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Dimers that Contain Unbridged W(IV)/W(IV) Double Bonds

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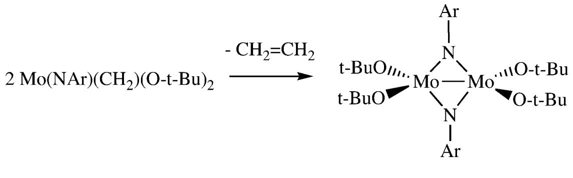
Compounds that contain an unbridged W═W bond can be prepared through bimolecular decomposition of various imido alkylidene complexes. One type of W═W species is $[W(NR)(CH_2\text{-t-Bu})(OR')]_2$ (R = 2,6-dimethylphenyl (Ar′) or 2,6-diisopropylphenyl (Ar); R′ = pentafluorophenyl or hexafluoroisopropyl), which is found in both heterochiral and homochiral forms. The other type is $[W(NR)(OR')_2]_2$ (R′ = trifluoro-*tert*-butyl or hexafluoro-*tert*-butyl). All species contain an unbridged W(IV)/W(IV) double bond with a W═W bond distance of 2.4−2.5 Å, a 90° angle between the imido ligands and the W═W bond, and an *anti* relationship of the imido ligands. There is no indication that W═W bonds are broken spontaneously; for example, heterochiral and homochiral $[W(NR)(CH_2\text{-t-Bu})(OR')]_2$ species do not interconvert.

Introduction

High oxidation state imido alkylidene complexes of tungsten and molybdenum, especially those of the type $M(NR)(CHR')(OR'')_2$, comprise a large class of well-defined olefin metathesis catalysts.[1] Although there is little doubt concerning many details of olefin metathesis reactions, relatively little is known about how catalytic intermediates decompose and the reverse of those reactions, i.e., if and how alkylidenes might be regenerated. Evidence suggests that there are two main deactivation pathways. One is rearrangement of intermediate metalacyclobutane complexes.[2] A second is bimolecular coupling of alkylidenes to give olefins.[3] The possibility that a third, formation of a cyclopropane, is operative in certain circumstances cannot be excluded. Bimolecular decomposition of alkylidenes is slowest for neopentylidene or neophylidene complexes and most rapid for methylene complexes. $M(NR)(OR'')_2$(olefin) complexes have been observed,[2] and in one case an ethylene complex has been isolated and crystallographically characterized.[4]

Alkylidenes were believed to decompose to give bimetallic species that contain bridging imido ligands.[2] The only crystallographically characterized species in the literature is $[Mo(\mu\text{-}NAr)(O\text{-t-Bu})_2]_2$ (Ar = 2,6-i-$Pr_2C_6H_3$; Mo−Mo = 2.654(1) Å), which is formed in a reaction between $Mo(NAr)(CH\text{-t-Bu})(O\text{-t-Bu})_2$ and ethylene (eq 1).[2] $[Mo(\mu\text{-}NAr)(O\text{-t-Bu})_2]_2$ has approximately a tetrahedral arrangement of ligands about each metal. However, the $Mo_2(O\text{-t-Bu})_4$ core is *not* flat; the O−M−M−O dihedral angle is ∼15°, and the O−Mo−O angle is ∼112°. Nevertheless, proton NMR spectra show no evidence of inequivalent *tert*-butoxide ligands at room temperature. Since no propylene was observed as a product of this reaction, $[Mo(\mu\text{-}NAr)(O\text{-t-Bu})_2]_2$ was proposed to form via bimolecular decomposition of intermediate $Mo(NAr)(CH_2)(O\text{-t-Bu})_2$ species (eq 1). Evidently neither an ethylene complex nor a molybdacyclopentane complex is stable with respect to formation of $[Mo(\mu\text{-}NAr)(O\text{-t-Bu})_2]_2$, and any back reaction between $[Mo(\mu\text{-}NAr)(O\text{-t-Bu})_2]_2$ and ethylene is slow. A compound with the empirical formula $W(NAr)[OCMe(CF_3)_2]_2$ (according to NMR and elemental analyses) was proposed to be a bimetallic complex bridged by imido ligands, i.e., $\{W(\mu\text{-}NAr)[OCMe(CF_3)_2]_2\}_2$.[5] This compound, which was isolated from the reaction between $W(NAr)(CH\text{-t-Bu})[OCMe(CF_3)_2]_2$ and 3-hexene, is formed upon decomposition of observable, but unstable, orange $W(NAr)(CHEt)[OCMe(CF_3)_2]_2$, via bimolecular coupling of propylidenes. Other propylidene complexes, $W(NAr)(CHEt)(OR)_2$ (OR = O-t-Bu, $OCMe_2CF_3$), were also found to be unstable with respect to formation of dimers via bimolecular decomposition.[5] An attempted X-ray study of brown crystalline "$W(NAr)[OCMe(CF_3)_2]_2$" was of sufficient quality to conclude that it was a dimeric species. However, severe disorder prevented a solution of this structure and even a conclusion as to whether bridging imido ligands were present or not. The ^{13}C NMR spectrum of "$W(NAr)[OCMe(CF_3)_2]_2$" revealed two CF_3 carbon resonances, which would be consistent with a structure in which no plane of symmetry runs through the W_2O_4 core.



(1)

Rhenium complexes of the type $Re(C\text{-t-Bu})(CH\text{-t-Bu})(OR)_2$,[6] which are isoelectronic with $W(NAr)(CH\text{-t-Bu})(OR)_2$ species, have been shown to be viable olefin metathesis catalysts when OR is sufficiently electron withdrawing (e.g., $OCMe(CF_3)_2 = OR_{F6}$).[7] Complexes in which OR is O-t-Bu or OR_{F6} react with CH_2═CHOEt to yield observable but unstable intermediate $Re(C\text{-t-Bu})(CHOEt)(OR)_2$ species that decompose to yield the $[Re(C\text{-t-Bu})(OR)_2]_2$ complexes (eq 2). X-ray studies showed that

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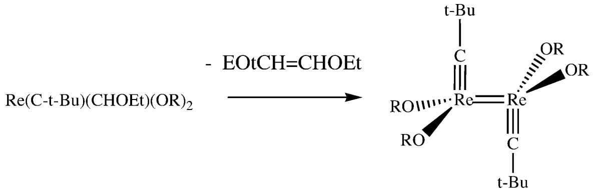

(2)

these decomposition products are M═M dimers that contain an *unbridged metal−metal double bond* (2.3836(8) Å when OR = OR_{F6} and 2.396(1) Å when OR = O-t-Bu) and a staggered, ethane-like geometry. These compounds reportedly do not react readily with various phosphines, olefins, or acetylenes, although their reactivity was not explored in great detail. Upon irradiation with 360 nm light, the $[Re(C\text{-}t\text{-}Bu)(OR)_2]_2$ complexes are transformed into $[Re(\mu\text{-}C\text{-}t\text{-}Bu)(OR)_2]_2$ species[8] whose structures appear to contain μ-C-t-Bu groups, according to NMR studies and an X-ray study of a derivative.

Our interest in the possibility of synthesizing M(NR)(CHR′)(OR″)$_2$ species in situ (M = Mo or W) led us to explore reactions between Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)$_2$[9] or W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)$_2$[10] and alcohols. We found that only one neopentyl group was protonated to yield species of the type M(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OR); in some cases M(NAr)(CH$_2$-t-Bu)$_3$(OR) was formed instead and then could be transformed into M(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OR) upon heating. As we began to explore the chemistry of M(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OR) and related complexes, we found that M(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$) complexes decompose bimolecularly to give dimers that do not contain bridging imido ligands, i.e., species analogous to the Re species shown in eq 2. We then revisited tungsten bisalkoxide complexes that we had assumed to contain bridging imido ligands and found that they too do not contain bridging ligands. The results of these investigations are reported in full here.

Results

Syntheses and Structures of [W(NAr)(CH$_2$-t-Bu)(OR)]$_2$ Complexes (OR = OC$_6$F$_5$ or OCH(CF$_3$)$_2$). W(NAr)(CH$_2$-t-Bu)$_3$(OC$_6$F$_5$) is formed upon addition of C$_6$F$_5$OH to W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)$_2$.[10] Although W(NAr)(CH$_2$-t-Bu)$_3$(OC$_6$F$_5$) is stable in solution at room temperature for hours, it decomposes in a first-order manner upon heating to 60 °C ($k = 10 \times 10^{-5}$ s^{-1} in C$_6$D$_6$) to give neopentane and W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$). A preparative reaction is more conveniently carried out at 80 °C. W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$) can be isolated only when the decomposition is carried out under relatively dilute conditions. We propose that W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$)[10] is a dimer in the solid state analogous to its molybdenum analogue, [Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$, which contains bridging pentafluorophenoxides that behave as donors *trans* to the neopentylidene ligand.[11] When relatively concentrated benzene or toluene solutions of W(NAr)(CH$_2$-t-Bu)$_3$(OC$_6$F$_5$) are heated at 80 °C for several hours, W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$) is formed but then decomposes to give di-*tert*-butylethylene and a sparingly soluble red compound. The ^{1}H NMR spectrum of this species shows only imido and neopentyl ligand resonances. A single septet is observed for the C*H*Me$_2$ protons in the NAr (N-2,6-i-Pr$_2$C$_6$H$_3$) ligand, and two resonances are observed for the isopropyl methyl groups, consistent with rapidly rotating Ar rings through which a mirror plane does not pass. The two doublets observed for the neopentyl methylene protons (3.09 and 2.47 ppm, J_{HH} = 14.5 Hz) are assigned to diastereotopic neopentyl methylene protons. The ^{19}F spectrum shows three distinct resonances for the five fluorine atoms of the OC$_6$F$_5$ ligand. All NMR data are consistent with a dimeric species in which no mirror plane passes through any ligand.

An X-ray diffraction study (Tables 1 and 2; Figures 1a and 1b) revealed that the compound is [W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ in which the W═W bond is not bridged. The structure adopts a staggered ethane-like geometry in which the two *terminal* imido ligands are *anti* with respect to one another and the two ends of the molecule are related by an inversion center. Therefore it is a *hetero*chiral dimer.

The most important feature of the structure of [W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ is the presence of the unbridged W(IV)/W(IV) double bond, even though imido and alkoxide ligands are present that could, and often do, bridge metal−metal bonds. Table 2 lists selected bond lengths and angles of *hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$. The W═W bond distance of 2.4443(2) Å is well within the range of W═W bond lengths found in other compounds reported here and others found in the literature (see Discussion section). The W−N bond length and W−N−C angle (1.745(2) Å and 165.37(19)°) are not unusual, while the W−C(19)−C(20) angle (119.25(19)°) is typical of a neopentyl group that is relatively undistorted by steric pressure. The relatively large W−O(1)−C(13) angle (146.57(18)°), on the other hand, must be ascribed to a significant degree of π bonding, possibly in combination with some steric pressure that opens up the W−O(1)−C(13) angle. Finally, a striking feature of the molecule is the virtual 90° angle (90.38(7)°) between the imido ligands and the W═W bond vector. (The *anti* orientation of neopentylidyne ligands in isoelectronic and isostructural $[Re(C\text{-}t\text{-}Bu)(OR)_2]_2$ (OR = O-t-Bu or OCMe(CF$_3$)$_2$) complexes is what one might expect on the basis of steric repulsions between alkylidyne ligands, although an analysis of the bonding and energetics of model compounds suggested that this arrangement is also preferred electronically.[12]) Since an electronic barrier to rotation about the Re═Re bond in $[Re(C\text{-}t\text{-}Bu)(OR)_2]_2$ species was predicted, we expect there to be a barrier to rotation about the W═W bond in *hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$.

When W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$) is treated with 2-pentene at room temperature, two products are formed, one of them being *hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$. This reaction is believed to involve formation of W(NAr)(CHR)(CH$_2$-t-Bu)(OC$_6$F$_5$) (R = Me or Et) species, which decompose more rapidly in a bimolecular fashion than does W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$). The same mixture is obtained when W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$) is added to a solution of 2-pentene at room temperature. In the more soluble product the CHMe$_2$ resonances are broad, consistent with a rate of rotation of the Ar rings in that species on the order of the NMR time scale. The C$_6$F$_5$ rings, however, are freely rotating on the ^{19}F NMR time scale, as they are in *hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$.

The second, more soluble product was found to be a C_2-symmetric analogue of *hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$, i.e., *homo*chiral [W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ (Tables 1 and 2; Figures 2a and 2b). Despite the inherent differences in the

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Table 1. Crystal Data and Structure Refinement for *Hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$, *Homo*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$, and *Homo*-{W(NAr)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$]}$_2$

empirical formula	$C_{46}H_{56}F_{10}N_2O_2W_2$	$C_{53}H_{64}F_{10}N_2O_2W_2$	$C_{40}H_{58}F_{12}N_2O_2W_2$
fw	1226.63	1318.76	1194.58
temp (K)	193(2)	194(2) K	194(2)
cryst syst	monoclinic	monoclinic	orthorhombic
space group	*P*2(1)/*c*	*P*2/*n*	*Pbca*
unit cell dimens			
a, Å	10.5289(6)	13.1211(15)	18.3215(7)
b, Å	9.9479(6)	11.1659(13)	19.8284(7)
c, Å	22.5331(14)	18.596(2)	26.2556(10
α, deg	90	90	90
β, deg	94.8380(10)	100.116(3)	90
γ, deg	90	90	90
volume (Å^3)	2351.7(2)	2682.2(5)	9538.3(6)
Z	2	2	8
density (calcd; Mg/m^3)	1.732	1.633	1.664
abs coeff (mm^{-1})	4.965	4.360	4.900
F(000)	1200	1300	4672
cryst size (mm^3)	0.45 × 0.41 × 0.30	0.20 × 0.12 × 0.07	0.95 × 0.90 × 0.75
θ range (deg)	1.81 to 27.88	1.82 to 26.02	1.70 to 28.29
index ranges	$-12 \le h \le 13$	$-16 \le h \le 14$	$-24 \le h \le 13$
	$-12 \le k \le 13$	$-13 \le k \le 13$	$-26 \le k \le 24$
	$-29 \le l \le 22$	$-22 \le l \le 15$	$-31 \le l \le 35$
no. of reflns collected	14 637	16 997	65 656
no. of indep reflns [*R*(int)]	5558 [*R*(int) = 0.0236]	5181 [*R*(int) = 0.0302]	11 836 [*R*(int) = 0.0508]
completeness to θ = 29.13°	99.2%	98%	99.9%
abs corr	semiempirical	semiempirical	semiempirical
max. and min. transmn	0.3174 and 0.2135	0.7500 and 0.4759	0.1203 and 0.0898
no. of data/restraints/params	5558/81/312	5181/343/418	11 836/17/535
goodness-of-fit on F^2	1.028	1.026	1.064
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0200	R1 = 0.0225	R1 = 0.0443
	wR2 = 0.0470	wR2 = 0.0504	wR2 = 0.1054
R indices (all data)	R1 = 0.0246	R1 = 0.0291	R1 = 0.0637
	wR2 = 0.0484	wR2 = 0.0531	wR2 = 0.1162
largest diff peak and hole (e Å^{-3})	0.756 and −0.774	0.902 and −0.493	2.920 and −0.898

[a] In all cases the wavelength was 0.71073 Å and the refinement method was full-matrix least-squares on F^2.

Table 2. Selected Bond Distances (Å) and Angles (deg) in Heterochiral and Homochiral [W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ and Homochiral {W(NAr)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$]}$_2$

	hetero-OC$_6$F$_5$	*homo*-OC$_6$F$_5$	*homo*-OCH(CF$_3$)$_2$	
W=W	2.4443(2)	2.4492(3)	2.4537(3)	
W−N	1.745(2)	1.747(3)	1.757(5)	1.747(5)
W−O	1.9339(18)	1.924(2)	1.908(4)	1.915(5)
W−C	2.135(3)	2.134(3)	2.123(6)	2.123(7)
N−W=W	90.38(7)	91.06(8)	91.55(14)	92.67(16)
N−W−O	132.40(9)	136.23(11)	131.0(2)	129.5(2)
N−W−C	106.28(11)	102.46(12)	105.9(2)	106.5(2)
O−W−C	110.23(10)	109.23(12)	109.3(2)	110.3(3)
O−W−W	113.15(6)	109.94(7)	112.89(14)	111.68(17)
C−W−W	97.99(7)	102.72(9)	101.86(17)	101.98(18)
C−N−W	165.37(19)	171.4(2)	166.4(4)	168.0(4)
C−O−W	146.57(18)	156.4(2)	146.7(4)	148.4(5)
C−C−W	119.25(19)	115.9(2)	117.8(4)	119.3(5)

molecular symmetry (C_2 vs C_i) and spectroscopic behavior of *homo*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ versus *hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ (vide supra), the bond lengths and angles in the coordination sphere of *homo*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ are virtually indistinguishable from those in *hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ (Table 2). However, the C−O−W−W dihedral angles in the two structures are significantly different. In *hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ the C−O−W−W dihedral angle is −118°, while in *homo*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ it is 41°. As a consequence, the C$_6$F$_5$ ring in the *hetero*chiral dimer is directed *away* from the imido ligand, while in the *homo*chiral dimer it is pointed *toward* the imido group. This structural difference might lead to slight differences in steric congestion in the two isomers and, therefore, to the observed slower rate of rotation of the i-Pr$_2$C$_6$H$_3$ rings in *homo*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$.

So far we have seen no interconversion of *hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ and *homo*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ upon heating solutions of one or the other. Apparently the W=W bonds do not cleave spontaneously into pseudo-trigonal W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$) fragments analogous to structurally characterized W(N-t-Bu)[OSi(t-Bu)$_3$]$_2$.[13] Most likely the large silox ligands in W(N-t-Bu)[OSi(t-Bu)$_3$]$_2$ prevent formation of {W(N-t-Bu)[OSi(t-Bu)$_3$]$_2$}$_2$, while the double bonds in *hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ and *homo*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ are simply too strong to cleave homolytically under relatively mild conditions.

Although W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$] is relatively stable thermally,[10] upon treating a concentrated solution of W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$] in pentane with 2-pentene, the initially yellow reaction mixture turned red within minutes and red crystals were deposited over a period of days at −30 °C. Two products were observed whose solubilities and NMR properties are analogous to those for *hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ and *homo*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$. Therefore we propose that these species are *hetero*-{W(NAr)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$]}$_2$ and *homo*-{W(NAr)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$]}$_2$; the more soluble isomer shows slower rotation of the NAr rings on the NMR time scale, as found for *homo*chiral [W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$.

An X-ray structural study of the more soluble product confirms that it is *homo*chiral {W(NAr)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$]}$_2$ (Tables 1 and 2, Figure 3). This compound shares the same general features as *homo*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$ shown in Figure 2, e.g., a staggered ethane-like geometry, *anti* imido groups, close to 90° N=W=W angles (91.55(14) and 92.67(16)°), and a W(IV)/W(IV) double bond (2.4537(3) Å). The C−O−W−W dihedral angle in *homo*-{W(NAr)(CH$_2$-t-Bu)-

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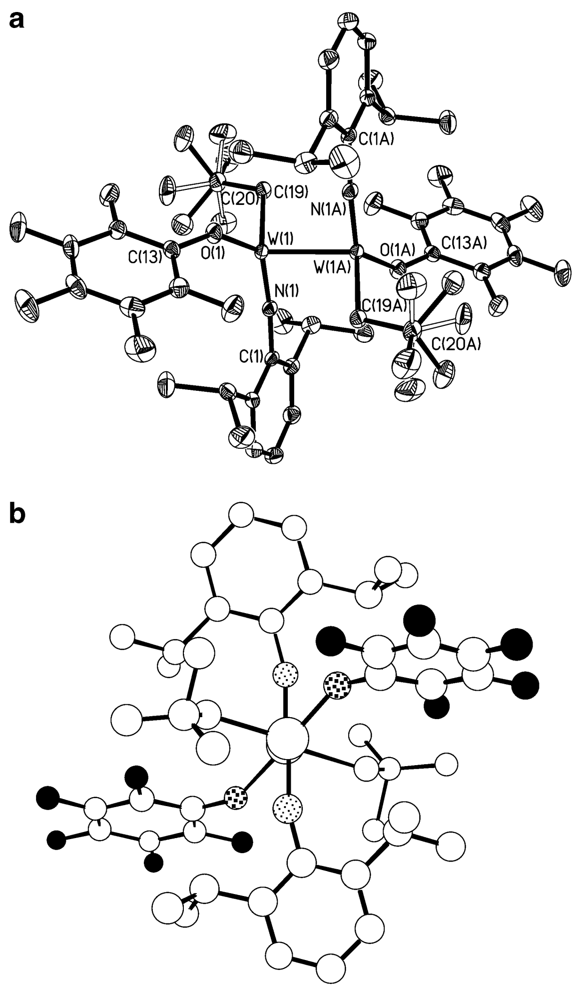


Figure 1. (a) Thermal ellipsoid drawing of the molecular structure of heterochiral $[W(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$. (b) Chem 3D view from the end of heterochiral $[W(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$.

$[OCH(CF_3)_2]\}_2$ is −9°, while it is 41° in *homo*-$[W(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$.

Synthesis of $[W(NAr')(CH_2\text{-t-Bu})(OC_6F_5)]_2$ (Ar′ = 2,6-$Me_2C_6H_3$). Bisalkoxide complexes of the type $W(NAr')(CH\text{-t-Bu})(OR)_2$ have been prepared from $W(NAr')(CH\text{-t-Bu})Cl_2(dme)$, which was prepared through base-catalyzed proton transfer in $W(NHAr')(C\text{-t-Bu})Cl_2(dme)$.[5] $W(NAr')(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$ has not been reported. It can be prepared from $W(NAr')(CH\text{-t-Bu})(OTf)_2(dme)$, which was synthesized in a manner analogous to that for $W(NAr)(CH\text{-t-Bu})(OTf)_2(dme)$, i.e., by treating $W(NAr')_2(CH\text{-t-Bu})_2$ with 2 equiv of triflic acid. The ^1H NMR spectrum of yellow-orange $W(NAr')(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$ shows a singlet at 6.87 ppm ($J_{HW} = 16$ Hz) for the neopentylidene proton. This is comparable to H_α of 6.74 ppm observed for $W(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$[5] and δ $H_\alpha = 6.61$ ppm reported for $W(NPh)(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$,[14] which was obtained as a red oil upon addition of $LiCH_2\text{-t-Bu}$ to $W(NPh)(CH_2\text{-t-Bu})_3Cl$. Attempts to synthesize $W(NAr')(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$ via alkylation of $W(NAr')Cl_4(THF)$ with 3 equiv of $t\text{-BuCH}_2MgCl$ at −78 °C consistently gave a mixture of $W(NAr')(CH_2\text{-t-Bu})_3Cl$ and $W(NAr')(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$, according to NMR spectra, and possibly other (unidentified) products, from which $W(NAr')(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$ could not be isolated in pure form.

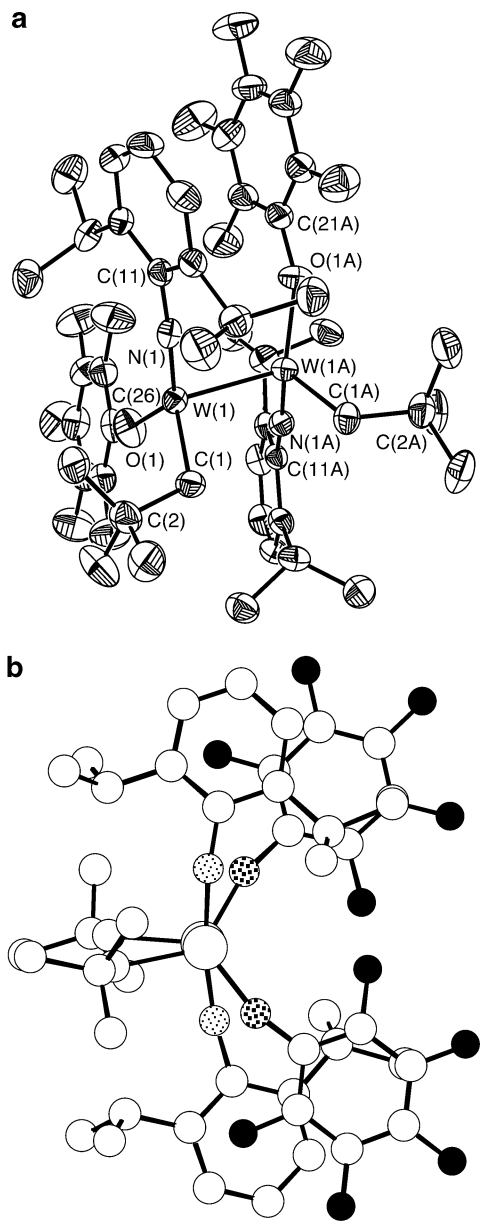
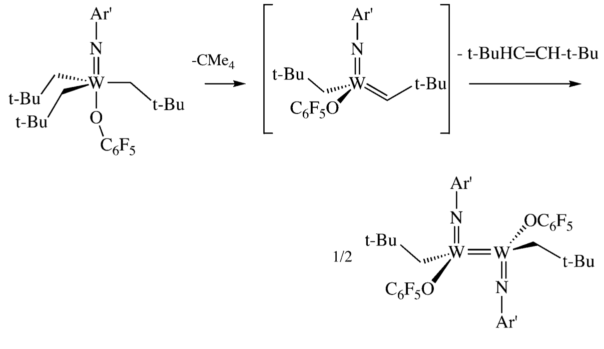


Figure 2. (a) Thermal ellipsoid drawing of the molecular structure of homochiral $[W(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$. (b) Chem 3D view from the end of homochiral $[W(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$.

Addition of pentafluorophenol to $W(NAr')(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$ yields $W(NAr')(CH_2\text{-t-Bu})_3(OC_6F_5)$, a product analogous to that obtained upon addition of pentafluorophenol to $W(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$.[10] Heating a toluene-$d_8$ solution (0.10 M) of $W(NAr')(CH_2\text{-t-Bu})_3(OC_6F_5)$ to 60 °C yields what we propose to be $W(NAr')(CH\text{-t-Bu})(CH_2\text{-t-Bu})(OC_6F_5)$ ($\delta H_\alpha = 9.36$ ppm), although all efforts to isolate this species proved unsuccessful as a consequence of its facile decomposition to yield t-BuCH═CH-t-Bu and $[W(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ (eq 3). The basic



(3)

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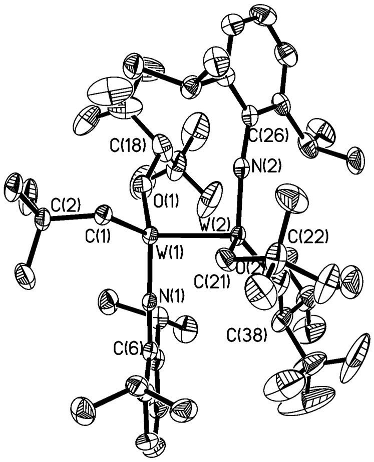


Figure 3. Thermal ellipsoid drawing of the molecular structure of homochiral [W(NAr)(CH_2-t-Bu)[OCH(CF_3)$_2$]]$_2$.

problem appears to be that W(NAr′)(CH_2-t-Bu)$_3$(OC_6F_5) is less sterically crowded than W(NAr)(CH_2-t-Bu)$_3$(OC_6F_5) and so decomposes to yield a neopentylidene complex more slowly than W(NAr)(CH_2-t-Bu)$_3$(OC_6F_5), while W(NAr′)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5), again for steric reasons, is *more* prone to decompose bimolecularly than is W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5). Therefore only a relatively small quantity of W(NAr′)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) (a maximum of ~10%) has been observed. As expected, [W(NAr′)(CH_2-t-Bu)(OC_6F_5)]$_2$ contains inequivalent neopentyl methylene protons, characteristic of dimeric species of this general type, and therefore almost certainly also contains an unsupported W(IV)/W(IV) double bond. We believe [W(NAr′)(CH_2-t-Bu)(OC_6F_5)]$_2$ to be a heterochiral dimer on the basis of its formation via coupling of neopentylidene complexes and the equivalence of all 2,6-*Me*$_2C_6H_3$N groups on the ^{1}H NMR time scale. However, it is possible that the hindered rotation of Ar rings in the homochiral dimers discussed above is a consequence of bulky isopropyl groups being present and not an intrinsic property of *all* homochiral dimers regardless of the nature of the imido group. Therefore we cannot say with certainty that [W(NAr′)(CH_2-t-Bu)(OC_6F_5)]$_2$ is in fact heterochiral.

Syntheses and Structures of {W(NAr′)[OCMe(CF_3)$_2$]$_2$}$_2$, [W(NAr′)($OCMe_2CF_3$)$_2$]$_2$ (Ar′ = 2,6-$Me_2C_6F_3$), and [W(NAr)($OCMe_2CF_3$)$_2$]$_2$. Upon discovery of the [W(NR)(CH_2-t-Bu)(OR′)]$_2$ complexes described above, we considered the possibility that only monoalkoxide species of this general type had unbridged M═M bonds. However, some inconsistensies in the literature concerning the products of decomposition of W(NAr)(CHR)(OR′)$_2$ complexes, as described in the Introduction, suggested that this may not be the case.

Unstable W(NAr′)(CHEt)[OCMe(CF_3)$_2$]$_2$ decomposes to yield "W(NAr′)[OCMe(CF_3)$_2$]$_2$", which was proposed to be {W(μ-NAr′)[OCMe(CF_3)$_2$]$_2$}$_2$.[5] Crystals of this compound suitable for X-ray diffraction studies were obtained in the same manner as described in the literature.[5] The X-ray study was marred by a complex disorder (see Experimental Section). However, the disorder was solved satisfactorily and this species was found to be {W(NAr′)[OCMe(CF_3)$_2$]$_2$}$_2$, in which the W═W bond is unsupported by bridging ligands (2.4751(4) Å; Tables 3 and 4 and Figure 4**)**. Structural features of this dimer are analogus to those for the monoalkoxide dimers described above.

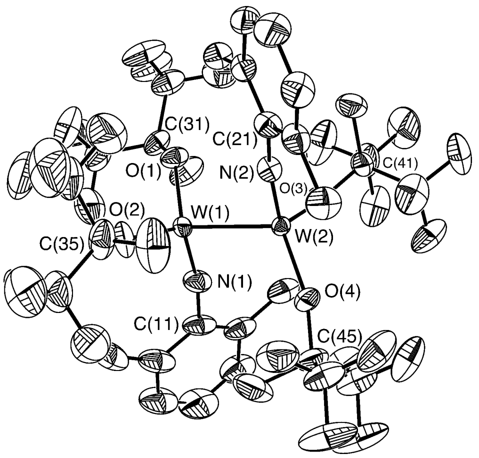
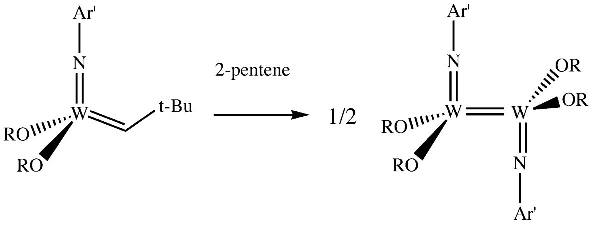


Figure 4. Thermal ellipsoid drawing of the molecular structure of {W(NAr′)[OCMe(CF_3)$_2$]$_2$}$_2$ (one molecule of two).

[W(NAr)($OCMe_2CF_3$)]$_2$ and [W(NAr′)($OCMe_2CF_3$)]$_2$ were prepared in a manner analogous to that employed to prepare {W(NAr′)[OCMe(CF_3)$_2$]$_2$}$_2$, as shown in eq 4. X-ray diffraction studies showed that both are unbridged dimers that are virtually identical to {W(NAr′)[OCMe(CF_3)$_2$]$_2$}$_2$ (Tables 3 and 4, Figures 5 and 6). In proton NMR spectra of both compounds, the two methyl groups of the OC*Me*$_2CF_3$ ligands are inequivalent, consistent with the C_i-symmetric structure. [W(NAr)($OCMe_2CF_3$)$_2$]$_2$ is the species reported here that is obtained in the lowest yield and not reproducibly. Clearly formation of the W═W bond is very sensitive to the size of the covalently bound ligands and conditions in a manner that is not yet quantifiable.



(4)

Discussion

There are relatively few examples of M═M bonds in the literature, and most of those that are known contain bridging ligands. For example, Casey reported (η^5-C_5Me_5)(CO)$_2$Re═Re(CO)$_2$(η^5-C_5Me_5), which contains a Re−Re double bond (2.723(1) Å) in which two of the carbonyl ligands are "semibridging".[15,16] Bridged W(IV)/W(IV) double bonds are found in [K(18-crown-6)$_{1.5}$][W_2(μ-H)(μ-O)(OC-t-Bu)$_6$] (2.445(1) Å),[17] [W_2(κ-O_2C-t-Bu)$_4$(μ-MeCCMe)$_2$] (2.4888(2) Å),[18] [W_2(κ-O_2C-t-Bu)$_4$(μ-PhCCMe)$_2$] (2.4925(2) Å),[18] and W_2(OCH_2-t-Bu)$_8$.[19] Examples of complexes that contain a metal−metal double bond and no potentially bridging ligands include macrocycle complexes such as [M(octaethylporphyrin)]$_2$ (M = Ru, Os)[20] and [Ru($C_{22}H_{22}N_4$)]$_2$.[21] The compound (i-PrO)$_4$WW(DMPE)$_2$(CO)[22] (no bridging ligands) could be said to be a d^2/d^6 dimer in which a

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Table 3. Crystal Data and Structure Refinement for [W(NAr′)(OR$_{F6}$)$_2$]$_2$, [W(NAr′)(OR$_{F3}$)$_2$]$_2$, and [W(NAr)(OR$_{F3}$)$_2$]$_2$

	[W(NAr′)(OR$_{F6}$)$_2$]$_2$	[W(NAr′)(OR$_{F3}$)$_2$]$_2$	[W(NAr)(OR$_{F3}$)$_2$]$_2$
empirical formula	$C_{32}H_{30}F_{24}N_2O_4W_2$	$C_{32}H_{42}F_{12}N_2O_4W_2$	$C_{40}H_{58}F_{12}N_2O_4W_2$
fw	1330.28	1114.38	1226.58
temp (K)	100(2)	193(2)	193(2) K
cryst syst	monoclinic	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*c*
unit cell dimens			
a, Å	17.1623(5)	10.4324(7)	19.7134(8)
b, Å	13.2753(4)	13.2926(9)	11.1767(4)
c, Å	36.7743(11)	14.0726(10)	21.4229(8)
α, deg	90	90	90
β, deg	96.4960(10)	97.1920(10)	90.0250(10)
γ, deg	90	90	90
volume (Å^3)	8324.7(4)	1936.1(2)	4720.1(3)
Z	8	2	4
density (calcd; Mg/m^3)	2.123	1.911	1.726
abs coeff (mm^{-1})	5.669	6.031	4.956
F(000)	5056	1072	2400
cryst size (mm^3)	0.15 × 0.15 × 0.05	0.11 × 0.06 × 0.05	0.30 × 0.17 × 0.15
θ range (deg)	1.26 to 29.57	2.12 to 28.27	1.90 to 28.28
index ranges	$-23 \le h \le 23$	$-13 \le h \le 12$	$-19 \le h \le 26$
	$0 \le k \le 18$	$-13 \le k \le 17$	$-14 \le k \le 14$
	$0 \le l \le 51$	$-18 \le l \le 18$	$-22 \le l \le 28$
no. of reflns collected	331 577	13 428	32 828
no. of indep reflns [*R*(int)]	23 350 [*R*(int) = 0.0594]	4790 [*R*(int) = 0.0185]	11 707 [*R*(int) = 0.0327]
completeness to $\theta = 29.13°$	100.0%	99.9%	100.0%
abs corr	semiempirical	semiempirical	semiempirical
max. and min. transmn	0.7647 and 0.4835	0.7525 and 0.5567	0.5235 and 0.3179
no. of data/restraints/params	23 352/3692/1403	4790/0/241	11 707/562/671
goodness-of-fit on F^2	1.275	1.029	1.087
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0622	R1 = 0.0218	R1 = 0.0404
	wR2 = 0.1385	wR2 = 0.0563	wR2 = 0.0976
R indices (all data)	R1 = 0.0727	R1 = 0.0249	R1 = 0.0572
	wR2 = 0.1438	wR2 = 0.0588	wR2 = 0.1045
largest diff peak and hole (e Å^{-3})	3.175 and −1.503	1.813 and −0.946	1.625 and −0.549

[a] In all cases the wavelength was 0.71073 Å and the refinement method was full-matrix least-squares on F^2.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in [W(NAr′)(OR$_{F6}$)$_2$]$_2$, [W(NAr′)(OR$_{F3}$)$_2$]$_2$, and [W(NAr)(OR$_{F3}$)$_2$]$_2$ Complexes

	[W(NAr′)(OR$_{F6}$)$_2$]$_2$	[W(NAr′)(OR$_{F3}$)$_2$]$_2$	[W(NAr)(OR$_{F3}$)$_2$]$_2$
W=W	2.4751(4)	2.4909(2)	2.4925(3)
W−N	1.755(7), 1.737(6)	1.751(2)	1.749(5), 1.754(5)
W−O	1.902(6), 1.892(5)	1.9239(18)	1.914(4), 1.919(4)
W−O	1.915(5), 1.909(5)	1.860(2)	1.878(4), 1.876(4)
N−W=W	92.4(2), 93.8(2)	92.59(7)	94.92(16), 93.75(15)
N−W−O	114.5(3), 111.8(3)	114.90(9)	114.86(18), 119.2(2)
N−W−O	117.2(3), 120.2(3)	119.55(9)	116.9(2), 117.0(2)
O−W−O	112.0(3), 112.6(3)	110.19(9)	109.80(19), 108.8(2)
O−W=W	104.88(18), 102.48(18)	104.29(6)	104.72(14), 104.10(14)
O−W=W	113.7(2), 113.10(18)	113.53(6)	112.41(14), 113.86(15)
C−N−W	170.3(7), 169.5(6)	172.42(9)	169.6(4), 166.7(4)
C−O−W	135.4(5), 132.9(5)	132.61(17)	137.5(4), 134.1(4)
C−O−W	151.4(6), 163.3(5)	153.09(18)	152.0(4), 159.9(4)

W=W bond is present (2.52429(9) Å), although alternative explanations are possible. We believe that unbridged M=M complexes of the type [Re(C-t-Bu)(OR)$_2$]$_2$,[23] and the W=W species reported here, are the only symmetric M=M complexes that are stable at room temperature and in which potentially bridging ligands are present. They also appear to contain the shortest W=W bonds known. The fact that they also have M=CHR relatives that are olefin metathesis catalysts is also a noteworthy feature of such species. Therefore one could view the relationship between the unbridged M=M bonds described here and M=C bonds in their relatives as analogous to the relationship between M≡M bonds and M≡C bonds[24] in alkyne metathesis catalysts; for example, alkynes can react with M≡M bonds to yield alkylidynes[25,26] reversibly.[27] The recent finding that M=M species can initiate olefin metathesis reactions[28] raises the possibility that M=M species can react with C=C bonds to yield M=C species, the reverse of the reaction in which they are formed. However, there are several alternative possibilities, so whether this is true or not is unknown.

The W=W bonded species reported here are characterized by a 90° W−W−N angle and a 180° N−W−W−N dihedral angle. The 90° W−W−N angle suggests that the three π bonds around the metal center are formed from the three mutually perpendicular, essentially pure d$_{xy}$, d$_{yz}$, and d$_{xz}$ orbitals, while the four σ bonds are formed from the three p orbitals and some combination of s and d$_{z^2}$ orbitals. In models of [Re(C-t-Bu)-

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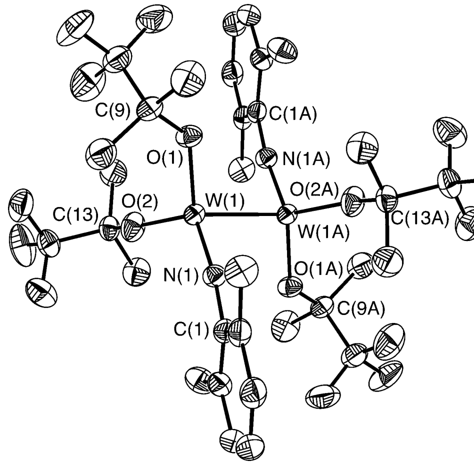


Figure 5. Thermal ellipsoid drawing of the molecular structure of [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$.

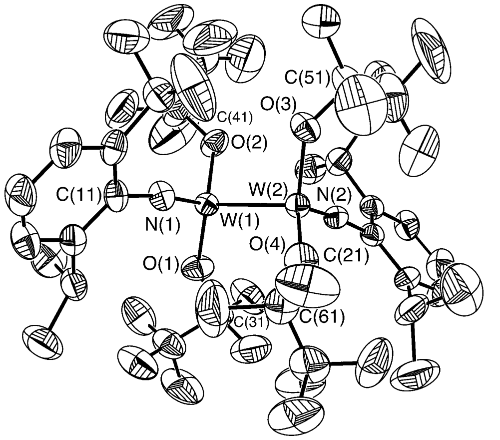
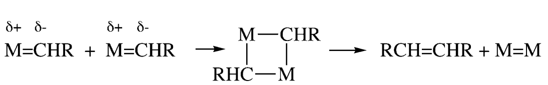


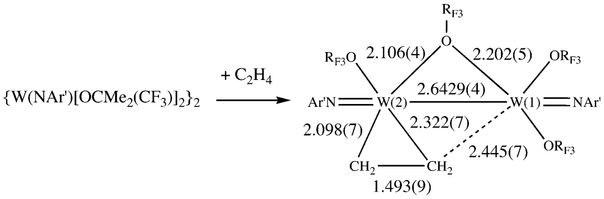
Figure 6. Thermal ellipsoid drawing of the molecular structure of [W(NAr)(OCMe$_2$CF$_3$)$_2$]$_2$.

(OR)$_2$]$_2$ (OR = O-t-Bu or OCMe(CF$_3$)$_2$) complexes[23] Bursten found[12] that the *anti* arrangement of the multiply bound alkylidyne ligands was energetically preferred. A staggered structure is sensible on the basis of steric arguments alone.



$$\overset{\delta+\ \ \delta-}{M=CHR} + \overset{\delta+\ \ \delta-}{M=CHR} \longrightarrow \begin{array}{c}M-CHR\\ |\qquad |\\ RHC-M\end{array} \longrightarrow RCH=CHR + M=M \qquad (5)$$

We can imagine that M=M bonds might be formed through coupling of alkylidenes as shown in eq 5. One ($\delta+$)M=C($\delta-$) bond effectively reacts in a manner analogous to a (polarized) C=C bond with the other ($\delta+$)M=C($\delta-$) bond to form a 1,3-dimetallacyclobutane intermediate. What amounts to a compound of this type recently has been observed through NMR studies.[29] The compound is [W(NAr)(^{13}CH$_2$)(Biphen)]$_2$ where Biphen^{2-} = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate. A key feature of its ^{13}C{^{1}H} NMR spectrum is a singlet resonance at 185.9 ppm flanked with *two* sets of tungsten satellites ($^1J_{WC}$ = 78.9, 36.7 Hz), characteristic of the methylene carbon being coupled to two different ^{183}W nuclei. The proton-coupled spectrum reveals that the methylene carbon is coupled to two inequivalent protons ($^1J_{CH}$ = 148, 131 Hz) located at 8.20 and 7.37 ppm in the proton NMR spectrum. The fact that this species can be observed and that no carbon−carbon bond has yet formed suggests that it may have to rearrange first to a 1,2-dimetalacyclic species from which olefin can be lost readily. In fact, a 1,2-dimetallacyclic species that contains one bridging alkoxide has been observed to form reversibly when ethylene is added to (CF$_3$Me$_2$CO)$_2$(Ar′N)W=W(NAr′)(OCMe$_2$CF$_3$)$_2$ (eq 6).[28] Moreover, (CF$_3$Me$_2$CO)$_2$(Ar′N)W=W(NAr′)(OCMe$_2$CF$_3$)$_2$ will metathesize certain olefins slowly.[28] Therefore there is some possibility that monomeric alkylidenes are formed from the 1,2-dimetalacyclobutane. That is not yet known. In any case it seems clear that M=M bonds form from alkylidenes in small steps as the olefin is formed and ejected. Whether a M=M bond actually forms is likely to depend on a number of factors, among them the overall steric bulk of the covalently bound ligands involved (imido, alkoxide, alkyl) and what ligands (e.g., olefins) bind to the metal in a monomer or dimer and thereby prevent formation of the M=M species.



(6)

Reduction of W(N-t-Bu)(Silox)$_2$Cl$_2$ (Silox = OSi(t-Bu)$_3$) has produced pseudo-trigonal planar W(N-t-Bu)(Silox)$_2$,[13] instead of hypothetical (Silox)$_2$(t-BuN)W=W(N-t-Bu)(Silox)$_2$, presumably because dimerization is prevented by the bulk of the Silox groups. Recently, reduction of W(NAr′)(OCMe$_2$CF$_3$)$_2$Cl$_2$ has been shown to yield (CF$_3$Me$_2$CO)$_2$(Ar′N)W=W(NAr′)(OCMe$_2$CF$_3$)$_2$,[28] while sodium amalgam reduction of Mo(N-t-Bu)[OSi(t-Bu)$_3$]$_2$Cl$_2$ has been reported to yield {Mo(N-t-Bu)[OSi(t-Bu)$_3$]$_2$}$_2$(μ-Hg).[30] The spectroscopy of {Mo(N-t-Bu)[OSi(t-Bu)$_3$]$_2$}$_2$(μ-Hg), along with calculations, allowed the strength of the π component of the Mo=Mo bond in [Mo(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$[9] to be estimated as ~27 kcal/mol. If the π component is worth 27 kcal/mol, we might guess that the entire double bond (including the σ portion) will be worth ~75 kcal/mol and that W=W bonds probably would be stronger than Mo=Mo bonds. The findings in this paper are consistent with W=W bonds being relatively strong and the failure to see scrambling between heterochiral and homochiral dimers. Future studies will be concerned with reactions that involve W=W bonds along the lines that have appeared in a preliminary study.[28]

Experimental Details

General Procedures. All air-sensitive work was carried out in a Vacuum Atmospheres drybox under a dinitrogen atmosphere or by standard Schlenk techniques. All solvents, except methylene chloride and dimethoxyethane, were sparged with nitrogen and passed through a column of activated alumina. Methylene chloride was distilled from CaH$_2$, while dimethoxyethane was distilled from benzophenone ketyl before being degassed (freeze−pump−thaw) three times. All deuterated solvents, as well as the alcohols and phenols used, were degassed before being brought into the box. All solvents were stored over 4 Å molecular sieves. All lithium alkoxides were prepared through addition of *n*-butyllithium to the alcohol. W(NAr)Cl$_4$(Et$_2$O),[5] W(NAr′)(CH-t-Bu)(OTf)$_2$(dme),[10] W(NAr)(CH-*t*-Bu)(OCMe$_2$CF$_3$)$_2$,[31] W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$],[10] and {W(NAr′)[OCMe(CF$_3$)$_2$]$_2$}$_2$[5] were prepared as described in the literature.

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Reported ^{1}H and ^{13}C NMR chemical shifts are listed in parts per million referenced to either the residual protons or ^{13}C atoms of the deuterated solvents. ^{19}F NMR shifts are reported relative to C$_6$F$_6$ used as an external reference. ^{1}H NMR spectra were obtained on an instrument operating at 300 MHz (unless otherwise noted), ^{13}C NMR spectra were obtained on an instrument operating at 125 MHz, while ^{19}F NMR spectra were obtained on a 282 MHz instrument. All spectra were recorded near 22 °C.

***Homo*- and *Hetero*-{W(NAr)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$]}$_2$.** To a rapidly stirred solution of W(N-2,6-i-Pr$_2$C$_6$H$_3$)(CH-t-Bu)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$] (470 mg, 0.704 mmol) in a minimum amount of pentane at room temperature was added dropwise 1.52 mL (14.1 mmol) of *cis*-2-pentene. The mixture was left to stir overnight. The volatiles were removed in vacuo to give a red oil. Minimum amount of pentane was added and the solution kept at −30 °C. Dark red crystals, formed over a period of two weeks, were collected on a frit and washed with 3 × 1 mL of cold pentane to give 60 mg of the product as a mixture of *homo*- and *hetero*chiral isomers in approximately a 7:1 ratio (11% yield). *Homo*-{W(NAr)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$]}$_2$: ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 7.10 (t, 2), 7.03 (d, 4), 4.89 (m, 2), 4.44 (m, 2), 3.07 (m, 2), 2.37 (d, 2, $J_{\mathrm{HW}} = 15$ Hz), 2.04 (d, 2, $J_{\mathrm{HW}} = 15$ Hz), 1.61 (d, 6), 1.32 (d, 6), 1.25 (d, 6), 1.02 (s, 18), 1.01 (d, 6). *Hetero*-{W(NAr)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$]}$_2$: ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 7.09 (t, 2), 7.01 (d, 4), 5.22 (m, 2), 3.85 (m, 4), 2.59 (d, 2, $J_{\mathrm{HH}} = 14$ Hz), 2.42 (d, 2, $J_{\mathrm{HH}} = 15$ Hz), 1.30 (d, 12), 1.23 (d, 12), 0.99 (s, 18). Anal. Calcd for C$_{20}$H$_{29}$NOF$_6$W: C, 40.22; H, 4.89; N, 2.35. Found: C, 40.36; H, 5.01; N, 2.32.

***Hetero*-[W(NAr)(CH$_2$CMe$_3$)(OC$_6$F$_5$)]$_2$.** A sample of W(NAr)(CH$_2$CMe$_3$)$_3$(OC$_6$F$_5$) (1.010 g) was dissolved in a minimum amount of toluene, and the solution was heated at 80 °C for 48 h. A red solid crystallized out of solution, was collected on a frit, and was washed liberally with pentane; yield 585 mg (70%): ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 7.17 (d, 4), 7.08 (t, 2), 3.86 (m, 4), 3.09 (d, 2, $J_{\mathrm{HH}} = 14.5$ Hz), 2.47 (d, 2, $J_{\mathrm{HH}} = 14.5$ Hz), 1.30 (d, 12), 1.01 (s, 18), 0.99 (d, 12); ^{19}F NMR (C$_6$D$_6$) δ −159.29 (d, 4), −164.80 (t, 4), −167.80 (t, 2). Anal. Calcd for C$_{23}$H$_{28}$NOF$_5$W: C, 45.04; H, 4.60; N, 2.28. Found: C, 44.88, H, 4.54, N, 2.33.

***Homo*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$.** A solution of W(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$) (700 mg, 1.024 mmol) in 10 mL of pentane was added dropwise to a rapidly stirred solution of 2.21 mL (20.85 mmol) of *cis*-2-pentene in 10 mL of pentane. Solids formed within 20 min. The dark red reaction mixture was stirred overnight. The insoluble product was collected on a frit, washed with liberal amounts of pentane (25 °C), and dried to give 40 mg of red-orange *hetero*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$, which was identical to the compound prepared via the preceding method. The filtrate was collected and concentrated to dryness. The residue was collected on a frit, washed with *cold* pentane, and dried to give 250 mg of red *homo*-[W(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$; yield 40%: ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 6.86 (br, 6), 4.49 (br, 2), 3.06 (br, 2), 2.60 (d, 2, $J_{\mathrm{HW}} = 15$ Hz), 2.19 (d, 2, $J_{\mathrm{HW}} = 15$ Hz), 1.72 (br, 6), 1.36 (br, 6), 1.25 (br, 6), 1.12 (s, 18), 0.88 (br, 6); ^{19}F NMR (C$_6$D$_6$) δ −158.6 (d, 4), −164.3 (t, 4), −167.1 (t, 2).

W(NAr′)(CH-t-Bu)(CH$_2$-t-Bu)$_2$. Neopentylmagnesium chloride (3.41 mL, 1.35 M) was added dropwise to a rapidly stirred solution of W(N-2,6-Me$_2$C$_6$H$_3$)(CH-t-Bu)(OTf)$_2$(dme) (1.75 g, 2.298 mmol) in 20 mL of ether at −30 °C. After 8 h, all volatiles were removed in vacuo. The product was taken up in 20 mL of pentane, the solution was filtered through a bed of Celite, and the filtrate was concentrated to dryness to give a yellow-orange solid (1.13 g) in 90% yield: ^{1}H NMR (C$_6$D$_6$) δ 7.00 (2, 3), 6.87 (t, 1), 6.78 (s,1, $J_{\mathrm{HW}} = 15.5$ Hz), 2.48 (s, 6), 2.37 (d, 2, $J_{\mathrm{HH}} = 14$ Hz), 1.18 (s, 9), 1.16 (s, 18), 0.78 (d, 2, $J_{\mathrm{HH}} = 14$ Hz). Anal. Calcd for WNC$_{23}$H$_{41}$: C, 53.6; H, 8.02; N, 2.72. Found: C, 53.48, H, 8.11, N, 2.71.

W(NAr′)(CH$_2$-t-Bu)$_3$(OC$_6$F$_5$). W(N-2,6-Me$_2$C$_6$H$_3$)(CH$_2$-t-Bu)(CH-t-Bu)$_2$ (500 mg, 0.970 mmol) was dissolved in pentane and was treated with 1 equiv of HOC$_6$F$_5$ (179 mg). The resulting yellow solution was stirred for 1 h, after which the volatiles were removed in vacuo. The residue was collected on a frit and washed with cold pentane to give a yellow powder; yield 420 mg (62%): ^{1}H NMR (C$_6$D$_6$) δ 6.91 (d, 2), 6.78 (t, 1), 4.15 (m,2), 2.61 (s, 6), 2.21 (s, 6, $J_{\mathrm{HW}} = 9.6$ Hz), 1.10 (s, 27); ^{19}F NMR (C$_6$D$_6$) δ −156.9 (d, 2), −165.2 (t, 2), −170.9 (t, 1). Anal. Calcd for WNOF$_5$C$_{29}$H$_{42}$: C, 49.8; H, 6.05; N, 2.00. Found: C, 49.75, H, 6.11, N, 1.95.

Observation of W(NAr′)(CH$_2$-t-Bu)$_3$[OCH(CF$_3$)$_2$]. Hexafluoroisopropyl alcohol (6.7 μL, 1.1 equiv) was added via syringe to a solution of W(NAr′)(CH-t-Bu)(CH$_2$-t-Bu)$_2$ (30 mg, 0.058 mmol) in 0.80 mL of C$_6$D$_6$ in an NMR (JY) tube. A proton NMR spectrum showed that W(NAr′)(CH$_2$-t-Bu)$_3$[OCH(CF$_3$)$_2$] had formed quantitatively: ^{1}H NMR (C$_6$D$_6$) δ 6.90 (d, 2), 6.78 (t, 1), 5.19 (m, 1), 2.57 (s, 6), 2.01 (s, 6), 1.07 (s, 27); ^{19}F NMR (C$_6$D$_6$) δ −71.33, −71.35.

W(NAr)(CH$_2$-t-Bu)$_3$[OCH(CF$_3$)$_2$]. To a solution of 300 mg (0.493 mmol) of W(NAr)(CH$_2$-t-Bu)$_3$(Cl) in 5 mL of benzene was added as a solid 1 equiv of LiOCH(CF$_3$)$_2$. The reaction mixture was heated at 60 °C overnight as it was being stirred, after which it was filtered through a bed of Celite, and the filtrate was concentrated to dryness to give the desired product as a red oil in virtually quantitative yield (320 mg): ^{1}H NMR (C$_6$D$_6$) δ 8.96 (s, 1, $J_{\mathrm{HW}} = 15$ Hz), 7.05 (m, 3), 4.50 (m, 1), 3.70 (m, 2), 2.58 (d, 1, $J_{\mathrm{HH}} = 15$ Hz), 2.13 (d, 1, $J_{\mathrm{HH}} = 15$ Hz), 1.28 (d, 6), 1.26 (d, 6), 1.14 (s, 9), 1.12 (s, 9); ^{19}F NMR (C$_6$D$_6$) δ −74.0 (q, 3) and −74.3 (q, 3).

[W(NAr′)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$. A solution of W(NAr′)(CH$_2$-t-Bu)$_3$(OC$_6$F$_5$) prepared as described above from 1.03 g (1.472 mmol) of W(NAr′)(CH-t-Bu)(CH$_2$-t-Bu)$_2$ in a minimum amount of benzene was heated at 60 °C for 48 h. The resulting red solution was cooled to −30 °C. The red solid that crystallized out of the solution was collected on a frit and washed with pentane. The filtrate was then concentrated to dryness, and the residue collected on a frit and washed with pentane to give a red powder. Combined yield: 427 mg (52%); ^{1}H NMR (toluene-d_8, 500 MHz) δ 6.98 (d, 4), 6.94 (t, 2), 3.08 (d, 2, $J_{\mathrm{HH}} = 14.5$ Hz), 2.46 (s, 12), 2.36 (d, 2, $J_{\mathrm{HH}} = 14.5$ Hz), 0.91 (s, 18); ^{19}F NMR (C$_6$D$_6$) δ −158.8 (d, 4), −164.2 (t, 4), −167.80 (t, 2). Anal. Calcd for C$_{19}$H$_{20}$NOF$_5$W: C, 40.96; H, 3.62; N, 2.51. Found: C, 40.84; H, 3.68; N, 2.57.

W(NAr′)(CH-t-Bu)(OCMe$_2$CF$_3$)$_2$. W(NAr′)(CH-*t*-Bu)(OTf)$_2$(dme) (1.00 g, 1.31 mmol) was dissolved in 30 mL of THF. The solution was cooled to −30 °C, and 352 mg (2.627 mmol) of LiOCMe$_2$CF$_3$ was added. The mixture was allowed to warm to room temperature as it was being stirred. After 12 h, the reaction mixture was concentrated to dryness in vacuo. The residue was then extracted into pentane, and the mixture was filtered. Removal of volatiles in vacuo afforded 670 mg of a yellow powder, which was pure by NMR (81% yield): ^{1}H NMR (C$_6$D$_6$) δ 8.48 ppm (s, 1), 6.93 (d, 2), 6.86 (t, 1), 2.28 (s, 6), 1.31 (s, 6), 1.25 (s, 6), 1.13 (s, 9); ^{19}F NMR (C$_6$D$_6$) δ −82.1 ppm (s). According to the NMR data and properties, this compound is identical to that published.[5]

[W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$. A solution of W(N-2,6-Me$_2$C$_6$H$_3$)(CH-t-Bu)(OCMe$_2$CF$_3$)$_2$ (4.70 g, 7.49 mmol) in 20 mL of pentane was treated with 10 equiv of 2-pentene (8.1 mL, 75 mmol) at room temperature. The yellow-orange solution immediately turned red. The mixture was stirred overnight, during which time yellowish-brown microcrystals were formed. The solids were collected on a frit, washed with liberal amounts of pentane, and dried in vacuo to give 3.48 g of product (83% yield): ^{1}H NMR (toluene-d_8) δ 6.99 (m, 6), 2.54 (s, 12), 1.26 (s, 12), 1.19 (s, 12); ^{19}F NMR (toluene-d_8) δ −82.72 (s). Anal. Calcd for C$_{32}$H$_{42}$F$_{12}$N$_2$O$_4$W$_2$: C, 34.49; H, 3.80; N, 2.51. Found: C, 34.28; H, 3.74; N, 2.49.

Single crystals suitable for X-ray diffraction studies were grown in toluene solution at −30 °C.

[W(NAr)(OCMe$_2$CF$_3$)$_2$]$_2$. *cis*-2-Pentene (1.58 mL, 14.6 mmol) was added to a rapidly stirred solution of W(N-2,6-i-Pr$_2$C$_6$H$_3$)(CH-t-Bu)(OCMe$_2$CF$_3$)$_2$ (500 mg, 0.732 mmol) in 5 mL of pentane at room temperature. The resulting red solution was stirred for 16 h. Removal of volatiles in vacuo gave a red oil, into which was added 1 mL of pentane. The solution was kept at −30 °C. Red-brown crystals suitable for X-ray diffraction studies were formed over a period of two weeks. Several crystals were manually isolated and subjected to crystallographic studies. The remaining product was collected on a frit, washed with 2 × 1 mL of cold pentane, and dried to give 18 mg of the product (5% yield): ^{1}H NMR (C_6D_6) δ 7.16 (m, 6), 4.02 (m, 4) 1.34 (s, 12) 1.31 (br s, 24), 1.25 (s, 12); ^{19}F NMR (C_6D_6) δ −82.2 (s).

X-ray Diffraction Studies. Low-temperature data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), performing φ- and ω-scans. All structures were solved by direct methods using SHELXS[32] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[33] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms (except hydrogen atoms on carbon that binds directly to tungsten) were included in the model at geometrically calculated positions and refined using a riding model. All hydrogen atoms bound to carbon atoms directly linked to tungsten have been taken from the difference Fourier synthesis and refined semi-freely with the help of distance restraints. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed in Tables 1 and 3.

Both the *homo*- and *hetero*-[W(NAr)(CH_2-t-Bu)(OC_6F_5)]$_2$ crystallize in monoclinic space groups with half a molecule in the asymmetric unit, and in both structures the one crystallographically independent t-Bu group is disordered. These disorders were refined with the help of similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The ratios were refined freely, while constraining the total occupancy of both components to unity. In addition to the half molecule of *homo*-[W(NAr)(CH_2-t-Bu)(OC_6F_5)]$_2$, there is half a toluene molecule in the asymmetric unit. This solvent molecule is disordered over four positions, involving the crystallographic 2-fold. It was necessary to constrain the six carbon atoms of the phenyl rings in both crystallographically independent components to be perfectly hexagonal.

The structures of [W(NAr′)(OR_{F6})$_2$]$_2$ and [W(NAr)(OR_{F3})$_2$]$_2$ both show whole-molecule disorder. In the structure of [W(NAr′)(OR_{F6})$_2$]$_2$, both crystallographically independent molecules show at least 3-fold (if not 4-fold) whole-molecule disorder. The major components have occupancies of 87.4% and 86.3%, respectively; the occupancies of the minor components refined to 8.8% and 3.9% for one molecule and 9.8% and 3.9% for the other. The whole-molecule disorder of [W(NAr)(OR_{F3})$_2$]$_2$ is only 2-fold, and the ratio converged at 95:5. In both structures, only some of the lighter atoms of the minor components can be found and the refinement of those positions was not stable. Therefore, only the tungsten positions were modeled as involved in the whole-molecule disorder and the occupancies of the lighter atoms were left at 100%. This leads to somewhat inflated looking thermal ellipsoids for those lighter atoms. Furthermore, in the structures of both [W(NAr′)(OR_{F6})$_2$]$_2$ and [W(NAr)(OR_{F3})$_2$]$_2$ several CF_3 and $CCH_3(CF_3)_2$ groups are disordered within the main component of the whole-molecule disorder. These disorders were refined with the help of similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The ratios were refined freely, while constraining the total occupancy of both components to unity.

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Supporting Information Available: Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for *hetero*-[W(NAr)(CH_2-t-Bu)(OC_6F_5)]$_2$ (03265A), *homo*-[W(NAr)(CH_2-t-Bu)(OC_6F_5)]$_2$ (04148), *homo*-{W(NAr)(CH_2-t-Bu)[$OCH(CF_3)_2$]}$_2$ (04097), {W(NAr′)[$OCMe(CF_3)_2$]}$_2$ (04231), [W(NAr′)($OCMe_2CF_3$)$_2$]$_2$ (04102), and [W(NAr)($OCMe_2CF_3$)$_2$]$_2$ (04107). This information is available free of charge via the Internet at http://pubs.acs.org. Data for the four structures are also available to the public at http://www.reciprocalnet.org/. The number in parentheses above identifies each structure at this site.

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