CH ₂ Cl ₂) ₂][WCl ₆]·6CH ₂ Cl ₂	2.336(4)	76
M⁵⁺		
[AsPh ₄][CrOCl ₄]	2.240(3)	77
[AsPh ₄][MoOCl ₄]	2.333(3)	78
[PPh ₄][WOCl ₄]	2.379(1)	79
[NH ₄][WCl ₆]	2.313(1), 2.327(1), 2.328(1)	76
M⁶⁺		
[Cp*CrOCl ₂]	2.231(2), 2.246(2)	80
[Cat][CrO ₃ Cl] ^k	2.189(1), 2.175(2), 2.182(1), 2.188(1), 2.158(1)	81
[MoO ₂ Cl ₂ (bipy)]	2.366(1), 2.3769(9)	82
MoO ₂ Cl ₂ (4,4'-Me ₂ bipy)]	2.370(2), 2.375(2)	83
[MoO ₂ Cl ₂ ((pyz) ₂ CH ₂)]	2.3570(7), 2.3877(5)	84
[MoO ₂ Cl ₂ (RSCH ₂ CH ₂ SR)]	2.3484(10), 2.3446(10) (R = Me); 2.3550(5) (R = Et)	85
[WOCl ₄ (NCPH)]	2.3027(12), 2.3091(13)	86
[WO ₂ Cl ₂ (1,3-dimethylalloxazine)]	2.3404(11), 2.3480(12)	87
[WO ₂ Cl ₂ (bis(1-methylimidazol-2-yl)ketone)]	2.349(3), 2.350(3)	87
[Et ₄ N][WOCl(1,2-benzenedithiolate) ₂]	2.436(2)	88

^aThis work. ^bdmpe = 1,2-bis(dimethylphosphino)ethane. ^cdepe = 1,2-bis(diethylphosphino)ethane. ^ddppe = 1,2-bis(diphenylphosphino)ethane. ^edppb = 1,2-bis(diphenylphosphino)benzene. ^fTerminal M–Cl bond length(s). ^gdippe = 1,2-bis(diisopropylphosphino)ethane. ^hHB(pz)₃ = hydridotris(pyrazolyl)borate(1-). ⁱHB(3,5-Me₂pz)₃ = hydridotris(3,5-dimethylpyrazolyl)borate(1-). ^jData are for the P₂/n polymorph. ^kFive independent structures reported. Cat = 1/2[4,4'-bipyridinedium]²⁺, [4-methylquinolinium]⁺, [6-methylquinolinium]⁺, [N,N'-ethylenediaminium]⁺, [5-Cl-2-pyridyl](2-pyridyl)NH₂⁺, respectively, for the five given Cr–Cl values.

Table 4. Calculated Metal–Ligand Bond Lengths, Angles for $[\text{MCl}_2(\text{Mes}^{\text{dad}}\text{Me})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$)

	$[\text{CrCl}_2(\text{Mes}^{\text{dad}}\text{Me})]$	$[\text{MoCl}_2(\text{Mes}^{\text{dad}}\text{Me})]$	$[\text{WCl}_2(\text{Mes}^{\text{dad}}\text{Me})]$
M–Cl, Å	2.20	2.33	2.30
M–N, Å	1.86	1.95	1.94
Cl–M–Cl, deg	138.10	138.00	128.82

Table 5. Unit Cell and Refinement Data for $[\text{ZnX}_2(\text{Mes}^{\text{dad}}\text{Me})] \cdot \text{CH}_2\text{Cl}_2$ ($\text{X} = \text{Cl}, \text{Br}$)

formula	$\text{C}_{23}\text{H}_{30}\text{Cl}_4\text{N}_2\text{Zn}$	$\text{C}_{23}\text{H}_{30}\text{Br}_2\text{Cl}_2\text{N}_2\text{Zn}$
fw	541.71	630.58
temperature, K	150	100
wavelength, Å	0.71073	0.71073
2θ range, deg	4.02–66.28	3.98–55.66
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a , Å	12.6703(2)	12.625(3)
b , Å	14.4861(2)	14.625(3)
c , Å	14.1761(2)	14.336(3)
α , deg	90	90
β , deg	90.837(1)	90.002(30)
γ , deg	90	90
volume, Å ³	2601.65(7)	2646.9(9)
Z	4	4
density, g/cm ³	1.378	1.582
μ , mm ^{−1}	1.367	4.162
crystal size	$0.12 \times 0.15 \times 0.21$	$0.10 \times 0.13 \times 0.17$
color, habit	yellow slab	yellow block
limiting indices, h	$-16 < h < 19$	$-16 < h < 16$
limiting indices, k	$-22 < k < 22$	$-19 < k < 19$
limiting indices, l	$-21 < l < 21$	$-18 < l < 18$
reflections collected	50166	29645
independent data	9919	4742
restraints	69	0
parameters refined	285	274
GOF ^a	1.118	0.964
$R_1, wR_2^{d,c}$	0.0514, 0.1343	0.0465, 0.1177
$R_1, wR_2^{d,e}$	0.0682, 0.1442	0.0640, 0.1225
largest diff peak, e·Å ^{−3}	1.340	0.926
largest diff hole, e·Å ^{−3}	−1.348	−1.204

^aGOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n = number of reflections and p is the total number of parameters refined. ^b $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$. ^c R indices for data cut off at $I > 2\sigma(I)$. ^d $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $P = (F_o^2 + 2F_c^2)/3$. ^e R indices for all data.

behavior resulting for nearly every atom of the diazadiene ligand.

Inspection of the crystallographic data files provided as Supporting Information for the crystal structures of **2c**·CH₂Cl₂, **3a**, and **3c**·CH₂Cl₂ reveals that the models refined against the diffraction data employed site occupancy factors for the metal

atoms — and only for the metal atoms — that were substantially less than unity: 0.775 for Mo in **2c**·CH₂Cl₂, 0.417 and 0.4005 for W in **3a** and **3c**·CH₂Cl₂, respectively.⁹⁴ While it is not uncommon to refine parts of a crystal structure with fractional site occupancies, for example, in a situation involving compositional disorder or partial occupancy by an interstitial solvent molecule, the effect of this selective treatment of the metal atoms is to cause them to behave as an element with proportionately smaller atomic number and scattering power. The *specific* site occupancy factors used are notably close to the ratios of the atomic numbers of Zn over Mo (30/42 = 0.714) and Zn over W (30/74 = 0.405), meaning that the *specific* lighter element whose appearance is deduced using the foregoing combination of heavier element scattering factors and offsetting partial site occupancies is zinc. For emphasis, Table 6 shows that, when the diffraction data collected for $[\text{ZnCl}_2(\text{Mes}^{\text{dad}}\text{Me})] \cdot \text{CH}_2\text{Cl}_2$ are refined with metal as Mo and partial site occupancy of 0.775, or as tungsten with partial site occupancy of 0.409, final refinement statistics are obtained that are nearly the same as with the correct model employing Zn at a site occupancy of 1.00 (cf. Tables 5 and 6).

As a final test of the general procedure reported for the synthesis of $[\text{WCl}_2(\text{dad})]$, we have applied it using $[\text{WBr}_4(\text{MeCN})_2]$ in place of the corresponding chloride and found it to produce yellow crystalline, diamagnetic $[\text{ZnBr}_2(\text{Mes}^{\text{dad}}\text{Me})]$, which we have identified by ¹H NMR spectroscopy, mass spectrometry, and X-ray crystallography (Table 5, Figure 3). The compound is isostructural and isomorphous to the chloride homologue, differing only in having slightly longer metal–halide bond lengths (2.3313(8), 2.3480(7) Å vs 2.2033(6), 2.2140(6) Å) that result in a slightly larger unit cell volume. The tungsten(IV) precursor, while it evidently undergoes some degree of reduction, appears to do so incompletely and to deposit from the crystallization mixture as an ill-defined brown oily material that is not amenable to further characterization.

SUMMARY AND CONCLUSIONS

The primary conclusion emerging from our examination of the crystallographic characterization of the chromium, molybdenum, and tungsten $[\text{M}^{\text{II}}\text{Cl}_2(\text{diazadiene})]$ complexes reported by Bouachir and co-workers is that the compounds isolated in their work were Zn species rather than the intended Group 6 complexes, zinc metal having been employed as common reducing agent in their synthesis from higher-valent precursors.

Table 6. Refinement Statistics for $[\text{ZnCl}_2(\text{Mes}^{\text{dad}}\text{Me})]$ Refined with $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$

	$[\text{CrCl}_2(\text{Mes}^{\text{dad}}\text{Me})]$	$[\text{MoCl}_2(\text{Mes}^{\text{dad}}\text{Me})]$		$[\text{WCl}_2(\text{Mes}^{\text{dad}}\text{Me})]$	
		SOF ^c = 1	SOF ^c = 0.775	SOF ^c = 1	SOF ^c = 0.409
R_1, wR_2^a	0.0926, 0.2712	0.0730, 0.2308	0.0530, 0.1311	0.1893, 0.5145	0.0529, 0.1371
R_1, wR_2^b	0.1154, 0.2997	0.0944, 0.2535	0.0747, 0.1469	0.2141, 0.5454	0.0753, 0.1561
GOF	1.056	1.048	1.044	2.399	1.015
residual density	3.687, −1.420	1.755, −2.232	1.307, −1.369	15.611, −4.687	1.364, −1.313

^aData cut at $I < 2\sigma I$. ^bAll data used. ^cSOF = site occupancy factor.

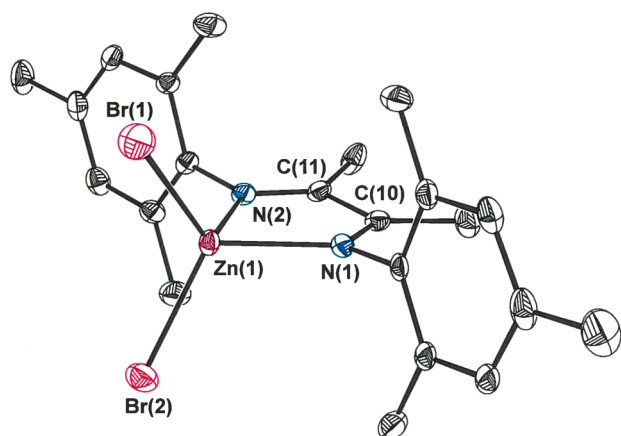


Figure 3. Thermal ellipsoid plot at the 50% probability level for $[\text{ZnBr}_2(\text{MesdadMe})]$. All H atoms are omitted for clarity.

The metal–chloride and metal–nitrogen bond lengths reported for the compounds identified as molybdenum and tungsten species are significantly shorter by ~ 0.1 Å than typical bond lengths of these kinds, as shown by a broad survey of structural data within the Cambridge Structural Database, and are consistent instead with the metal being a first row element. We emphasize that the M–Cl bond lengths in the putative $[\text{WCl}_2(\text{dad})]$ compound (**3a**, Figure 1, Table 1) are significantly shorter than any W–Cl bond length we have been able to identify for any complex of tungsten in any oxidation state. Similarly, unit cell volumes among the set of $[\text{MCl}_2(\text{dad})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) complexes are at variance with the clear trend of larger volumes for tungsten complexes versus their chromium counterparts among isostructural, isomorphous Group 6 complexes. Rather high R_1 and wR values for the final, refined crystal structures, especially when all data are included, are further suggestive of structural models that are fundamentally incorrect. That acceptable thermal ellipsoids are observed for the published images of **2c**· CH_2Cl_2 , **3a**, and **3c**· CH_2Cl_2 has been found to be due to the incorrect usage of partial site occupancy factors that cause Mo and W to appear as zinc. An effort to prepare $[\text{WBr}_2(\text{MesdadMe})]$ from $[\text{WBr}_4(\text{MeCN})_2]$ and Zn^0 by the published procedure produced, in our hands, $[\text{ZnBr}_2(\text{MesdadMe})]$ instead.

Collectively taken, the foregoing observations disprove the synthetic and structural results reported in the series of papers published by Bouachir and co-workers. The incorrect formulation of a crystallographically characterized compound by element misidentification can easily occur when the elements in question are similar in diffracting power (e.g., S and Cl)⁹⁵ and when a heavy reliance upon X-ray diffraction as a tool of qualitative analysis has been — or must be — made. We are unaware, however, of a documented instance in which the elements in question differ as much as they do in the present case. The error notwithstanding, we submit that the work we have reviewed and sought to correct presents an instructive case study for the crystallography student looking for awareness of the potential pitfalls of highly automated crystal structure solving and refining. It offers also a reminder to the reviewing community that such mundane aspects of crystal structures as bond lengths are important details for scrutiny when the structures of unusual or implausible species are reported.

EXPERIMENTAL SECTION

$[\text{ZnCl}_2(\text{MesdadMe})]$. A 15 mL CH_2Cl_2 solution of the MesdadMe ligand (0.531 g, 1.66 mmol), prepared according a literature procedure,⁹⁶ was treated with an excess (several grams) of commercial $\text{ZnCl}_2 \cdot \text{Et}_2\text{O}$ in 25 mL of H_2O . This heterogeneous, two-phase mixture was stirred in air for 36 h, whereupon it was diluted with 50 mL portions each of CH_2Cl_2 and H_2O . The organic layer was separated, and the aqueous phase extracted with additional portions of CH_2Cl_2 (2×50 mL). The combined organic portions were dried over anhydrous Na_2SO_4 , filtered, and reduced to a solid residue under reduced pressure. The residue was redissolved in a minimal volume of CH_2Cl_2 (~ 15 mL). Slow evaporation of the solution afforded a mixture of crystalline $[\text{ZnCl}_2(\text{MesdadMe})] \cdot \text{CH}_2\text{Cl}_2$ and free MesdadMe ligand, as determined by X-ray crystallography.⁹⁷ The more soluble free ligand was separated by extraction with CH_2Cl_2 (2×1 mL), and the remaining yellow $[\text{ZnCl}_2(\text{MesdadMe})]$ was recrystallized by diffusion of *n*-pentane vapor into a saturated THF solution. R_f (1:1, CH_2Cl_2 /hexanes): 0.26. ^1H NMR (δ , ppm in CDCl_3): 6.94 (s, 4H, aromatic C–H), 2.28 (s, 6H, $-\text{N}=\text{C}-\text{CH}_3$), 2.21 (s, 6H, mesityl *p*- CH_3), 1.54 (s, 12H, mesityl *o*- CH_3). MALDI MS: m/e $\text{C}_{22}\text{H}_{28}\text{Cl}_2\text{N}_2\text{Zn}$, 454.756; Observed: 418.868 (M–Cl).

$[\text{ZnBr}_2(\text{MesdadMe})]$. The procedure and crystallization method of Bouachir et al.⁴ was followed using $[\text{WBr}_4(\text{MeCN})_2]$ ⁹⁸ in place of $[\text{WCl}_4(\text{MeCN})_2]$. After the crystalline compound thus obtained was identified as $[\text{ZnBr}_2(\text{MesdadMe})]$, the reaction was repeated on a scale employing 0.967 g of $[\text{WBr}_4(\text{MeCN})_2]$ (1.60 mmol), 1.54 g of MesdadMe (4.82 mmol), and 0.525 g of Zn dust (8.03 mmol). After 48 h of stirring, the reaction mixture was filtered, and the filtrate was reduced to dryness to afford 0.419 g of crude solid. This solid was redissolved in a minimal volume of CH_2Cl_2 and purified on a silica column eluted with the same solvent. The leading yellowish band was collected and identified as a mixture of $[\text{ZnBr}_2(\text{MesdadMe})]$ and free MesdadMe ligand. The MesdadMe ligand was separated by extracting the mixture of solids with CH_2Cl_2 (2×1 mL). The resulting yellow solid residue could be recrystallized by the diffusion of *n*-pentane vapor into a saturated THF or CH_2Cl_2 solution. R_f (1:1, CH_2Cl_2 /hexanes): 0.30. ^1H NMR (δ , ppm in CDCl_3): 6.94 (s, 4H, aromatic C–H), 2.29 (s, 6H, $-\text{N}=\text{C}-\text{CH}_3$), 2.25 (s, 6H, mesityl *p*- CH_3), 1.54 (s, 12H, mesityl *o*- CH_3). MALDI MS: m/e $\text{C}_{22}\text{H}_{28}\text{Br}_2\text{N}_2\text{Zn}$, 545.676; observed: 465.077 (M–Br). Anal. Calcd for $[\text{ZnBr}_2(\text{MesdadMe})] \cdot \frac{3}{4} \text{CH}_2\text{Cl}_2$, $\text{C}_{22.75}\text{H}_{29.5}\text{Br}_2\text{Cl}_{1.5}\text{N}_2\text{Zn}$: C, 44.84; H, 4.88; N, 4.60. Found: C, 44.72; H, 4.88; N, 4.58.

$[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{Cl}]$. This compound was isolated as single crystals arising from a reaction between $[\text{W}(\text{CO})_4(\text{piperidine})_2]$ ⁹⁹ and *cis*-2,3-dithiolato-2-butene(2-)/ $\text{Et}_4\text{N}^+\text{Cl}^-$. Being an unintended product, it was not characterized further beyond an X-ray crystal structure. The W–Cl bond length in this anion is included in Table 3 to assist the comparison between W–Cl and Cr–Cl bond lengths in related compounds.

$[\text{fac-}\text{WCl}_3(\text{PMe}_3)_3]$. This compound was identified as an adventitious byproduct attending the synthesis of $[\text{W}^{\text{IV}}\text{Cl}_4(\text{PMe}_3)_3]$ from WCl_6 and PMe_3 in the presence of Zn^0 as reducing agent. A deliberate synthesis has been reported by Sharp.¹⁹ The compound was characterized structurally by X-ray crystallography but not subjected to other physical methods. The W–Cl bond lengths in this compound are included in Table 3 to assist the comparison between W–Cl and Cr–Cl bond lengths in compounds of the same or similar type.

CALCULATIONS

All calculations were performed using the Gaussian09 package. Geometry optimizations were calculated at a B3LYP level of theory using the default pruned fine grids for energies (75 302) and the default pruned coarse grids (35 110) for Hessians and gradients for all atoms except tungsten. All structures were confirmed by ensuring that imaginary frequencies were not present. The basis set chosen for all main group elements, except hydrogen, is the 6-31G(d,p). For chromium, molybdenum, and tungsten, the LANL2DZ with effective core potential

was implemented, and a split valence (SV) basis set was used for all hydrogen atoms.

■ ASSOCIATED CONTENT

Supporting Information

Spectroscopic data for $[\text{ZnCl}_2(\text{Mes}^{\text{d}}\text{ad}^{\text{Me}})]$ and $[\text{ZnBr}_2(\text{Mes}^{\text{d}}\text{ad}^{\text{Me}})]$. Full description of procedures for crystal growth, diffraction data collection and processing, and structure solution and refinement; complete crystallographic data for all new structures in CIF format; thermal ellipsoid plots with complete atom labeling; table of unit cell volumes for isostructural, isomorphous Cr and W compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The Louisiana Board of Regents is thanked for enhancement Grant LEQSF-(2002-03)-ENH-TR-67 with which Tulane's X-ray diffractometer was purchased, and Tulane University is acknowledged for its ongoing support with operational costs for the diffraction facility. Support from the National Science Foundation (Grant CHE-0845829 to J.P.D.) and from the Louisiana Board of Regents and the IBM Corporation (to A.F.G.) is gratefully acknowledged.

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