

## Imido Alkylidene Bispyrrolyl Complexes of Tungsten

Thorsten Kreickmann, Stefan Arndt, Richard R. Schrock,\* and Peter Müller

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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We have prepared tungsten bispyrrolyl (Pyr) or bis-2,5-dimethylpyrrolyl (Me<sub>2</sub>Pyr) complexes W(NAr)-(CHCMe<sub>2</sub>Ph)(η<sup>1</sup>-Pyr)<sub>2</sub>(DME) (**1**), W(NAr)(CHCMe<sub>2</sub>Ph)(η<sup>1</sup>-Me<sub>2</sub>Pyr)(η<sup>5</sup>-Me<sub>2</sub>Pyr) (**2**), W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)-(η<sup>1</sup>-Pyr)<sub>2</sub>(DME) (**3b**), and W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(η<sup>1</sup>-Me<sub>2</sub>Pyr)(η<sup>5</sup>-Me<sub>2</sub>Pyr) (**4**) (Ar = 2,6-diisopropylphenyl, Ar<sub>Cl</sub> = 2,6-dichlorophenyl) in excellent yields by treating the appropriate W(NR)(CHCMe<sub>2</sub>R')(OTf)<sub>2</sub>(DME) species with LiPyr or LiMe<sub>2</sub>Pyr. Compounds **2** and **4** react with ethylene slowly to yield stable methylene complexes, W(NAr)(CH<sub>2</sub>)(η<sup>1</sup>-Me<sub>2</sub>Pyr)(η<sup>5</sup>-Me<sub>2</sub>Pyr) (**5**) and W(NAr<sub>Cl</sub>)(CH<sub>2</sub>)(η<sup>1</sup>-Me<sub>2</sub>Pyr)(η<sup>5</sup>-Me<sub>2</sub>Pyr) (**6**). In contrast, treatment of what is believed to be a fortuitous 1:1 mixture of **3b** and [W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(η<sup>1</sup>-Pyr)<sub>2</sub>][W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(η<sup>1</sup>-Pyr)(η<sup>5</sup>-Pyr)] with ethylene leads to formation of [W(μ-NAr<sub>Cl</sub>)(η<sup>1</sup>-Pyr)<sub>2</sub>]<sub>2</sub> (**7**) in moderate (54%) yield. Compounds **2** and **4** react with [HNMe<sub>2</sub>Ph]-[B(Ar<sub>F</sub>)<sub>4</sub>] (Ar<sub>F</sub> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) in dichloromethane to yield cationic species that contain one η<sup>5</sup>-Me<sub>2</sub>-Pyr ligand and one 2,5-dimethylpyrrolenine ligand formed through addition of a proton to C(2) of a dimethylpyrrolyl ligand, e.g., [W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(Me<sub>2</sub>Pyr){NC<sub>4</sub>(H<sub>3</sub>-2,3,4)(Me<sub>2</sub>-2,5)}]<sup>+</sup>[B(Ar<sub>F</sub>)<sub>4</sub>]<sup>-</sup> (**9**). X-ray studies were carried out on **1**, **2**, **6**, **7**, and **9**.

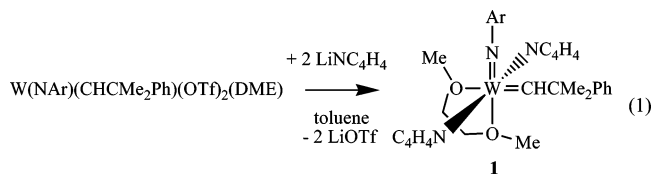
### Introduction

We reported recently that bispyrrolyl (or bispyrrolide)<sup>1</sup> molybdenum complexes can be prepared that have the empirical formula Mo(NR)(CHCMe<sub>2</sub>R')(pyrrolyl)<sub>2</sub> (where pyrrolyl = NC<sub>4</sub>H<sub>4</sub> (Pyr)<sup>2</sup> or 2,5-NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub> (Me<sub>2</sub>Pyr),<sup>3</sup> R' = Ph or Me, and R = 2,6-diisopropylphenyl, 1-adamantyl, or 2-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>). An X-ray study of Mo(N-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(CHCMe<sub>2</sub>Ph)(Pyr)<sub>2</sub> showed it to be a dimer in which the coordination at one end is of the type Mo(NAr)(CHCMe<sub>2</sub>Ph)(η<sup>1</sup>-Pyr)(η<sup>5</sup>-Pyr), where Mo has an 18-electron count, and that at the other end is of the type Mo(NAr)(CHCMe<sub>2</sub>Ph)(η<sup>1</sup>-Pyr)<sub>2</sub>(donor), where the lone pair on the nitrogen atom in the η<sup>5</sup>-Pyr ligand is bound to the second Mo. Low-temperature NMR spectra are consistent with the dimer being the lowest energy species in solution. In contrast, low-temperature NMR studies of Mo(NR)(CHCMe<sub>2</sub>R')(Me<sub>2</sub>-Pyr)<sub>2</sub> species suggested that they are 18e monomers of the type Mo(NR)(CHCMe<sub>2</sub>R')(η<sup>1</sup>-Me<sub>2</sub>Pyr)(η<sup>5</sup>-Me<sub>2</sub>Pyr).<sup>3</sup> Both Pyr and Me<sub>2</sub>Pyr complexes are highly fluxional on the NMR time scale in solution at room temperature as a consequence of interconversion of η<sup>1</sup>-pyrrolyl and η<sup>5</sup>-pyrrolyl ligands. The Pyr and Me<sub>2</sub>-Pyr complexes are of interest in their own right in view of the paucity of pyrrolyl complexes in general, and especially those of Mo and W. However, we are interested in pyrrolyl complexes primarily as precursors to monoalkoxide or bisalkoxide complexes that are formed upon addition of alcohols to bispyrrolyl complexes in solution<sup>2,3</sup> or upon addition of bispyrrolyl

complexes to SiOH on a silica surface.<sup>4</sup> We became interested in extending this type of chemistry to tungsten. In this paper we report W(NR)(CHCMe<sub>2</sub>R')(pyrrolyl)<sub>2</sub> complexes where R is 2,6-diisopropylphenyl or 2,6-dichlorophenyl and the pyrrolyl is Pyr or Me<sub>2</sub>Pyr, along with some reactions involving them.

### Results

**Synthesis of Pyrrolyl Complexes That Contain the NAr Ligand.** The reaction between W(NAr)(CHCMe<sub>2</sub>Ph)(OTf)<sub>2</sub>(DME) (Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, OTf = OSO<sub>2</sub>CF<sub>3</sub>)<sup>5</sup> and 2 equiv of LiNC<sub>4</sub>H<sub>4</sub> in toluene at 20 °C produces yellow W(NAr)-(CHCMe<sub>2</sub>Ph)(Pyr)<sub>2</sub>(DME) (**1**) in 80% yield (eq 1). Compound **1** can be recrystallized from pentane. An X-ray study showed **1** to have a structure analogous to that of Mo(NAr)(CHCMe<sub>3</sub>)-(OTf)<sub>2</sub>(DME),<sup>6</sup> i.e., a distorted octahedron containing a *syn* alkylidene ligand, *trans* η<sup>1</sup>-pyrrolyl ligands, and dimethoxyethane bound *trans* to the imido and alkylidene ligands (Table 1 and Figure 1). Bond distances and angles are unexceptional.<sup>7</sup> (See figure caption for selected values.) Compound **1** has an 18-electron count at the metal if the lone pair on the imido nitrogen is included.



The proton NMR spectrum of **1** at 20 °C in C<sub>6</sub>D<sub>6</sub> shows sharp resonances for two types of pyrrolyl protons at 6.77 and 6.44

\* Corresponding author. E-mail: rrs@mit.edu.

(1) In analogy with cyclopentadienide, “pyrrolide” describes an often main group salt containing the anion of pyrrole, e.g., lithium pyrrolide. “Pyrrolide” has also been employed to describe transition metal species, sometimes regardless of the hapticity and mode of coordination of the pyrrolide. However, in analogy with cyclopentadienyl, “pyrrolyl” appears to be the preferred term for transition metals. Therefore “pyrrolyl” is the descriptor employed in this paper.

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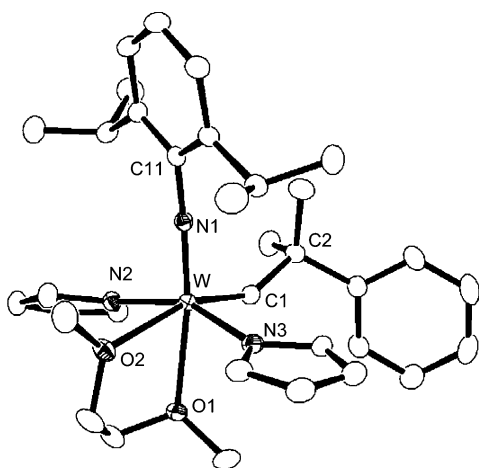
(6) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

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**Table 1. Crystal Data and Structure Refinement for W(NAr)(CHCMe<sub>2</sub>Ph)( $\eta^1$ -Pyr)<sub>2</sub>(DME) (1) and W(NAr)(CHCMe<sub>2</sub>Ph)( $\eta^1$ -Me<sub>2</sub>Pyr)( $\eta^5$ -Me<sub>2</sub>Pyr) (2a)<sup>a</sup>**

	1	2a
empirical formula	C <sub>34</sub> H <sub>47</sub> N <sub>3</sub> O <sub>2</sub> W	C <sub>34</sub> H <sub>45</sub> N <sub>3</sub> W
fw	713.60	679.58
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>
unit cell dimens	<i>a</i> = 11.4402(10) Å <i>b</i> = 18.7872(17) Å <i>c</i> = 15.4030(14) Å $\alpha$ = 90° $\beta$ = 92.817(2)° $\gamma$ = 90°	<i>a</i> = 9.8595(8) Å <i>b</i> = 30.930(3) Å <i>c</i> = 10.6710(8) Å $\alpha$ = 90° $\beta$ = 108.8770(10)° $\gamma$ = 90°
volume	3306.6(5) Å <sup>3</sup>	3079.1(4) Å <sup>3</sup>
Z	4	4
density (calcd)	1.433 Mg/m <sup>3</sup>	1.466 Mg/m <sup>3</sup>
absorb coeff	3.526 mm <sup>-1</sup>	3.777 mm <sup>-1</sup>
<i>F</i> (000)	1448	1376
cryst size	0.20 × 0.15 × 0.10 mm <sup>3</sup>	0.20 × 0.15 × 0.10 mm <sup>3</sup>
$\theta$ range for data collection	1.71 to 29.48°	2.12 to 29.57°
index ranges	-15 ≤ <i>h</i> ≤ 15 -26 ≤ <i>k</i> ≤ 26 -21 ≤ <i>l</i> ≤ 21	-13 ≤ <i>h</i> ≤ 13 -42 ≤ <i>k</i> ≤ 42 -14 ≤ <i>l</i> ≤ 14
no. of refls collected	71 413	68 232
no. of indep refls	9193 [ <i>R</i> (int) = 0.0634]	8621 [ <i>R</i> (int) = 0.0455]
completeness to $\theta_{\max}$	100.0%	99.8%
max. and min. transmn	0.711 and 0.540	0.7038 and 0.5188
no. of data/restraints/params	9193/1/372	8621/1/356
goodness-of-fit on <i>F</i> <sup>2</sup>	1.018	1.045
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0224 w <i>R</i> 2 = 0.0535	<i>R</i> 1 = 0.0197 w <i>R</i> 2 = 0.0440
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0280 w <i>R</i> 2 = 0.0564	<i>R</i> 1 = 0.0231 w <i>R</i> 2 = 0.0454
largest diff peak and hole	1.029 and -0.785 e Å <sup>-3</sup>	0.826 and -0.924 e Å <sup>-3</sup>

<sup>a</sup> In both cases the temperature was 100(2) K, the wavelength was 0.71073 Å, the absorption correction was semiempirical from equivalents, and the refinement method was full-matrix least-squares on *F*<sup>2</sup>.

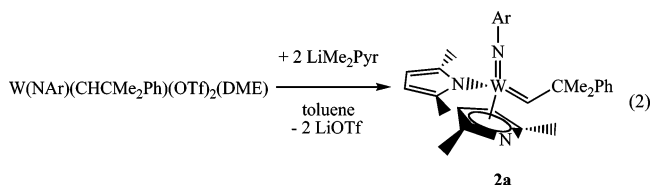


**Figure 1.** Molecular structure of W(NAr)(CHCMe<sub>2</sub>Ph)(Pyr)<sub>2</sub>(DME) (1) in the solid state. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: W–C(1) = 1.905(2); W–N(1) = 1.7422(17); W–N(2) = 2.1144(17); W–N(3) = 2.1221(18); W–O(1) = 2.3446(15); W–O(2) = 2.3374(15); N(1)–W–C(1) = 101.86(8); N(1)–W–O(1) = 167.77(7); N(2)–W–N(3) = 155.97(7); C(1)–W–O(2) = 159.59(8); W–C(1)–C(2) = 146.60(16); W–N(1)–C(11) = 175.61(15).

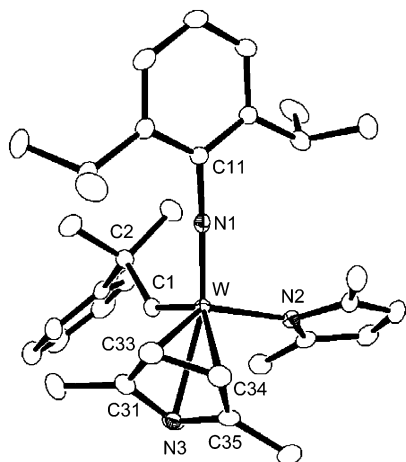
ppm, a resonance for the *syn* alkylidene proton at 10.58 ppm (*J*<sub>CH</sub> = 121 Hz), and one set of resonances for the coordinated dimethoxyethane; no resonance for the *anti* alkylidene proton can be observed. A fluxional process that is rapid on the NMR time scale at room temperature is responsible for the NMR observations at 20 °C. At -50 °C singlet resonances are observed for each of the methyl and methylene groups in bound dimethoxyethane, consistent with the observed structure in the

solid state. At -63 °C spectra are observed that reflect a slowing of rotation (on the NMR time scale) of the imido ligand about the N–C axis and a slowing of rotation of each pyrrolyl ligand about its W–N axis (see Experimental Section).

W(NAr)(CHCMe<sub>2</sub>Ph)(OTf)<sub>2</sub>(DME) also reacts with 2 equiv of Li-2,5-Me<sub>2</sub>NC<sub>4</sub>H<sub>4</sub> in toluene to give yellow W(NAr)(CHCMe<sub>2</sub>Ph)(Me<sub>2</sub>Pyr)<sub>2</sub> (2a) in 70% yield (eq 2). Complex 2a can be recrystallized readily from pentane. An X-ray study revealed that 2a has a pseudotetrahedral structure (Table 1 and Figure 2) in which one pyrrolyl ring is  $\eta^1$ -bound and the other is  $\eta^5$ -bound. Two “short” (W–C(31) = 2.370(2) and W–C(33) = 2.3667(19) Å) and two “long” (W–C(34) = 2.4674(19) and W–C(35) = 2.4928(19) Å) W–C bond distances are observed to the carbon atoms in the  $\eta^5$ -bound pyrrolyl ring, although the C–N bond distances within the  $\eta^5$ -pyrrolyl ring are essentially the same (C(35)–N(3) = 1.379(3) Å; C(31)–N(3) = 1.389(3) Å). The W–N distance (W–N(3)) is 2.4381(17) Å. Steric interactions are likely to be responsible for the slightly “slipped” nature of the  $\eta^5$ -Me<sub>2</sub>Pyr ligand. An 18-electron count is also reached in 2a. It should be noted that the  $\beta$ -carbon atom of the alkylidene ligand lies in the C(1)–W–N(1) plane. Therefore the orientation of the alkylidene ligand appears to be controlled by the imido ligand, not by the (arguably) “metallocene-like” nature of the (imido)W( $\eta^5$ -pyrrolyl) unit.



Complex 2a also shows fluxional behavior at 20 °C on the NMR time scale. Only broad pyrrolyl CH and CH<sub>3</sub> resonances



**Figure 2.** Molecular structure of  $W(NAr)(CHCMe_2Ph)(Me_2Pyr)_2$  (**2a**) in the solid state. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]:  $W-C(1) = 1.932(2)$ ;  $W-N(1) = 1.7541(16)$ ;  $W-N(2) = 2.0733(17)$ ;  $W-N(3) = 2.4381(17)$ ;  $W-C(31) = 2.370(2)$ ;  $W-C(33) = 2.3667(19)$ ;  $W-C(34) = 2.4674(19)$ ;  $W-C(35) = 2.4928(19)$ ;  $N(3)-C(31) = 1.389(3)$ ;  $C(31)-C(33) = 1.412(3)$ ;  $C(33)-C(34) = 1.426(3)$ ;  $C(34)-C(35) = 1.405(3)$ ;  $C(35)-N(3) = 1.379(3)$ ;  $C(1)-W-N(1) = 99.16(8)$ ;  $C(1)-W-N(2) = 100.45(7)$ ;  $N(1)-W-N(2) = 102.09(7)$ ;  $W-C(1)-C(2) = 135.77(15)$ ;  $W-N(1)-C(11) = 177.15(14)$ .

are observed for protons in equivalent pyrrolyl ligands as a consequence of interconversion of  $\eta^1$  and  $\eta^5$  forms. At  $-70$  °C, four sharp resonances are observed for protons on the pyrrolyl rings, consistent with the structure observed in the solid state, with the metal center being chiral, and with the  $\eta^1$ -pyrrolyl rotating slowly about the  $W-N$  bond on the NMR time scale at  $-70$  °C. Two resonances at 2.35 and 2.10 ppm can be assigned to the methyl groups of the  $\eta^5$ -coordinated pyrrolyl ring, but other resonances between 1.77 and 0.91 ppm cannot be assigned unambiguously. Nevertheless, the number of resonances and their integrals at  $-70$  °C are consistent with the structure observed in the solid state. Similar NMR behavior has been observed for  $Mo(NR)(CHCMe_2R')(Me_2Pyr)_2$  complexes in solution,<sup>3</sup> which suggests that they have structures analogous to that found for **2a**.

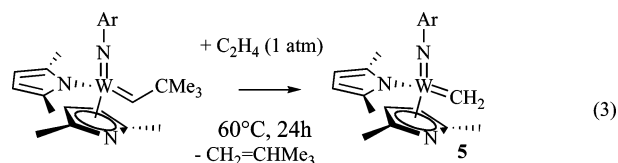
$W(NAr)(CHCMe_3)(OTf)_2(DME)$  also reacts with 2 equiv of  $Li-2,5-Me_2NC_4H_4$  in toluene to give yellow  $W(NAr)(CHCMe_3)(Me_2Pyr)_2$  (**2b**) in 79% yield. Compound **2b** is entirely analogous to **2a**.

**Synthesis of Pyrrolyl Complexes That Contain the  $NAr_{Cl}$  Ligand.** The reaction between  $W(NAr_{Cl})(CHCMe_3)(OTf)_2(DME)^8$  and 2 equiv of  $LiNC_4H_4$  in toluene gave a product whose proton NMR spectra at room temperature are consistent with a  $W(NAr_{Cl})(CHCMe_3)(Pyr)_2$  compound that contains 0.5 equiv of dimethoxyethane (**3a**). Upon recrystallization of **3a** from pentane in the presence of DME,  $W(NAr_{Cl})(CHCMe_3)(Pyr)_2(DME)$  (**3b**) was isolated in the form of yellow-orange microcrystals in 68% yield on a 3.7 mmol scale. Proton NMR studies of **3b** suggest that it has a structure analogous to **1**. The precise nature of **3a** could not be elucidated through NMR studies; we propose that **3a** is a fortuitous  $\sim 1:1$  mixture of **3b** and fluxional  $[W(NAr_{Cl})(CHCMe_3)(\eta^1-NC_4H_4)]_2[W(NAr_{Cl})(CHCMe_3)(\eta^1-NC_4H_4)(\eta^5-NC_4H_4)]$ , a compound whose structure would be analogous to that reported for  $[Mo(NAr)(CHCMe_2Ph)(\eta^1-NC_4H_4)_2][Mo(NAr)(CHCMe_2Ph)(\eta^1-NC_4H_4)(\eta^5-NC_4H_4)]$ .<sup>2</sup> Variable-temperature proton NMR spectra of **3b** in

$CD_2Cl_2$  are analogous to those for **1**; a fluxional process at room temperature is consistent with partial dissociation of DME, thereby equilibrating the two ends of DME, while at low temperatures DME is strongly bound on the NMR time scale.

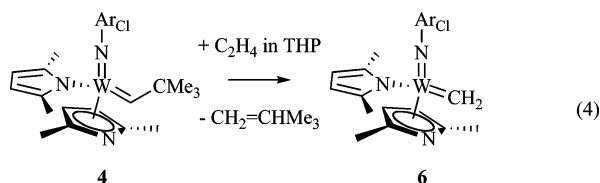
The reaction between  $W(NAr_{Cl})(CHCMe_3)(OTf)_2(DME)$  and 2 equiv of  $Li-2,5-Me_2NC_4H_4$  in toluene gave  $W(NAr_{Cl})(CHCMe_3)(Me_2Pyr)_2$  (**4**) as a yellow powder in 82% yield on a 12.5 mmol scale. All NMR data suggest that **4** has a structure analogous to **2** (eq 2). At 22 °C in  $CD_2Cl_2$  the  $^1H$  NMR spectrum of **4** exhibits a broad alkylidene resonance at 11.09 ppm ( $^1J_{CH} = 128$  Hz) as well as broad singlets for the pyrrolyl CH and methyl protons, consistent with a fluxional process in which the  $\eta^1$ -pyrrolyl and  $\eta^5$ -pyrrolyl rings exchange. At  $-60$  °C, the proton NMR spectrum of **4** is consistent with a molecule with no symmetry and restricted rotation about the imido  $N-C$  and the  $\eta^1$ -pyrrolyl  $N-W$  bond. It is especially clear in this case (vs the low-temperature spectrum of **2a**) that the two pyrrolyl ligands give rise to four sharp resonances for the methyl groups (at 2.93, 2.10, 1.90, and 1.52 ppm) and four sharp resonances for the pyrrolyl protons in the 3 and 4 positions (at 6.36, 6.06, 5.85, and 5.78 ppm) in the low-temperature limiting spectrum. The chemical shift of the alkylidene resonance is essentially invariant with temperature between  $-60$  and 20 °C. No alkylidene H resonance could be found for the *anti* isomer.

**Reactions of Pyrrolyl Complexes with Ethylene.** The reaction between **2** and 1 atm of ethylene in  $C_6D_6$  is exceedingly slow at 22 °C. However, at 60 °C **2b** reacts with ethylene (1 atm) cleanly and virtually completely to yield the product of the initial metathesis reaction and a methylene species **5** (eq 3). Compound **5** can be isolated as a yellow powder in 65%

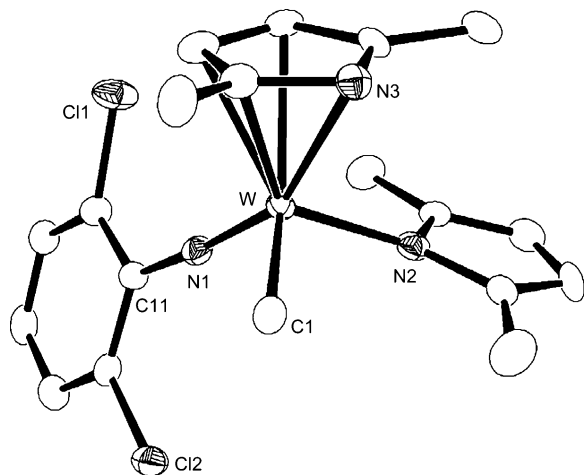


yield. It will be shown below that the structure of the analogous  $NAr_{Cl}$  species is the same as that proposed for **5** in eq 3. At  $-40$  °C the crucial features of the proton NMR spectrum are methylene proton resonances at 12.03 and 10.97 ppm, pyrrolyl proton resonances at 6.46, 5.82, 5.79, and 5.66 ppm, and pyrrolyl methyl resonances at 2.93, 2.07, 1.84, and 1.58 ppm.

A solution of **4** in tetrahydropyran (THP) reacts with ethylene over a period of 4 days to yield a mixture of tungsten-containing species. (THP has been found to be superior to THF in situations where formation of polyTHF appears to complicate workup.)<sup>8</sup> Workup of the crude product mixture led to isolation of the 18 valence electron methylidene complex  $W(NAr_{Cl})(CH_2)(\eta^1-Me_2Pyr)(\eta^5-Me_2Pyr)$  (**6**) as yellow crystals on a 3 mmol scale in 32% yield (eq 4). The methylidene protons appear as sharp



doublets in the  $^1H$  NMR spectrum at 20 °C (12.55 and 10.98 ppm,  $^2J_{HH} = 7.6$  Hz,  $^1J_{CH} = 145$  Hz). At 20 °C the four methyl groups of the two 2,5-dimethylpyrrolyl ligands give rise to one broad resonance at 2.3 ppm in the  $^1H$  NMR spectrum, and the protons in 3- and 4-position of the 2,5-dimethylpyrrolyl ligands vanish in the baseline. At  $-20$  °C all protons appear as sharp

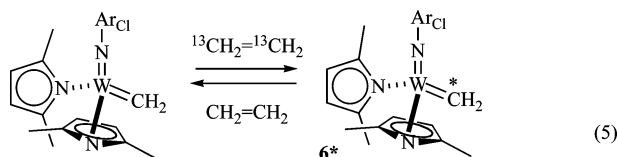


**Figure 3.** Molecular structure of  $W(NArCl)(CH_2)(Me_2Pyr)_2$  (**6**) in the solid state. One of the two independent molecules is shown. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]:  $W-C(1) = 1.941(5)$ ;  $W-N(1) = 1.754(4)$ ;  $W-N(2) = 2.069(4)$ ;  $W-N(1)-C(11) = 175.5(4)$ .

resonances in the  $^1H$  NMR spectrum ( $CD_2Cl_2$ ). Four singlets are found for both the four methyl groups and the four aromatic protons of the two 2,5-dimethylpyrrolyl ligands, whereas the resonances of the methylidene protons were found to be essentially invariant with temperature within the range examined ( $-60$  to  $+60$  °C). The fluxionality of **6** resembles that for **5**.

Single crystals of **6** suitable for X-ray crystallography were grown from a toluene solution at  $-40$  °C. The structure of the methylidene complex shown in Figure 3 is analogous to the structure of **2a** described earlier. The  $W=C$  bond ( $1.941(5)$  Å) is slightly longer than the  $W=C$  bond in **2a** ( $W-C(1) = 1.932(2)$  Å), but shorter than the  $Ta=C$  bond in  $Ta(\eta^5-C_5H_5)_2(CH_2)(CH_3)$  ( $2.026(10)$  Å).<sup>9</sup> Bending of the  $NArCl$  ligand in **6** ( $W-N(1)-C(11) = 175.5(4)^\circ$ ) is significantly less pronounced than in related tungsten complexes that contain the 2,6-dichloroimido ligand such as  $W(NArCl)(C_3H_6)(Biphen)$  ( $158.9(3)^\circ$ ) ( $Biphen^{2-} = 3,3'$ -di-*t*-Bu-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate).<sup>8</sup> Although the methylene protons in **6** were not found, we assume that they lie in the  $C-W-N$  plane on the basis of what is found in **2a**.

Complex **6** reacted immediately with  $^{13}CH_2=^{13}CH_2$  to give the  $^{13}C$ -labeled analogue (**6\***, eq 5), which could be isolated on a 200  $\mu$ mol scale in 97% yield. The immediate reaction of  $W(NArCl)(CH_2)(\eta^1-Me_2Pyr)(\eta^5-Me_2Pyr)$  with  $^{13}C$ -labeled ethylene to yield  $W(NArCl)(^{13}CH_2)(\eta^1-Me_2Pyr)(\eta^5-Me_2Pyr)$  almost certainly can be ascribed to the ready formation of 14-electron  $W(NArCl)(CH_2)(\eta^1-Me_2Pyr)_2$ , with which ethylene then reacts rapidly. No tungstacyclobutane intermediate is observed.

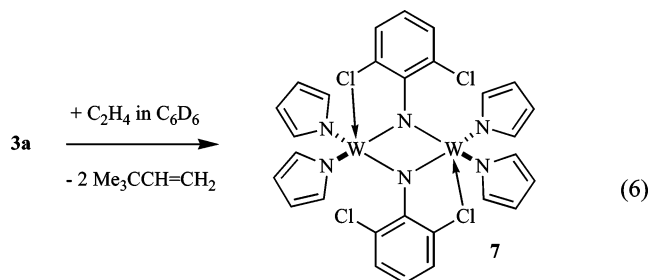


When an NMR sample of **3a** in  $C_6D_6$  was exposed to 1 atm of ethylene at 22 °C, the color of the solution immediately changed from yellow-orange to purple. After 1 h, a purple supernatant was decanted away from a crop of purple micro-



**Figure 4.** Molecular structure of  $[W(\mu-NArCl)(Pyr)_2]_2$  (**7**) in the solid state. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]:  $W-N(1) = 1.920(2)$ ;  $W-N(1') = 2.023(2)$ ;  $W-N(2) = 2.017(2)$ ;  $W-N(3) = 2.013(2)$ ;  $W-Cl(1) = 2.5687(6)$ ;  $W-W' = 2.5080(3)$ ;  $Cl(1)-W-N(1') = 176.50(6)$ ;  $N(2)-W-N(1) = 114.40(9)$ ;  $N(2)-W-N(3) = 123.17(10)$ .

crystals. The  $^1H$  NMR spectrum of the purple microcrystals in  $THF-d_8$  is consistent with this product being an alkylidene-free dimer,  $[W(\mu-NArCl)(NC_4H_4)_2]_2$  (**7**), in which rotation about the  $N-C$  bond of the imido ligands is not restricted by coordination of an *ortho* chlorine to  $W$  (eq 6). Purple **7** could be isolated in

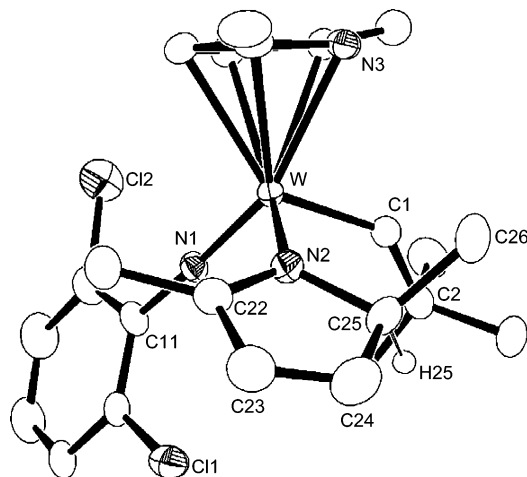


54% yield upon reaction of **3a** with ethylene in benzene on a 1 mmol scale. In an analogous experiment where **3b** was employed instead of **3a**, no **7** could be isolated and the products could not be elucidated. We propose that in the reaction of **3a** with ethylene, effectively only the DME-free dimer,  $[W(NArCl)(CHCMe_3)(Pyr)_2]_2$ , is converted into  $W(NArCl)(CH_2)(Pyr)_2$ , which then decomposes bimolecularly to yield **7** and ethylene readily into  $[W(\mu-NArCl)(Pyr)_2]_2$ . The reaction between **1** and ethylene (1 atm) led to a mixture from which no product could be identified readily.

Single crystals of **7** suitable for X-ray crystallography were obtained by slow diffusion of ethylene into a toluene solution of **3a**. The structural features of  $[W(\mu-NArCl)(Pyr)_2]_2$  in the solid state (Figure 4) are reminiscent of those for purple  $[W(\mu-NArCl)\{OC(CF_3)_2CMe_3\}_2]_2$ .<sup>8</sup> The interatomic  $W-W'$  distance in  $[W(\mu-NArCl)(NC_4H_4)_2]_2$  ( $2.5080(3)$  Å) is slightly longer than in related  $[W(NR)(OR')_2]_2$  complexes that contain an unsupported  $W=W$  double bond ( $2.4445(3)$ – $2.4925(3)$  Å).<sup>10</sup> All non-hydrogen atoms of the imido group in **7** lie approximately in a plane that is orthogonal to the plane that contains both tungsten atoms and the four pyrrolyl nitrogen atoms. The geometry around each tungsten atom is approximately a trigonal bipyramid

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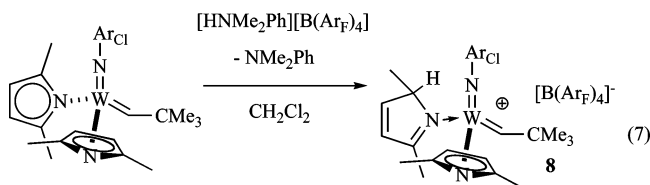
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**Figure 5.** Molecular structure of the cation in  $[W(NArCl)(CHCMe_3)(Me_2Pyr)\{NC_4(H_3-2,3,4)(Me_2-2,5)\}]^+[B(Ar_F)_4]^-$  (**8**) in the solid state. Hydrogen atoms except for H(25) are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: W–C(1) = 1.927(3); W–N(1) = 1.753(3); W–N(2) = 2.136(3); N(2)–C(22) = 1.313(4); C(22)–C(23) = 1.458(5); C(23)–C(24) = 1.327(6); C(24)–C(25) = 1.494(5); C(25)–N(2) = 1.492(4); W–N(1)–C(11) = 177.1(3); W–C(1)–C(2) = 139.2(2); C(24)–C(25)–N(2) = 103.1(3); N(2)–C(25)–C(26) = 113.2(3); C(24)–C(25)–C(26) = 113.5(3).

with one bridging chloride and one imido nitrogen atom in the apical position; equatorial positions are occupied by the other bridging imido nitrogen and two pyrrolyl nitrogens. The “equatorial” W–N(1) distance is shorter (1.920(2) Å) than the “axial” W–N(1) distance (2.023(2) Å) in the bridging imido ligands. A greater degree of  $\pi$  bonding to the nitrogen in an “equatorial” position around W(1) is believed to be the reason for the shorter W–N(1) bond. The W–Cl distance (W–Cl(1) = 2.5687(6) Å) is shorter than that in  $\{W(\mu-NArCl)[OC(CF_3)_2CMe_3]_2\}_2$  (2.6136(5) Å) and the Mo–Cl bond length in the Schiff base complex  $Mo(C_{13}H_8Cl_2N)Cl(CO)_3$  that contains a dative aryl Cl to Mo interaction (2.624(1) Å).<sup>11</sup> As in  $[W(\mu-NArCl)\{OC(CF_3)_2CMe_3\}_2]_2$ , the chlorides (Cl(1) and Cl(1')) are bound in approximately axial positions *trans* to the imido nitrogens.

**Protonation of Pyrrolyl Complexes.** Our interest in preparing (rare) cationic imido alkylidene complexes led to an exploration of the reaction between **4** and  $[HNMe_2Ph][B(Ar_F)_4]$  (where  $Ar_F = 3,5-(CF_3)_2C_6H_3$ ) in dichloromethane; the cationic species **8** shown in eq 7 is obtained as yellow crystals in 69% yield on a 1 mmol scale. Single crystals suitable for X-ray



crystallography were grown from dichloromethane at  $-40$  °C. A drawing of the structure of the cationic complex is shown in Figure 5. The cationic portion of **8** can be described as a Lewis base (L) adduct of a tungsten imido alkylidene  $\eta^5$ -pyrrolyl complex, i.e.,  $[W(NArCl)(CHCMe_3)(Me_2Pyr)(L)]^+$ , where L is

the 2,5-dimethylpyrrolenine that is formed upon protonation of C(2) in a 2,5-dimethylpyrrolyl ligand. The metric parameters of the substituted five-membered heterocycle are consistent with this scenario. The bond lengths N(2)–C(22) (1.313(4) Å) and C(23)–C(24) (1.327(6) Å) are indicative of double bonds, whereas C(22)–C(23) (1.458(5) Å), C(24)–C(25) (1.494(5) Å), and C(25)–N(2) (1.492(4) Å) are shorter than normal single bonds. A similar alternation of bond lengths has been observed in pyrrolenine complexes such as  $[Re(PMe_2Ph)_3Cl_2(NC_4H_5)]^+$ .<sup>12</sup> The angles at C(25) indicate largely  $sp^3$  hybridization of C(25) (C(24)–C(25)–N(2) = 103.1(3)°, N(2)–C(25)–C(26) = 113.2(3)°, and C(24)–C(25)–C(26) = 113.5(3)°). The neopentylidene ligand adopts the *syn* conformation with respect to the imido group and the W=C(1) bond length is 1.927(3) Å. The W–N(2) distance (2.136(3) Å) should be compared with the W–N<sub>pyrrolyl</sub> distance of 2.311(6) Å in  $[W(NAr)(CHCMe_2Ph)(OTf)_2(\text{dimethoxyethane})]$  and  $KTp'$  ( $Tp' = \text{hydrotris}(3,5\text{-dimethyl-1-pyrrolyl})\text{borate}$ ).<sup>13</sup> We cannot say whether the  $\eta^1$ -pyrrolyl ligand is protonated initially at C(2) or whether the  $\eta^5$ -pyrrolyl ligand is protonated at nitrogen followed by rearrangement to dimethylpyrrolenine.

The <sup>1</sup>H NMR spectrum of **8** in  $CD_2Cl_2$  is consistent with the structure observed in the solid state. The resonance for the proton on C(25) (Figure 5) appears as a multiplet at 4.48 ppm. The protons in the 3 and 4 positions of the dimethylpyrrolenine ligand appear at lower field (7.83 and 6.75 ppm) relative to those of the dimethylpyrrolyl ligand (6.63 and 6.20 ppm). The <sup>1</sup>H NMR spectrum exhibits four methyl resonances between 3.05 and 1.42 ppm for the two heterocyclic ligands. The doublet at 1.42 ppm (<sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz) can be assigned to the methyl group on C(25) of the dimethylpyrrolenine ligand.

Proton and carbon NMR spectra of **8** in THF-*d*<sub>8</sub> suggest that 1 equiv of 2,5-dimethylpyrrole is formed along with what we propose is a cationic species that contains coordinated THF, i.e.,  $[W(NArCl)(CHCMe_3)(Me_2Pyr)(THF-d_8)_x]^+[B(Ar_F)_4]^-$ . We did not attempt to isolate this species. In the <sup>1</sup>H NMR spectrum at 20 °C the alkylidene proton resonance is found at 11.09 ppm (<sup>1</sup>*J*<sub>CH</sub> = 119.2 Hz, <sup>1</sup>*J*<sub>WH</sub> = 11.9 Hz) in the <sup>1</sup>H NMR spectrum and the alkylidene carbon resonance at 285.8 ppm in the <sup>13</sup>C NMR spectrum. In the <sup>1</sup>H NMR spectrum the aromatic protons of the dimethylpyrrolyl group appear as multiplets at 5.87 and 5.74 ppm, and the methyl groups as singlets at 2.45 and 2.24 ppm. Resonances at 5.32 and 2.14 are indicative of free 2,5-dimethylpyrrole. We propose that 2,5-dimethylpyrrole is formed when THF displaces 2,5-dimethylpyrrolenine, which then rapidly rearranges to 2,5-dimethylpyrrole.

Compound **2b** reacts with  $[HNMe_2Ph][B(Ar_F)_4]$  in dichloromethane to yield the W=NAr analogue (**9**) of the cationic species **8** shown in eq 7. The NMR spectra of **9** are entirely analogous to those of **8**; the pyrrolenine-CHMe resonance is found at 4.46 ppm and the CHMe resonance at 1.44 ppm in the proton NMR spectrum in  $CD_2Cl_2$ . Compound **9** has limited stability in  $CD_2Cl_2$ , decomposing partially overnight at 22 °C; the nature of the decomposition product or products was not investigated.

## Discussion

Tungsten pyrrolyl complexes are rare. Dias and co-workers reported that treatment of  $WCl_4(\text{DME})$  with 2 equiv of Li-

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2,3,4,5-NC<sub>4</sub>Me<sub>4</sub> produced diamagnetic W( $\eta^5$ -NC<sub>4</sub>Me<sub>4</sub>)<sub>2</sub>Cl<sub>2</sub> in 6.5% yield.<sup>14</sup> Alkylation of W( $\eta^5$ -NC<sub>4</sub>Me<sub>4</sub>)<sub>2</sub>Cl<sub>2</sub> with LiMe produced W( $\eta^5$ -NC<sub>4</sub>Me<sub>4</sub>)<sub>2</sub>Me<sub>2</sub>, also in low yield (15.8%). No X-ray study of either compound was reported. Mayr reported the synthesis and X-ray structure of W(CPh)(PMe<sub>3</sub>)<sub>3</sub>(CO)(Pyr),<sup>15</sup> in which the  $\eta^1$ -pyrrolyl ligand is bound *trans* to the benzylidene ligand with a W–N bond length of 2.238(6) Å. We could find no example of a W(VI) complex in the literature that contains a monodentate pyrrolyl, although Odom has prepared M(NR)<sub>2</sub>(dpma) complexes for all group VI metals where dpma = *N,N*-di(pyrrolyl- $\alpha$ -methyl)-*N*-methylamine.<sup>16</sup> The only example of a molybdenum pyrrolyl complex other than the Mo(VI) species we have prepared<sup>2,3</sup> is Mo{HB(3,5-Me<sub>2</sub>C<sub>3</sub>N<sub>2</sub>H)<sub>3</sub>}(NO)( $\eta^1$ -NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub>.<sup>17,18</sup>

Isolable high oxidation state methylene complexes of Mo or W are also rare. W(O)(CH<sub>2</sub>)(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (18e count) could be isolated upon treating W(O)(CHCMe<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> in dichloromethane with ethylene in the presence of a trace of AlCl<sub>3</sub>.<sup>19</sup> It could be isolated when the reaction was carried out in benzene in the presence of 1/3 equiv of AlCl<sub>3</sub>.<sup>20</sup> W(NAr)(CH<sub>2</sub>)(OR)<sub>2</sub>(PMe<sub>3</sub>) complexes (Ar = 2,6-diisopropylphenyl, R = OCMe(CF<sub>3</sub>)<sub>2</sub> or OC(CF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>)(CF<sub>3</sub>)<sub>2</sub>) were isolated upon treatment of the tungstacyclobutane complexes, W(NAr)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(OR)<sub>2</sub>, with trimethylphosphine.<sup>21</sup> They are unusually stable for 16-electron complexes, most likely because of tight binding of PMe<sub>3</sub> and significant steric demands of the other ligands present that prevent bimolecular decomposition. Mo(NAr)(CH<sub>2</sub>)[OCMe(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(dimethoxyethane) can be observed in dme-*d*<sub>10</sub> upon addition of ethylene to Mo(NAr)(CHCMe<sub>3</sub>)[OCMe(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>. Upon addition of 2,2'-bipyridyl to the solution, Mo(NAr)(CH<sub>2</sub>)[OCMe(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(bipy) could be isolated and characterized.<sup>22</sup> Finally, W(NAr<sub>Cl</sub>)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(Biphen) decomposed to yield (*inter alia*) the dimeric, heterochiral methylene complex [W(NAr<sub>Cl</sub>)(Biphen)( $\mu$ -CH<sub>2</sub>)]<sub>2</sub> (Ar<sub>Cl</sub> = 2,6-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Biphen<sup>2-</sup> = 3,3'-di-*t*-Bu-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate), which was characterized crystallographically.<sup>23</sup> Heterochiral [W(NAr<sub>Cl</sub>)(Biphen)( $\mu$ -CH<sub>2</sub>)]<sub>2</sub> was found to decompose to yield homochiral [W(NAr<sub>Cl</sub>)(Biphen)]<sub>2</sub>( $\mu$ -CH<sub>2</sub>CH<sub>2</sub>), necessarily through cleavage of the heterochiral dimer and recombination of 14-electron W(NAr<sub>Cl</sub>)(Biphen)( $\mu$ -CH<sub>2</sub>) fragments. Although at least some of the above species almost certainly would yield crystals suitable for an X-ray study, to our knowledge 18-electron W(NAr<sub>Cl</sub>)(CH<sub>2</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> is the only monomeric methylene complex of W(VI) that has been characterized crystallographically.

The isolation of bispyrrolyl methylene complexes that are relatively stable toward bimolecular decomposition results from an unusual combination of circumstances. First, although the Me<sub>2</sub>Pyr complexes are relatively unreactive 18-electron species,

14-electron W(NR)(CHR')( $\eta^1$ -Me<sub>2</sub>Pyr)<sub>2</sub> species are likely to be intermediates in the fluxional process that involves interconversion of  $\eta^1$ - and  $\eta^5$ -pyrrolyl ligands. Second, although bispyrrolyl complexes appear to be relatively unreactive toward ordinary internal and terminal olefins, they will react with ethylene under forcing conditions. Third, metallacyclobutane bispyrrolyl complexes are disfavored relative to alkylidenes, most likely for steric reasons. Finally, the Me<sub>2</sub>Pyr methylene species do not decompose readily in a bimolecular fashion, again for steric reasons and because the concentration of 14-electron W(NR)(CH<sub>2</sub>)( $\eta^1$ -Me<sub>2</sub>Pyr)<sub>2</sub> species in solution is low. In effect the steric demands of  $\eta^5$ -pyrrolyl ligands and the ready interconversion of  $\eta^1$ - and  $\eta^5$ -pyrrolyls creates a type of "intramolecular protection" against bimolecular decomposition of alkylidenes, yet 18e pyrrolyl can access species with a 14e count. Less significant steric hindrance at the metal in W(NAr<sub>Cl</sub>)(CH<sub>2</sub>)( $\eta^1$ -Pyr)<sub>2</sub> and perhaps also intermolecular Cl–W interactions explain why W(NAr<sub>Cl</sub>) species decompose bimolecularly to dimers that contain bridging imido ligands (eq 6). Circumstances that make possible the isolation of a relatively stable methylene species upon reaction of a neopentylidene or neophylidene species with ethylene, especially under the conditions observed for **5** (60 °C), are rare. Formation of W(O)(CH<sub>2</sub>)(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> upon treating W(O)(CHCMe<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> in dichloromethane with ethylene in the presence of a trace of AlCl<sub>3</sub> is one other example that was noted above.<sup>24</sup>

As mentioned in the Introduction, we are interested in pyrrolyl complexes as precursors to alkoxides formed upon addition of 1 or 2 equiv of an alcohol, or to cationic alkylidene complexes upon addition of acid in which the anion is relatively noncoordinating.<sup>25</sup> Although there are numerous reports in the literature concerning pyrrolenine (also called 2H-pyrrole) complexed with Lewis acids and transition metals, pyrrolenine has never been observed in free form.<sup>26</sup> Calculations place the difference in the energy of pyrrolenine versus pyrrole between 10.0 and 19.3 kcal/mol.<sup>27–30</sup> Reaction of pyrrole with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> leads to formation of a pyrrolenine adduct.<sup>31</sup> This adduct also can be isolated upon treatment of Li pyrrolide with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, followed by addition of HCl.<sup>31,32</sup> Several examples of formation of pyrrolenine complexes upon protonation of a coordinated pyrrolyl are known for Os,<sup>33,34</sup> Re,<sup>12,35,36</sup> and W.<sup>36</sup> Usually pyrrolenine binds to the metal center through the nitrogen, but it also is known to bind through a  $\beta$ -carbon atom<sup>12,35,37</sup> or to be

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$\eta^2$ -coordinated through a C=C or C=N bond.<sup>33,34,36</sup> In view of the isolation of the 2,5-dimethylpyrrolenine adducts **8** and **9** we must consider the possibility that facile protonation of pyrrolyl ligands is the consequence of addition of a proton directly to C(2) in an  $\eta^1$ -pyrrolyl or  $\eta^5$ -pyrrolyl complex. We suspect that in certain circumstances attempts to protonate a pyrrolyl ligand in an imido alkylidene complex with other "acids" such as ROH might lead to formation of a pyrrolenine complex<sup>38</sup> and that this species might be relatively unreactive toward some olefins in metathesis reactions. Generally speaking, however, a donor functionality (even THF) can displace the pyrrolenine, thereby allowing it to rearrange to the pyrrole. It remains to be determined under what conditions relatively unreactive pyrrolenine complexes might lead to complications in metathesis reactions.

An interesting finding is that the Mo analogues of the W complexes do *not* react with ethylene to produce methylene species under similar conditions.<sup>39</sup> When a temperature is reached that leads to some reaction with ethylene, largely decomposition is observed. Evidently the initial reaction of the neopentylidene or neophylidene complex with ethylene is too slow and decomposition of the resulting methylene species is too fast to observe any significant buildup of intermediate methylene species.

The observations reported here raise a couple of interesting questions. First, do one or both Me<sub>2</sub>Pyr ligands in W methylene species protonate readily to yield mono- or bisalkoxide (or diolate) methylene species and how do those species decompose in the absence of substrates with which they would react (e.g., alkenes or alkynes)? Second, in view of the high reactivity of mono- or bisalkoxide methylene species, would bispyrrolyl methylene species be the preferred initiators in a variety of catalytic studies in which a catalyst is prepared through addition of alcohols *in situ* in the presence of substrates? Studies directed toward answering these and related questions are under way.

## Experimental Section

**General Procedures.** All operations were performed under a nitrogen atmosphere in the absence of oxygen and moisture in a glovebox or using standard Schlenk procedures. The glassware, including NMR tubes, were flame- and/or oven-dried prior to use. Benzene, ether, dichloromethane, pentane, and toluene were degassed with dinitrogen and passed through activated alumina columns. <sup>1</sup>H and <sup>13</sup>C NMR spectra were acquired in C<sub>6</sub>D<sub>6</sub> at 20 °C (unless otherwise noted) using a Bruker 400 or Varian 300 or 500 spectrometers (<sup>1</sup>H 400 MHz, <sup>13</sup>C 100 MHz) and referenced to the residual protio solvent peaks. Coupling constants (*J*<sub>CH</sub>) were determined on a Bruker Avance 600 spectrometer through HMQC studies. Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Neopentylmagnesium chloride was titrated with butanol in diethyl ether solution using 1,10-phenanthroline as an indicator immediately prior to use. W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(OTf)<sub>2</sub>(DME) was prepared according to published procedures.<sup>8</sup> Pyrrole and 2,5-dimethylpyrrole were purchased from Aldrich and distilled from CaH<sub>2</sub> prior to use. All other reagents were obtained from commercial suppliers and used as received unless otherwise noted.

**W(NAr)(CHCMe<sub>3</sub>Ph)(Pyr)<sub>2</sub>(DME) (1).** A cold solution of W(NAr)(CH<sub>2</sub>CMe<sub>2</sub>Ph)(OTf)<sub>2</sub>(DME) (1.00 g, 1.136 mmol) in toluene (15 mL) was added to a cold (−35 °C) suspension of LiNC<sub>4</sub>H<sub>4</sub> (166 mg, 2.273 mmol) in toluene (5 mL). The solution

turned orange as a white precipitate began to form. Stirring was continued overnight at ambient temperature, and the mixture was filtered through Celite. The solvent was removed *in vacuo*, and the residue was extracted with pentane (20 mL). The extract was filtered through Celite, and the solvent was removed from the filtrate to yield an orange powder. The crude product was recrystallized from pentane at −40 °C to form orange crystals; yield 650 mg (910 mmol, 80%): <sup>1</sup>H NMR (300 MHz)  $\delta$  10.86 (s, 1H, CHC(CH<sub>3</sub>)<sub>2</sub>Ph), 7.55 (dd, 2H, Ar-H), 7.26 (t, 2H, Ar-H), 7.11–7.07 (m, 3H, Ar-H), 6.97 (dd, 1H, Ar-H), 6.80 (t, 4H, pyr-H), 6.50 (t, 4H, pyr-H), 3.69 (sept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.87 (s, 6H, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 2.36 (s, 4H, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 1.83 (s, 6H, CHC(CH<sub>3</sub>)<sub>2</sub>Ph); <sup>13</sup>C NMR (75 MHz)  $\delta$  278.8 (CHC(CH<sub>3</sub>)<sub>2</sub>Ph), 152.2, 150.5, 149.3, 134.6, 128.6, 127.4, 126.5, 126.1, 123.4, 108.9, 70.9, 61.7, 53.8, 32.9, 27.2, 25.2; <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 500 MHz, −60 °C)  $\delta$  10.90 (s, 1H, CHCMe<sub>2</sub>Ph), 7.45 (d, 2H, Ar-H), 7.20 (s, 2H, Ar-H), 7.03 (t, 1H, Ar-H), 6.93–6.83 (m, 3H, Ar-H), 6.74 (s, br, 4H, Pyr-H), 6.56 (s, 4H, Pyr-H), 3.67 (sept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.78 (s, 3H, OCH<sub>3</sub>), 2.38 (s, 3H, OCH<sub>3</sub>), 2.12 (s, 2H, OCH<sub>2</sub>), 1.80 (s, br, CHC(CH<sub>3</sub>)<sub>2</sub>Ph and OCH<sub>2</sub>), 1.20 (dd, 12H, CH(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>34</sub>H<sub>47</sub>N<sub>3</sub>O<sub>2</sub>W: C 57.23, H 6.64, N 5.89. Found: C, 57.06; H, 6.55; N, 5.81.

**W(NAr)(CHCMe<sub>2</sub>Ph)(Me<sub>2</sub>Pyr)<sub>2</sub> (2a).** A cold solution of W(NAr)(CHCMe<sub>2</sub>Ph)(OTf)<sub>2</sub>(DME) (1 g, 1.136 mmol) in toluene (15 mL) was added to a cold (−35 °C) suspension of LiC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub> (216 mg, 2.273 mmol) in toluene (5 mL). The compound was prepared as described for **1** and isolated as orange crystals (540 mg, 795 mmol, 70%): <sup>1</sup>H NMR (300 MHz)  $\delta$  10.58 (s, 1H, CHC(CH<sub>3</sub>)<sub>2</sub>Ph), 7.36 (d, 2H, Ar-H), 7.15 (d, 2H, Ar-H), 7.08–7.01 (m, 4H, Ar-H), 5.95 (s, 4H, Pyr-CH), 3.49 (sept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.14 (s, 12H, Pyr-CH<sub>3</sub>), 1.67 (s, 6H, CHC(CH<sub>3</sub>)<sub>2</sub>Ph), 1.56 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (75 MHz)  $\delta$  277.2 (CHC(CH<sub>3</sub>)<sub>2</sub>Ph), 149.5, 149.1, 148.9 (Ar-C), 144.1 (Pyr-C), 126.5, 125.0, 124.4, 124.0, 121.6 (Ar-C), 105.2 (Pyr-C), 53.3, 30.8, 25.7, 22.4, 16.2 (Pyr-C); <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 500 MHz, −70 °C)  $\delta$  10.87 (s, 1H, CHCMe<sub>2</sub>Ph), 7.24 (d, 2H, Ar-H), 7.11 (t, 2H, Ar-H), 6.99 (t, 1H, Ar-H), 6.88 (m, 3H, Ar-H), 6.50 (s, 1H, Pyr-H), 6.39 (s, 1H, Pyr-H), 5.13 (s, 1H, Pyr-H), 4.93 (s, 1H, Pyr-H), 3.50 (sept, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.26 (sept, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.35 (s, 3H, Pyr-CH<sub>3</sub>), 2.10 (s, 3H, Pyr-CH<sub>3</sub>), 1.77 (s, 3H), 1.75 (s, 3H), 1.59 (s, 3H), 1.51 (s, 3H), 1.24 (d, 6H), 1.08 (d, 4H), 0.91 (s, 2H).

**W(NAr)(CHCMe<sub>3</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> (2b).** A cold solution of W(NAr)(CHCMe<sub>3</sub>)(OTf)<sub>2</sub>(DME) (650 mg, 0.795 mmol) in toluene (15 mL) was added to a cold (−35 °C) suspension of LiNMe<sub>2</sub>C<sub>4</sub>H<sub>2</sub> (161 mg, 1.59 mmol) in toluene (5 mL). The solution turned orange, and a white precipitate began to form. Stirring was continued overnight at ambient temperature, and the solution was filtered through Celite. The solvent was removed *in vacuo*, and the residue was extracted with pentane (20 mL). The extract was passed through Celite, and the solvent was removed *in vacuo* to yield an orange powder, which was recrystallized from pentane at −40 °C to form orange crystals (388 mg, 0.628 mmol, 79%): <sup>1</sup>H NMR (300 MHz)  $\delta$  10.49 (s, 1H, CHC(CH<sub>3</sub>)<sub>3</sub>), 7.36 (d, 2H, Ar-H), 7.04–6.94 (m, 3H, Ar-H), 6.00 (s, 4H, Pyr-CH), 3.48 (sept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.28 (s, 12H, Pyr-CH<sub>3</sub>), 1.20 (s, 9H, CHC(CH<sub>3</sub>)<sub>3</sub>), 1.14 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (75 MHz) 279.9 (CHC(CH<sub>3</sub>)<sub>3</sub>), 151.6, 146.5 (Ar-H), 140.1 (Pyr-C), 127.5, 124.1, (Ar-C), 108.4 (Pyr-C), 49.4, 34.6, 28.2, 24.9, 19.1 (Pyr-C). Anal. Calcd for C<sub>29</sub>H<sub>42</sub>N<sub>3</sub>W: C, 56.51; H, 7.02; N, 6.80. Found: C, 56.18; H, 7.10; N, 6.72.

**W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(Pyr)<sub>2</sub>(DME) (3a/3b).** Toluene (80 mL) was added to a mixture of W(NArCl)(CHCMe<sub>3</sub>)(OTf)<sub>2</sub>(DME) (3.00 g, 3.74 mmol) and LiNC<sub>4</sub>H<sub>4</sub> (546 mg, 7.48 mmol), and the suspension was stirred for 2 h at 25 °C. The colorless deposit was filtered off and washed with toluene (5 mL) to give an orange filtrate. All volatiles were removed from the filtrate under reduced pressure to leave behind an oily yellow-orange residue. Trituration with pentane (40 mL) produced a yellow-orange powder, which

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was isolated by filtration and washed with pentane (3 × 10 mL). On the basis of elemental analysis and recrystallization to give W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub>(DME) (see below), the crude product was assigned to be an approximate 1:1 mixture (per W) of W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub>(DME) and [W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub>. The crude product mixture was suspended in pentane (40 mL), and DME (3 mL) was added. After the suspension was stored at -40 °C overnight, analytically pure W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub>(DME) was obtained as an orange-yellow microcrystalline deposit (1.62 g, 68% yield): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 10.57 (s, <sup>1</sup>J<sub>CH</sub> = 112.4 Hz, 1H, WCH), 7.24 (d, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 2H, NAr<sub>Cl</sub>-3 and NAr<sub>Cl</sub>-5), 6.96 (t, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 1H, NAr<sub>Cl</sub>-4), 6.86 (br, 2 × 2H, NC<sub>4</sub>H<sub>4</sub>), 6.07 (br, 2 × 2H, NC<sub>4</sub>H<sub>4</sub>), 3.66 (s, 2 × 3H, DME), 3.30 (s, 2 × 2H, DME), 1.25 (s, 9H, CHCCH<sub>3</sub>); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, T = -60 °C) δ 10.63 (s, 1H, WCH), 7.22 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, NAr<sub>Cl</sub>-3 and NAr<sub>Cl</sub>-5, NC<sub>4</sub>H<sub>4</sub>), 6.95 (t, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 1H, NAr<sub>Cl</sub>-4), 6.81 (s, 2 × 2H, NC<sub>4</sub>H<sub>4</sub>), 6.00 (s, 2 × 2H, NC<sub>4</sub>H<sub>4</sub>), 3.94 (s, 3H, OCH<sub>3</sub>), 3.60 (s, 2H, OCH<sub>2</sub>), 3.35 (s, 3H, OCH<sub>3</sub>), 2.81 (s, 2H, OCH<sub>2</sub>), 1.16 (s, 9H, CHC(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 284.4 (s, <sup>1</sup>J<sub>WC</sub> = 179.8 Hz, <sup>1</sup>J<sub>CH</sub> = 112.4 Hz, WCH), 149.9, 135.1, 133.7, 128.5, 126.5, 108.1, 72.1, 61.3, 47.0, 33.3. Anal. Calcd for C<sub>23</sub>H<sub>31</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>W: C, 43.42; H, 4.91; N, 6.60. Found: C, 43.18; H, 4.99; N, 6.72.

**W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> (4).** Toluene (160 mL) was added to a mixture of W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(OTf)<sub>2</sub>(DME) (10.0 g, 12.5 mmol) and LiNC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub> (2.60 g, 25.7 mmol), and the suspension was stirred for 5 h at 25 °C. The colorless deposit was filtered off and washed with toluene (50 mL) to give a dark yellow filtrate. All volatiles were removed under reduced pressure to leave behind a dark yellow oily residue. Trituration with pentane (50 mL) produced a yellow powder, which was isolated by filtration and washed with pentane (50 mL); yield 6.17 g (82%): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 11.09 (br s, <sup>1</sup>J<sub>CH</sub> = 127.3 Hz, 1H, WCH), 7.32 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, NAr<sub>Cl</sub>-3 and NAr<sub>Cl</sub>-5), 7.03 (t, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 1H, NAr<sub>Cl</sub>-4), 6.03 (br, 2 × 2H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 2.19 (br, 4 × 3H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 1.18 (s, 9H, CHCCH<sub>3</sub>); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, T = -60 °C) δ 11.24 (s, 1H, WCH), 7.32 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 1H, NAr<sub>Cl</sub>-3), 7.27 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 1H, NAr<sub>Cl</sub>-5), 7.02 (t, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 1H, NAr<sub>Cl</sub>-4), 6.36 (s, 1H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 6.06 (s, 1H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 5.85 (s, 1H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 5.78 (s, 1H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 2.93 (s, 3H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 2.10 (s, 3H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 1.90 (s, 3H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 1.52 (s, 3H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 1.08 (s, 9H, CHCCH<sub>3</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 289.5 (br, <sup>1</sup>J<sub>CH</sub> = 127.3 Hz, WCH), 150.1, 132.4, 129.0, 126.1, 106.9, 48.7, 33.9, 18.7. Anal. Calcd for C<sub>23</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>3</sub>W: C, 45.87; H, 4.85; N, 6.98. Found: C, 45.73; H, 4.22; N, 6.87.

**W(NAr)(CH<sub>2</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> (5).** W(NAr)(CHCMe<sub>3</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> (350 mg, 0.567 mmol) was dissolved in benzene (15 mL), and the solution was degassed by three freeze-pump-thaw cycles and cooled to -78 °C. The reaction mixture was exposed to an atmosphere of ethylene (1 atm) and stirred for 48 h at 60 °C. The solvent was removed *in vacuo*, and the brownish residue was washed with pentane. Titration of the crude product with pentane gave pure W(NAr)(CH<sub>2</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> as a yellow powder (206 mg, 0.369 mmol, 65%): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 20 °C) δ 12.12 (d, <sup>2</sup>J<sub>HH</sub> = 7.3 Hz, 1H, WCH<sub>2</sub>), 11.10 (d, <sup>2</sup>J<sub>HH</sub> = 7.3 Hz, 1H, WCH<sub>2</sub>), 7.07-6.97 (m, 3H, Ar-H), 5.90 (s, br, 4H, Pyr-CH), 3.61 (sept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.18 (s, br, 12H, Pyr-CH<sub>3</sub>), 1.13 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz, -40 °C) δ 12.03 (d, 1H, WCH<sub>2</sub>), 10.97 (d, 1H, WCH<sub>2</sub>), 7.17-7.09 (m, 3H, Ar-H), 6.46 (s, 1H, Pyr-CH), 5.82 (s, 1H, Pyr-CH), 5.79 (s, 1H, Pyr-CH), 5.66 (s, 1H, Pyr-CH), 3.53 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.93 (s, 3H, Pyr-CH<sub>3</sub>), 2.07 (s, 3H, Pyr-CH<sub>3</sub>), 1.84 (s, 3H, Pyr-CH<sub>3</sub>), 1.58 (s, 3H, Pyr-CH<sub>3</sub>), 1.20 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.03 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz, 20 °C) δ 253.3 (<sup>1</sup>J<sub>WC</sub> = 164 Hz, W=CH<sub>2</sub>), 150.4, 145.4, 126.1, 122.7 (Ar-C), 27.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 18.3 (br, Pyr-CH<sub>3</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125 MHz, -40 °C) δ 252.6

(WCH<sub>2</sub>), 151.2, 149.3, 144.2, 141.2, 135.2, 134.7, 125.2, 122.0, 108.4, 107.1, 102.4, 97.1, 27.1, 23.0, 22.3, 20.3, 18.2, 17.7, 12.5.

**W(NAr<sub>Cl</sub>)(CH<sub>2</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> (6).** A thick-walled 250 mL glass vessel was charged with a solution of W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> (2.00 g, 3.32 mmol) in tetrahydrofuran (100 mL). The mixture was degassed by three freeze-pump-thaw cycles and then cooled to -78 °C. The reaction mixture was exposed to ethylene (1 atm), sealed, and warmed to 25 °C. After stirring for 4 days, all volatiles were removed under reduced pressure to leave behind an oily dark yellow residue. Trituration with pentane gave a yellow-brownish powder, which was washed with pentane (3 × 10 mL). Recrystallization of the crude product (1.42 g) from toluene (30 mL) gave W(NAr<sub>Cl</sub>)(CH<sub>2</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> as yellow crystals (585 mg, 32%): <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, T = 60 °C) δ 12.27 (d, <sup>2</sup>J<sub>HH</sub> = 7.3 Hz, 1H, WCH<sub>2</sub>), 10.93 (d, <sup>2</sup>J<sub>HH</sub> = 7.3 Hz, 1H, WCH<sub>2</sub>), 7.32 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, NAr<sub>Cl</sub>-3 and NAr<sub>Cl</sub>-5), 6.99 (t, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 1H, NAr<sub>Cl</sub>-4), 6.04 (br, 4H, NC<sub>4</sub>H<sub>2</sub>), 2.15 (br, 4 × 3H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 20 °C) δ 12.55 (d, <sup>2</sup>J<sub>HH</sub> = 7.6 Hz, <sup>1</sup>J<sub>CH</sub> = 147.3 Hz, 1H, WCH<sub>2</sub>), 10.98 (d, <sup>2</sup>J<sub>HH</sub> = 7.6 Hz, <sup>1</sup>J<sub>CH</sub> = 144.5 Hz, 1H, WCH<sub>2</sub>), 6.82 (d, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 2H, NAr<sub>Cl</sub>-3 and NAr<sub>Cl</sub>-5), 6.18 (t, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 1H, NAr<sub>Cl</sub>-4), 2.33 (br, 4 × 3H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>); the NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub> resonances were obscured by the resonances of the 2,6-dichloroimido group; <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 20 °C) δ 255.4 (s, <sup>1</sup>J<sub>WC</sub> = 159.5 Hz, WCH<sub>2</sub>), 150.5, 133.0, 129.3, 126.7, 109.5 (br), 19.5 (br); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, -20 °C) δ 12.44 (d, <sup>2</sup>J<sub>HH</sub> = 7.6 Hz, 1H, WCH<sub>2</sub>), 10.92 (d, <sup>2</sup>J<sub>HH</sub> = 7.6 Hz, 1H, WCH<sub>2</sub>), 7.32 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, NAr<sub>Cl</sub>-3 and NAr<sub>Cl</sub>-5), 6.99 (t, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 1H, NAr<sub>Cl</sub>-4), 6.55 (m, 1H, NC<sub>4</sub>H<sub>2</sub>), 5.91 (m, 1H, NC<sub>4</sub>H<sub>2</sub>), 5.84 (m, 1H, NC<sub>4</sub>H<sub>2</sub>), 5.81 (m, 1H, NC<sub>4</sub>H<sub>2</sub>), 2.92 (s, 3H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 2.12 (s, 3H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 1.85 (s, 3H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>), 1.61 (s, 3H, NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>). Anal. Calcd for C<sub>19</sub>H<sub>21</sub>Cl<sub>2</sub>N<sub>3</sub>W: C, 41.79; H, 3.88; N, 7.69. Found: C, 42.07; H, 3.78; N, 7.48.

**W(NAr<sub>Cl</sub>)(<sup>13</sup>CH<sub>2</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> (6\*).** A degassed solution of W(NAr<sub>Cl</sub>)(CH<sub>2</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> (113 mg, 207 μmol) in methylene chloride (15 mL) was treated with <sup>13</sup>CH<sub>2</sub>=<sup>13</sup>CH<sub>2</sub> (~12 equiv). After the solution was stirred for 20 min at 25 °C, it was degassed and treated with another 12 equiv of <sup>13</sup>CH<sub>2</sub>=<sup>13</sup>CH<sub>2</sub>. The reaction mixture was stirred for 20 min at 25 °C, and all volatiles were removed to yield yellow microcrystals, which were washed with cold toluene (1.5 mL); yield 110 mg (97%).

**[W(μ-NAr<sub>Cl</sub>)(Pyr)<sub>2</sub>]<sub>2</sub> (7).** A degassed solution of "W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub>(DME)<sub>0.5</sub>" (**3a**, 500 mg, 846 μmol) in benzene (20 mL) was exposed to ethylene (1 atm), and the reaction mixture was stirred at 25 °C for 24 h. The supernatant was decanted from purple microcrystals, which were washed with pentane (5 mL); yield 216 mg (54%): <sup>1</sup>H NMR (THF-*d*<sub>8</sub>) δ 8.00 (br, 2H, NAr<sub>Cl</sub>-3 and NAr<sub>Cl</sub>-5), 7.22 (t, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2 × 2H, NAr<sub>Cl</sub>-4), 5.94, 5.49 (s, 2 × 4H, NC<sub>4</sub>H<sub>4</sub>). Due to the insolubility of [W(NAr<sub>Cl</sub>)(μ-NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub>, a complete set of NMR spectra could not be obtained. Anal. Calcd for C<sub>28</sub>H<sub>22</sub>Cl<sub>4</sub>N<sub>6</sub>W<sub>2</sub>: C, 35.33; H, 2.33; N, 8.83; Found: C, 35.15; H, 2.38; N, 8.75.

In an analogous experiment where **3b** was employed instead of **3a**, no [W(μ-NAr<sub>Cl</sub>)(NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub> could be isolated.

**[W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(Me<sub>2</sub>Pyr){NC<sub>4</sub>(H<sub>3</sub>-2,3,4)(Me<sub>2</sub>-2,5)}]<sup>+</sup>[B(Ar<sub>F</sub>)<sub>4</sub>]<sup>-</sup> (8).** A stirred solution of W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> (500 mg, 830 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL, -40 °C) was treated with neat [HNMe<sub>2</sub>Ph][B(Ar<sub>F</sub>)<sub>4</sub>] (818 mg, 830 μmol). After the reaction mixture was stirred for 1 h at 25 °C, all volatiles were removed under reduced pressure to leave behind a yellow powder, which was washed with pentane (3 × 5 mL). The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and a layer of pentane (10 mL) was added. After it was kept for 3 days at -40, yellow crystals were obtained from the reaction mixture and washed with pentane/CH<sub>2</sub>Cl<sub>2</sub> (1:1 mixture, 3 × 1 mL, -40 °C) to yield analytically pure [W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>-2,5){NC<sub>4</sub>(H<sub>3</sub>-2,3,4)(Me<sub>2</sub>-2,5)}]<sup>+</sup>[B(Ar<sub>F</sub>)<sub>4</sub>]<sup>-</sup> (843 mg, 69%): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 12.06 (s, 1H, WCH), 7.83 (d, <sup>3</sup>J<sub>HH</sub> = 5.3 Hz, 1H, NC<sub>4</sub>H<sub>3</sub>-4), 7.72 (m, 4 × 2H,



**Table 2. Crystal Data and Structure Refinement for  $W(NAr_{Cl})(CH_2)(Me_2Pyr)_2$  (6),  $[W(\mu-NAr_{Cl})(Pyr)_2]_2$  (7), and  $[W(NAr_{Cl})(CHCMe_3)(Me_2Pyr)\{NC_4(H_3-2,3,4)(Me_2-2,5)\}]^+[B(Ar_F)_4]^-$  (8)<sup>a</sup>**

	6	7	8
empirical formula	C <sub>19</sub> H <sub>21</sub> Cl <sub>2</sub> N <sub>3</sub> W	C <sub>38</sub> H <sub>33</sub> Cl <sub>4</sub> N <sub>6</sub> W <sub>2</sub>	C <sub>55</sub> H <sub>42</sub> BCl <sub>2</sub> F <sub>24</sub> N <sub>3</sub> W
fw	546.14	1083.20	1466.48
temperature	90(2) K	193(2) K	90(2) K
cryst syst	orthorhombic	tetragonal	triclinic
space group	<i>Pca</i> 2(1)	<i>P4</i> (2)/ <i>n</i>	<i>P</i> 1
unit cell dimens	<i>a</i> = 14.205(4) Å <i>b</i> = 12.476(3) Å <i>c</i> = 21.561(6) Å $\alpha$ = 90° $\beta$ = 90° $\gamma$ = 90°	<i>a</i> = 13.2320(9) Å <i>b</i> = 13.2320(9) Å <i>c</i> = 21.410(3) Å $\alpha$ = 90° $\beta$ = 90° $\gamma$ = 90°	<i>a</i> = 12.699(3) Å <i>b</i> = 13.444(4) Å <i>c</i> = 17.522(4) Å $\alpha$ = 90.570(4)° $\beta$ = 105.392(4)° $\gamma$ = 95.365(5)°
volume	3821.2(18) Å <sup>3</sup>	3748.7(6) Å <sup>3</sup>	2869.8(13) Å <sup>3</sup>
Z	8	4	2
density (calcd)	1.899 Mg/m <sup>3</sup>	1.919 Mg/m <sup>3</sup>	1.697 Mg/m <sup>3</sup>
absorp coeff	6.332 mm <sup>-1</sup>	6.454 mm <sup>-1</sup>	2.224 mm <sup>-1</sup>
<i>F</i> (000)	2112	2076	1444
cryst size	0.15 × 0.15 × 0.04 mm <sup>3</sup>	0.30 × 0.20 × 0.15 mm <sup>3</sup>	0.25 × 0.20 × 0.15 mm <sup>3</sup>
$\theta$ range for data collection	2.17 to 29.57°	2.18 to 29.57°	1.52 to 29.57°
index ranges	-19 ≤ <i>h</i> ≤ 19 -17 ≤ <i>k</i> ≤ 17 -29 ≤ <i>l</i> ≤ 29	-18 ≤ <i>h</i> ≤ 18 -18 ≤ <i>k</i> ≤ 18 -29 ≤ <i>l</i> ≤ 29	-17 ≤ <i>h</i> ≤ 17 -18 ≤ <i>k</i> ≤ 18 -24 ≤ <i>l</i> ≤ 24
no. of reflns collected	80 281	82 886	63 761
no. of indep reflns	10 714 [ <i>R</i> (int) = 0.0758]	5251 [ <i>R</i> (int) = 0.0460]	16 060 [ <i>R</i> (int) = 0.0536]
completeness to $\theta = 29.57^\circ$	100.0%	100.0%	99.7%
max. and min. transmn	0.7858 and 0.4501	0.4444 and 0.3859	0.7314 and 0.6063
no. of data/restraints/params	10 714/1198/546	5251/112/269	16 060/3020/932
goodness-of-fit on <i>F</i> <sup>2</sup>	1.016	1.108	1.052
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0261 w <i>R</i> 2 = 0.0608	<i>R</i> 1 = 0.0197 w <i>R</i> 2 = 0.0408	<i>R</i> 1 = 0.0368 w <i>R</i> 2 = 0.0963
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0336 w <i>R</i> 2 = 0.0646	<i>R</i> 1 = 0.0303 w <i>R</i> 2 = 0.0455	<i>R</i> 1 = 0.0413 w <i>R</i> 2 = 0.0995
abs struct param	0.051(9)		
largest diff peak and hole	1.129 and -1.101 e Å <sup>-3</sup>	0.425 and -0.628 e Å <sup>-3</sup>	3.127 and -1.188 e Å <sup>-3</sup>

<sup>a</sup> In all cases the wavelength was 0.71073 Å, the absorption correction was semiempirical from equivalents, and the refinement method was full-matrix least-squares on *F*<sup>2</sup>.

Ar<sub>F</sub>-2 and Ar<sub>F</sub>-6), 7.56 (br, 4H, Ar<sub>F</sub>-4), 7.34 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.1 Hz, 2H, Ar<sub>Cl</sub>-3 and Ar<sub>Cl</sub>-5), 7.13 (t, <sup>3</sup>*J*<sub>HH</sub> = 8.1 Hz, 1H, Ar<sub>Cl</sub>-4), 6.75 (dd, <sup>3</sup>*J*<sub>HH</sub> = 5.3 Hz, 1.3 Hz, 1H, NC<sub>4</sub>H<sub>3</sub>-3), 6.63 (d, <sup>3</sup>*J*<sub>HH</sub> = 2.5 Hz, 1H, NC<sub>4</sub>H<sub>2</sub>), 6.20 (d, <sup>3</sup>*J*<sub>HH</sub> = 2.5 Hz, 1H, NC<sub>4</sub>H<sub>2</sub>), 4.48 (m, 1H, NC<sub>4</sub>H<sub>3</sub>-2), 3.05 (s, *J*<sub>WC</sub> = 15.2 Hz, 3H, NC<sub>4</sub>H<sub>2</sub>CH<sub>3</sub>), 2.57 (d, <sup>4</sup>*J*<sub>HH</sub> = 2.8 Hz, 3H, NC<sub>4</sub>H<sub>3</sub>CH<sub>3</sub>), 2.26 (s, 3H, NC<sub>4</sub>H<sub>2</sub>CH<sub>3</sub>), 1.42 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, 3H, NC<sub>4</sub>H<sub>3</sub>CH<sub>3</sub>), 1.15 (s, 9H, CHCCH<sub>3</sub>). Anal. Calcd for C<sub>55</sub>H<sub>42</sub>BCl<sub>2</sub>F<sub>24</sub>N<sub>3</sub>W: C, 45.05; H, 2.89; N, 2.87. Found: C, 45.00; H, 2.85; N, 2.82.

**[W(NAr)(CHCMe<sub>3</sub>)(Me<sub>2</sub>Pyr){NC<sub>4</sub>(H<sub>3</sub>-2,3,4)(Me<sub>2</sub>-2,5)}]<sup>+</sup>[B(Ar<sub>F</sub>)<sub>4</sub>]<sup>-</sup> (9).** [HNMe<sub>2</sub>Ph][B(Ar<sub>F</sub>)<sub>4</sub>] (226 mg, 0.23 mmol) was added to a stirred solution of W(NAr)(CHCMe<sub>3</sub>)(Me<sub>2</sub>Pyr)<sub>2</sub> (142 mg, 0.23 mmol) in cold (-40 °C) CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The solution immediately turned red and was stirred overnight at ambient temperature. All volatiles were removed *in vacuo*, and the reddish-brown residue was washed with pentane. Yellow crystals were obtained from a solution of the crude product in CH<sub>2</sub>Cl<sub>2</sub>/pentane (1:1) at -40 °C (148 mg, 0.1 mmol, 43%): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  12.25 (s, 1H, CHCMe<sub>3</sub>), 7.93 (d, <sup>3</sup>*J*<sub>HH</sub> = 5.3 Hz, 1H, pyrrolenine-H1), 7.77 (m, 8H, (BAr<sub>F</sub>)-CH), 7.60 (s, 4H, (BAr<sub>F</sub>)-CH), 7.26–7.16 (m, 3H, Ar-H), 6.83 (dd, <sup>3</sup>*J*<sub>HH</sub> = 5.3 Hz, <sup>3</sup>*J*<sub>HH</sub> = 1.3 Hz, 1H, pyrrolenine-CH), 6.52 (d, <sup>3</sup>*J*<sub>HH</sub> = 2.2 Hz, 1H, Pyr-CH), 5.98 (d, <sup>3</sup>*J*<sub>HH</sub> = 2.2 Hz, 1H, Pyr-CH), 4.46 (m, 1H, pyrrolenine-CHMe), 3.08 (s, 3H, Pyr-CH<sub>3</sub>), 2.91 (s, br, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.68 (d, <sup>4</sup>*J*<sub>HH</sub> = 2.9 Hz, 3H, pyrrolenine-CH<sub>3</sub>), 2.26 (s, 3H, Pyr-CH<sub>3</sub>), 1.44 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.7 Hz, 3H, pyrrolenine-CHCH<sub>3</sub>), 1.19 (s, 9H, CH(CH<sub>3</sub>)<sub>3</sub>), 1.17 (s, br, 12H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  299.6 (CHCMe<sub>3</sub>), 190.8 (pyrrolenine-C=N), 166.7, 151.8, 140.6, 134.9, 130.1, 128.4, 123.8, 123.0, 117.7, 104.6, 102.9, 89.1, 52.3, 34.4, 32.0, 28.0, 23.1, 22.5, 19.7, 16.1, 15.1, 14.0.

**Observation of [W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(Me<sub>2</sub>Pyr)(THF-*d*<sub>8</sub>)<sub>2</sub>]<sup>+</sup>[B(Ar<sub>F</sub>)<sub>4</sub>]<sup>-</sup>.** Yellow crystals of [W(NAr<sub>Cl</sub>)(CHCMe<sub>3</sub>)(Me<sub>2</sub>Pyr){NC<sub>4</sub>

(H<sub>3</sub>-2,3,4)(Me<sub>2</sub>-2,5)][B(Ar<sub>F</sub>)<sub>4</sub>] were dissolved in THF-*d*<sub>8</sub>: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>)  $\delta$  11.09 (s, <sup>1</sup>*J*<sub>CH</sub> = 119.2 Hz, <sup>1</sup>*J*<sub>WH</sub> = 11.9 Hz, 1H, WCH), 7.82 (m, 4 × 2H, Ar<sub>F</sub>-2 and Ar<sub>F</sub>-6), 7.61 (br, 1H, Ar<sub>F</sub>-4), 7.45 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.1 Hz, 2H, Ar<sub>Cl</sub>-3 and Ar<sub>Cl</sub>-5), 7.19 (t, <sup>3</sup>*J*<sub>HH</sub> = 8.1 Hz, 1H, Ar<sub>Cl</sub>-4), 5.87 (m, 1H, NC<sub>4</sub>H<sub>2</sub>), 5.74 (m, 1H, NC<sub>4</sub>H<sub>2</sub>), 2.45 (s, 3H, NC<sub>4</sub>H<sub>2</sub>CH<sub>3</sub>), 2.25 (s, 3H, NC<sub>4</sub>H<sub>2</sub>CH<sub>3</sub>), 1.31 (s, 9H, CHCCH<sub>3</sub>); <sup>13</sup>C NMR (THF-*d*<sub>8</sub>)  $\delta$  285.8 (br, <sup>1</sup>*J*<sub>CH</sub> = 119.2 Hz, WCH), 162.9 (quart, <sup>1</sup>*J*<sub>CB</sub> = 49.6 Hz, Ar<sub>F</sub>-1), 149.7, 135.7 (br, Ar<sub>F</sub>-2 and Ar<sub>F</sub>-6), 135.0, 131.1, 130.1 (quart, <sup>2</sup>*J*<sub>FC</sub> = 30.7 Hz, Ar<sub>F</sub>-3 and Ar<sub>F</sub>-5), 125.9, 125.6 (quart, <sup>1</sup>*J*<sub>CF</sub> = 271.4 Hz, CF<sub>3</sub>), 118.3 (m, Ar<sub>F</sub>-4), 111.1, 110.9, 106.1, 49.6, 33.0, 18.9, 15.4, 13.1. One equivalent of 2,5-dimethylpyrrole was formed in the process.

**X-ray Crystallography.** Crystals for the X-ray studies were obtained from the solvents employed in each case. (See the Experimental Section above.) Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å), performing  $\phi$ - and  $\omega$ -scans. The structures were solved by direct methods using SHELXS<sup>40</sup> and refined against *F*<sup>2</sup> on all data by full-matrix least-squares with SHELXL-97.<sup>41</sup> All non-hydrogen atoms were refined anisotropically. All hydrogen atoms (except hydrogen atoms on carbon that binds directly to tungsten, which have been taken from the difference Fourier synthesis and refined semifreely with the help of distance restraints) were included into the model at geometrically calculated positions and refined using a riding model. 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

(40) Sheldrick, G. M. *Acta Crystallogr. A* **1990**, *46*, 467.

(41) Sheldrick, G. M. *SHELXL 97*; Universität Göttingen: Göttingen, Germany, 1997.

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 2.

The asymmetric unit of the structure of  $W(NAr_{Cl})(CH_2)(Me_2Pyr)_2$  contains two molecules. One of the two crystallographically independent molecules is well-behaved, while the other one shows whole molecule disorder. The ratio between the two components was refined freely and converged at 0.832(9). Equivalent atoms of the two components of the disordered molecule were constrained to have identical anisotropic displacement parameters, and similarity restraints on 1–2 and 1–3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters were applied. No restraints on anisotropic displacement parameters were applied to the first molecule and similarity restraints only insofar as geometrically relating the two crystallographically independent molecules. All bond lengths and angles specified and discussed throughout this publication are those of the nondisordered molecule. The structure was refined as a racemic twin; the twin ratio converged at 0.051(9).

Several disorders in  $[B(Ar_F)_4]^-$  in the structure of **8** 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.

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**Supporting Information Available:** Labeled thermal ellipsoid drawings, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for all crystallographically characterized compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>. Data for  $W(NAr)(CHCMe_2Ph)(\eta^1-Pyr)_2(DME)$  (06238),  $W(NAr)(CHCMe_2Ph)(Me_2Pyr)_2$  (07007),  $W(NAr_{Cl})(CH_2)(Me_2Pyr)_2$  (07053),  $[W(\mu-NAr_{Cl})(Pyr)_2]_2$  (06211), and  $[W(NAr_{Cl})(CHCMe_3)(Me_2Pyr)\{NC_4(H_3-2,3,4)(Me_2-2,5)\}]^+[B(Ar_F)_4]^-$  (07043) are also available to the public at <http://www.reciprocalnet.org/>.

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