Syntheses, Structures, and Reactivity of a Series of (Pentamethylcyclopentadienyl)molybdenum(V) and -tungsten(V) Imido Complexes

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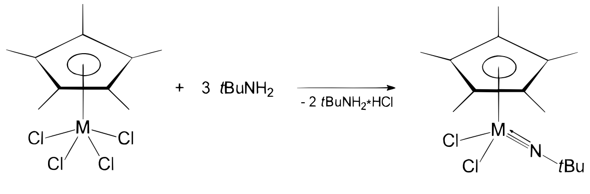
Reactions of the (pentamethylcyclopentadienyl)molybdenum(V) and -tungsten(V) tetrachlorides ($(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}_4$) (M = Mo, W) with the primary amines RNH_2 (R = *t*-Bu, *i*-Pr, C_6F_5, and 2,6-(*i*-Pr)$_2$C$_6$H$_3$) lead to the formation of the imido complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{M(NR)Cl}_2]$ (**3a**−**h**). X-ray structure analyses of **3a**, **3c**, and **3e** reveal their monomeric nature. **3c** and **3e** crystallize in the monoclinic space group $P2_1/c$ with the lattice parameters a = 15.171(3) Å, b = 7.615(2) Å, c = 14.758(3) Å, β = 90.29(3)°, and V = 1704.9(7) Å^3 for **3e** and a = 10.4502(7) Å, b = 10.6897(8) Å, c = 15.915(2) Å, β = 94.342(8)°, and V = 1772.7(3) Å^3 for **3c**. **3a** crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 8.6040(10) Å, b = 12.0490(10) Å, c = 17.020(2) Å, and V = 1764.5(3) Å^3. The metal−nitrogen distances of these 17-electron complexes (1.719(3) Å for **3a**, 1.716(12) Å for **3e**, and 1.748(2) Å for **3c**) correspond to a triple bond. $(\eta^5\text{-C}_5\text{Me}_5)\text{W(NC}_6\text{F}_5)\text{Cl}_2$ (**3g**) decomposes in the presence of air to the half-sandwich tungsten(VI) imido complex $(\eta^5\text{-C}_5\text{Me}_5)\text{W(NC}_6\text{F}_5)\text{Cl}_3$ (**4**) and a green solid. Further hydrolysis of **3g** results in the dinuclear tungsten(VI) oxo complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{WO}_2]_2(\mu\text{-O})\cdot\text{C}_6\text{F}_5\text{NH}_2$ (**5**) with a linear W−O−W bridge. The complexes have been characterized by X-ray diffraction. **4** crystallizes in the triclinic space group $P\bar{1}$, with a = 7.3843(1) Å, b = 11.529(2) Å, c = 11.558(2) Å, α = 77.38(2)°, β = 80.15(2)°, γ = 79.88(2)°, and V = 936.2(3) Å^3; **5** crystallizes in the monoclinic space group $P2_1/n$, with a = 1.3246(3) Å, b = 1.0042(3) Å, c = 1.4102(3) Å, β = 104.37(3)°, and V = 1.8173(6) Å^3.

Introduction

The role of transition-metal imido complexes[1] as reactive intermediates in industrial[2] and laboratory organic[3] syntheses has received increased attention in recent years. The selective ammonoxidation of propylene to acrylonitrile is the most significant reaction of this type. Since it is known that in the ammonoxidation ammonia is activated by formation of an imido species (Mo=NH), it has been the subject of industrial research and mechanistic studies.[4] In recent years several structural investigations on half-sandwich imido complexes of the early transition metals have been reported, e.g.: $[(\eta^5\text{-C}_5\text{H}_5)\text{V(N-}t\text{-Bu)Cl}_2]$,[5] $[(\eta^5\text{-C}_5\text{R}_5)\text{M(N-}t\text{-Bu)Cl}_2]$ (R = H, Me; M = Nb, Ta),[6] $[(\eta^5\text{-C}_5\text{R}_5)\text{M(N-}t\text{-Bu)}_2\text{Cl}]$ (R = H, Me; M = W, Mo),[7] and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re(N-}t\text{-Bu)Cl}_2]$.[8] Although the chemistry of imido complexes of molybdenum(VI) and tungsten(VI) is well established,[7,9] little is known however of imido compounds of the lower oxidation state (V).[10] $[(\text{C}_5\text{H}_5)\text{Mo(N-}t\text{-Bu)Cl}_2]$ is so far the only example of a structurally characterized compound of this class. Herein we describe a convenient synthetic route for the preparation of a variety of pentamethylcyclopentadienyl imido complexes of molydenum(V) and tungsten(V) containing imido groups of different steric and electronic properties and their behavior against hydrolyses.

Results and Discussion

(a) Syntheses. The direct aminolysis of the pentamethylcyclopentadienyl tetrachlorides $(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}_4$ (**1a** or **1b**) with 3 equiv of *t*-BuNH$_2$ leads to the formation of the half-sandwich imido complexes **3a** and **3e**. This method is nevertheless limited to the case of *t*-BuNH$_2$. Using *i*-PrNH$_2$ in an analogous reaction



(1)

1a: M = Mo
1b: M = W

3a: M = Mo
3e: M = W

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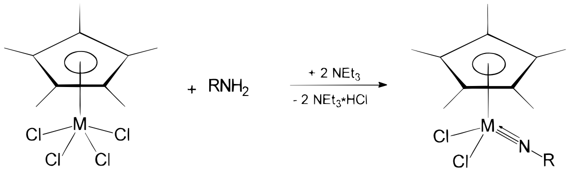
leads to modest yields, which are in both cases (**3b**,**f**) under 20%. The aromatic amines only react in the presence of a base like triethylamine.

Therefore the imido complexes **3a**−**h** were prepared by treatment of the tetrachlorides ($(\eta^5\text{-}C_5Me_5)MCl_4$ (**1a**,**b**) with a primary amine (**2**) in the presence of triethylamine. It is also possible to obtain the *t*-Bu-derivatives **3a** and **3e** by this method; however, using the direct aminolyses always resulted in higher yields.



(2)

1a: M = Mo
1b: M = W

2a: R = *t*Bu
2b: R = *i*Pr
2c: R = C_6F_5
2d: R = 2,6-$(i\text{Pr})_2C_6H_3$

3a-h

3	a	b	c	d	e	f	g	h
M	Mo	Mo	Mo	Mo	W	W	W	W
R	*t*-Bu	*i*-Pr	C_6F_5	2,6-(*i*-Pr)$_2$-C_6H_3	*t*-Bu	*i*-Pr	C_6F_5	2,6-(*i*-Pr)$_2$-C_6H_3

All reactions are carried out at room temperature in toluene. The molybdenum complexes are yellow-brown (**3a**,**b**), red-orange (**3c**), and brown (**3d**); the analogous tungsten compounds are green-yellow (**3e**,**f**), green (**3g**), and dark-yellow (**3h**) microcrystalline solids. Complexes containing an aliphatic imido group are soluble in hexane; compounds with an aromatic group are soluble in toluene. All compounds are sensitive to air and moisture.

Recently Geoffroy *et al.* reported on the synthesis and characterization of the oxo-imido complex $(\eta^5\text{-}C_5Me_5)WO(N\text{-}t\text{-}Bu)Cl$,[10b] which can be obtained by oxidation of $(\eta^5\text{-}C_5Me_5)W(N\text{-}t\text{-}Bu)Cl_2$ in the presence of moist air, but no crystallographic characterization has been made. In recent years a number of cyclopentadienyl oxo complexes of tungsten and molybdenum have been prepared and characterized, but the structural characterization by X-ray diffraction was done exclusively on molybdenum complexes. In order to get more detailed information about structures of oxo complexes of tungsten, we attempted to prepare similar compounds like $(\eta^5\text{-}C_5Me_5)WO(N\text{-}t\text{-}Bu)Cl$. Therefore a green toluene solution of $(\eta^5\text{-}C_5Me_5)W(NC_6F_5)Cl_2$ (**3g**) was stirred for 15 min while exposed to air. During this reaction the color changed from green to yellow. Yellow crystals could be removed from the toluene solution, and the structure has been determined by single crystal X-ray diffraction. To our surprise no oxygen could be found in the structure. The $(\eta^5\text{-}C_5Me_5)W(NC_6F_5)Cl_2$ (**3g**) decomposed in the presence of air forming the cyclopentadienylimidotungsten(VI) complex $(\eta^5\text{-}C_5Me_5)W(NC_6F_5)Cl_3$ (**4**) and a green solid, which could not be characterized. **4** is comparable to the tungsten- and molybdenum complexes $(\eta^5\text{-}C_5R_5)M(N\text{-}t\text{-}Bu)Cl_3$ (R = H, Me), (M = Mo, W)[7b,9] recently described by Sundermeyer *et al.* using a different synthetic approach. However, **4** is the first crystallographically characterized half-sandwich imido complex of tungsten(VI) as well as the first compound of this class containing an aromatic imido ligand. Further exposure to air of complex **3g** over a period of 2 days leads to the formation of pale-yellow crystals, which could be separated from the toluene solution and characterized crystallographically as the dinuclear tungsten(VI) oxo complex $[(\eta^5\text{-}C_5Me_5)WO_2]_2(\mu\text{-}O)\cdot C_6F_5NH_2$ (**5**). The decomposition of the tungsten(V) imido complex **3g** could be seen as the first step of the hydrolysis. By further stepwise hydrolysis of the tungsten chloride and imido bonds, the oxo complex **5** is formed. The formed amine cocrystallizes with the oxo complex.

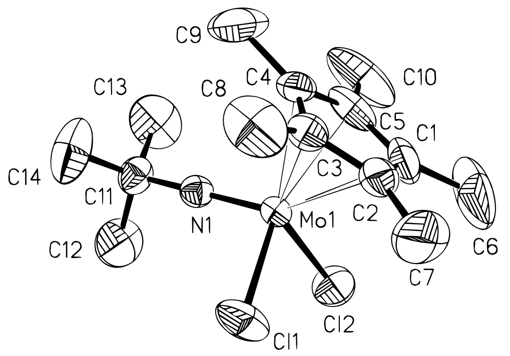


Figure 1.

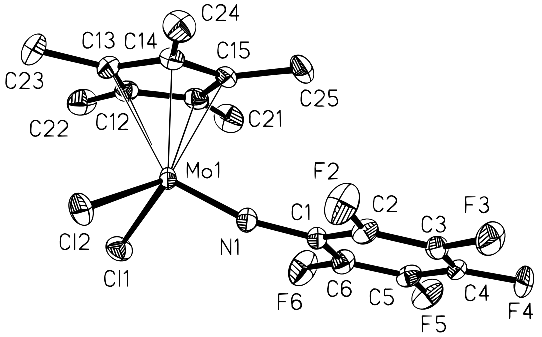


Figure 2.

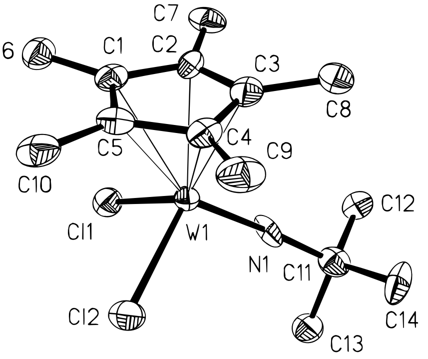


Figure 3.

(b) Molecular Structures. The X-ray crystal structures of compounds **3a**, **3c**, **3e**, **4**, and **5** have been determined. The molecular structures are shown in Figure 1 (**3a**), Figure 2 (**3c**), Figure 3 (**3e**), Figure 4 (**4**) and Figure 5 (**5**). The crystal data are given in Table 1.

The structure of $(\eta^5\text{-}C_5Me_5)Mo(N\text{-}t\text{-}Bu)Cl_2$ (**3a**), which crystallizes from *n*-hexane at 2 °C in the orthorhombic space group $P2_12_12_1$, is exactly analogous to the molecular structure of the tungsten complex $(\eta^5\text{-}C_5Me_5)W(N\text{-}t\text{-}Bu)Cl_2$ (**3e**), which also crystallizes from *n*-hexane at 2 °C, but in the monoclinic space group $P2_1/c$. For both of these monomeric 17-electron complexes the metal−nitrogen distance is in agreement with the value expected for a triple bond[1] (1.719 Å for the Mo−N bond and 1.716 Å for the W−N bond) as a result of sp-

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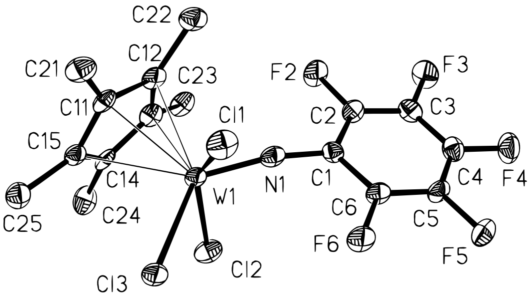

Figure 4.

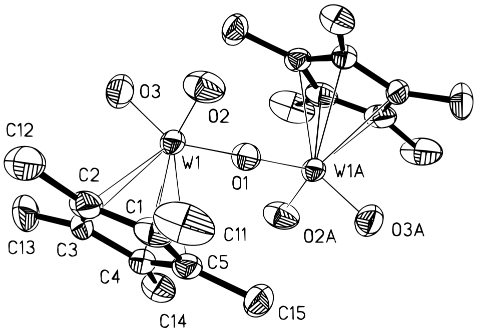

Figure 5.

hybridization at the N-atom and donation of the nitrogen lone pair to the metal. The triply bonded nature of the M−N bond can also be seen in the linearity of the M−N−C moiety [C11−N1−Mo1 177.3(2)° and C11−N1−W1 177.1(1)°]. The M−N bond lengths and the M−N−C angles in both the molybdenum and tungsten complexes **3a** and **3e** are very similar to those found in (η^5-C$_5$H$_5$)Mo(N-*t*-Bu)Cl$_2$[10a] [Mo-N 1.712(2) Å, Mo−N−C 170.1(2)°] and (η^5-C$_5$Me$_5$)Re(N-*t*-Bu)Cl$_2$[8] [Re−N 1.709 Å, Re−N−C 170.5(2)°].

(η^5-C$_5$Me$_5$)(MoNC$_6$F$_5$)Cl$_2$ (**3c**) crystallizes from toluene at −20 °C in the monoclinic space group $P2_1/c$. The molybdenum center in **3c** has the usual pseudotetrahedral arrangement of the cyclopentadienyl ring, the imido ligand, and the two chlorine atoms as the *tert*-butyl derivatives **3a** and **3e**. All complexes (**3a, 3c** and **3e**) are monomeric in the solid state, adopting a three-legged piano-stool structure. The Cl2−Mo1−Cl1 angle of 92.90(3)° for **3c** compares well to the Cl−M−Cl angles of 92.38(4)° found in **3a** and 91.11(1)° in **3e**, respectively. The Mo1−N1 bond distance of 1.748(2) Å is close to the bond length found in previously reported compounds, e.g. (η^5-C$_5$H$_5$)Nb(N-*t*-Bu)Cl$_2$[6a] [Nb−N 1.774(3) Å] and (η^5-C$_5$H$_5$)Ta(N-2,6-(*i*-Pr)$_2$C$_6$H$_3$)Cl$_2$[6a] [1.780(5) Å]. A comparison of **3a, 3c**, and **3e** show a slight deviation from linearity for (η^5-C$_5$Me$_5$)Mo(NC$_6$F$_5$)Cl$_2$ (C1−N1−Mo1 163.3(2)°). This is due to the primary interaction of one of the nitrogen lone pairs with a metal orbital projecting *trans* to the ring.[6a,11]

In all complexes the pentamethylcyclopentadienyl ligand is not coordinated in an ideal η^5 fashion, but a trend toward η^3 coordination can be observed. This can be seen in the difference between the longest and the shortest M−C bond. The range of this deviation is from 0.113 Å for **3e** and 0.154 Å for **3a** to 0.186 Å for **3c**, respectively and compares well with values of 0.106 and 0.122 Å for the two independent molecules of (η^5-C$_5$H$_5$)Mo(N-*t*-Bu)Cl$_2$.[10a]

(η^5-C$_5$Me$_5$)W(NC$_6$F$_5$)Cl$_3$ (**4**) crystallizes in the triclinic space group $P\bar{1}$. The five coordinated tungsten atom has a square-pyramidal coordination geometry if the ring centroid is taken as the apex of the pyramid. There is a slight distortion in the square base, which could be seen in the average bond angle of 82.9°. The W1−N1 bond distance of 1.754(4) Å is close to the bond length found in **3e** and likewise longer as the value expected for a metal nitrogen triple bond. The W1−N1−C1 bond angle of 169.2(3)° shows a slight deviation from linearity.

The X-ray determination of **5** shows that the oxo complex [(η^5-C$_5$Me$_5$)WO$_2$]$_2$(μ-O)·C$_6$F$_5$NH$_2$ crystallizes as a pentaoxo dimer with a linear oxygen bridge [W1−O1−W1A 180.0°]. The oxo groups as well as the pentamethylcyclopentadienyl ligands are *trans* to each other. Each tungsten atom has a pseudotetrahedral geometry if the ring centroids of the cyclopentadienyl rings are taken as one tops. Both tetrahedrons are bridged by one oxygen atom. The distances of the W−O double bonds (average 1.722 Å) are in the same range than the corresponding metal-oxygen bond lengths (average 1.73 Å) in the dinuclear complex [(η^5-C$_5$Me$_5$)(CO)$_3$W−W(O)$_2$(η^5-C$_5$Me$_5$).[12] The W−O distance of the bridging unit is as expected longer than the double bonds [W1−O1 1.882(7) Å] and comparable to the Mo−O bond length found in [(η^5-C$_5$H$_5$)MoCl(O)]$_2$O [Mo−O 1.847(1) Å].[13]

In complexes **4** and **5** the deviation of the pentamethylcyclopentadienyl ligands from the η^5 coordination can also be noticed. The individual tungsten−carbon bond distances ranges from 2.308(4) Å to 2.578(4) Å in **4** and from 2.320(6) to 2.466(5) Å in **5**.

Experimental Section

All reactions were carried out under purified nitrogen by standard Schlenk-techniques. Solvents were dried by standard methods and distilled under nitrogen prior to use.

(η^5-C$_5$Me$_5$)WCl$_4$[14] and (η^5-C$_5$Me$_5$)MoCl$_4$[15] were prepared by literature methods. The primary amines RNH$_2$ (R = *t*-Bu, *i*-Pr, 2,6-(*i*-Pr)$_2$C$_6$H$_3$) and triethylamine were distilled over CaH$_2$; pentafluoroaniline was purified by vacuum sublimation.

IR: Nujol mulls and CsI cells, Perkin Elmer Bio-Rad FTS-7. Elemental analyses: Analytisches Labor of the Institute of Inorganic Chemistry, Göttingen, Germany. MS: Finnigan MAT 8230 and Varian MAT CH5. Melting points: sealed capillaries, uncorrected.

Preparation of (η^5-C$_5$Me$_5$)Mo(N-*t*-Bu)Cl$_2$ (3a). Method a. A dark purple suspension of (η^5-C$_5$Me$_5$)MoCl$_4$ (**1a**) (1.12 g, 3.0 mmol) in toluene (40 mL) was treated with N-*t*-BuH$_2$ (**2a**) (2.20 g, 30 mmol) at room temperature. After the reaction mixture was stirred for 3 h, the *tert*-butylammoniumhydrochloride was filtered off and all volatile compounds were removed in vacuo. Recrystallization of the residue from *n*-hexane (40 mL) yields 0.62 g (55%) of brown-yellow crystals, mp 110 °C.

Method b. A toluene suspension of equimolar amounts of (η^5-C$_5$Me$_5$)MoCl$_4$ (**1a**) (1.12 g, 3.0 mmol) and *t*-BuNH$_2$ (**2a**) (0.22 g, 3.0 mmol) was treated with triethylamine (0.63 g, 6.2 mmol) at room temperature for 4 h in toluene (60 mL). After the triethylammonium chloride was filtered off, the solvent was removed in vacuo, and the brown residue was recrystallized from *n*-hexane (40 mL) to yield 0.38 g (34%) of **3a**. IR (CsI, cm^{-1}): 1260 (m), 1208 (s), 1104 (s), 1024 (s), 802 (s), 385 (m), 349 (m). MS (EI) *m/z* (%): 374 (26) [M$^+$], 318 (100) [M − *t*-Bu]. Anal. Calcd for C$_{14}$H$_{24}$Cl$_2$MoN: C, 45.02; H, 6.43; N, 3.75; Cl, 19.00. Found: C, 44.03; H, 6.37; N, 3.74; Cl, 19.13.

Preparation of (η^5-C$_5$Me$_5$)Mo(N-*i*-Pr)Cl$_2$ (3b). In a manner similar to that used for **3a** (method b), (η^5-C$_5$Me$_5$)MoCl$_4$ (**1a**) (0.75 g, 2.0 mmol), *i*-PrNH$_2$ (**2b**) (0.12 g, 2.0 mmol), and triethylamine (0.42 g, 4.2 mmol) yield 0.47 g (65%) of **3b** as a brown solid, mp 164 °C. IR

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Table 1. Crystal Data for **3a**, **3c, 3e**, **4**, and **5**

compd	**3a**	**3e**	**3c**	**4**	**5**
formula	$C_{14}H_{24}Cl_2NMo$	$C_{14}H_{24}Cl_2NW$	$C_{16}H_{15}Cl_2F_5MoN$	$C_{16}H_{15}Cl_3F_5NW$	$C_{16}H_{17}F_5NO_{2.5}W$
fw	373.18	436.87	483.13	606.49	542.16
temp/K	2230(2)	150(2)	153(2)	153(2)	153(2)
wavelength/Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst size/mm	0.4 × 0.4 × 0.3	0.7 × 0.5 × 0.2	0.25 × 0.25 × 0.25	0.70 × 0.25 × 0.25	0.40 × 0.30 × 0.30
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	8.6040(10)	15.171(3)	10.4502(7)	7.3843(1)	13.246(3)
b/Å	12.0490(10)	7.615(2)	10.6897(1)	11.529(2)	10.043(2)
c/Å	17.020(2)	14.758(3)	15.915(2)	11.558(2)	14.102(3)
β/deg		90.29(3)	94.342(8)	80.15(2)	104.37(3)
V/Å^3	1764.5(3)	1704.9(7)	1772.7(3)	936.2(3)	1817.3(6)
Z	4	4	4	2	4
d_{calcd}/Mg/m^3	1.405	1.796	1.810	2.151	1.982
abs coeff/mm^{-1}	1.032	7.074	1.089	6.645	6.417
F(000)	764	892	956	576	1036
θ range for data collcn	3.59−22.51	3.79−22.50	2.57−22.55	2.82−25.01	4.06−22.48
no. of reflcs collcd	8121	6587	3067	4718	3977
no. of indep reflcns	2294 ($R_{int} = 0.0394$)	2210 ($R_{int} = 0.1021$)	2341 ($R_{int} = 0.0116$)	2548 ($R_{int} = 0.0468$)	2349 ($R_{int} = 0.0326$)
R,[a] wR2[b] ($I > 2\sigma I$)	0.0213, 0.0561	0.038, 0.093	0.0194, 0.0440	0.0206, 0.0542	0.0295, 0.0735
R, wR2 (all data)	0.0217, 0.0570	0.0534, 0.1395	0.0239, 0.0753	0.0211, 0.0548	0.0316, 0.0765
goodness of fit S[c]	1.057	1.050	1.052	1.063	1.055
data/restraints/params	2293/0/171	2210/0/172	2239/0/231	2548/0/240	2245/0/237
largest diff peak and hole/e nm^{-3}	247 and −414	2528 and −2783	249 and −230	717 and −814	1037 and −1227

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)^2]/\sum(n - p)]^{1/2}$.

(CsI, cm^{-1}): 1261 (m), 1212 (s), 1096 (m), 1064 (m), 1022 (s), 801 (s), 398 (s), 386 (s), 330 (s). MS (EI) *m/z* (%): 360 (96) [M$^+$], 282 (100) [M − *i*-Pr − Cl]. Anal. Calcd for $C_{13}H_{22}Cl_2MoN$: C, 43.43; H, 6.12; N, 3.90; Cl, 19.74. Found: C, 42.61; H, 6.45; N, 3.56; Cl, 19.86.

Preparation of (η^5-C_5Me_5)Mo(NC_6F_5)Cl_2 (3c). To a suspension of (η^5-C_5Me_5)$MoCl_4$ (**1a**) (1.12 g, 3.0 mmol) and pentafluoroaniline (**2c**) (0.55 g, 3.0 mmol) in toluene (40 mL) was added triethylamine (0.63 g, 6.2 mmol) at room temperature. After the resulting solution was stirred for 12 h, the triethylammonium chloride was filtered off and the solvent was removed in vacuo to give an orange-red solid. Recrystallization from toluene (50 mL) yields 1.07 g (74%) of dark red crystals of **3c**, mp 204 °C. IR (CsI, cm^{-1}): 1262 (m), 1224 (s), 1060 (s), 1023 (m), 993 (s), 796 (s), 460 (m), 394 (s), 362 (m), 338 (s). MS (EI) *m/z* (%): 484 (100) [M$^+$]. Anal. Calcd for $C_{16}H_{15}Cl_2F_5MoN$: C, 39.74; H, 3.10; N, 2.90; Cl, 14.69. Found: C, 39.79; H, 3.39; N, 2.67; Cl, 14.65.

Preparation of (η^5-C_5Me_5)Mo(N-2,6-(*i*-Pr)$_2C_6H_3$)Cl_2 (3d). In a manner similar to that used for **3c**, (η^5-C_5Me_5)$MoCl_4$ (**1a**) (0.80 g, 2.1 mmol), 2,6-(*i*-Pr)$_2C_6H_3$-NH_2 (**2d**) (0.38 g, 2.1 mmol), and triethylamine (0.44 g, 4.4 mmol) yield after 2 days 0.40 g (39%) brown crystals of **3d**, mp 242 °C. IR (CsI, cm^{-1}): 1262 (m), 1100 (m), 1073 (m), 1020 (s), 809 (s), 393 (m), 353 (m), 305 (m). MS (EI) *m/z* (%): 478 (100) [M$^+$]. Anal. Calcd for $C_{22}H_{32}Cl_2MoN$: C, 55.31; H, 6.70; N, 2.93; Cl, 14.86. Found: C, 50.14; H, 6.57; N, 3.17; Cl, 15.32.

Preparation of (η^5-C_5Me_5)W(N-*t*-Bu)Cl_2 (3e). Method a. An orange suspension of (η^5-C_5Me_5)WCl_4 (**1b**) (1.38 g, 3.0 mmol) in toluene (40 mL) was treated with N-*t*-BuH_2 (**2a**) (2.19 g, 30 mmol) at room temperature. After the reaction mixture was stirred for 4 h, the *tert*-butylammonium chloride was filtered off and all volatile compounds were removed in vacuo. Recrystallization of the residue from *n*-hexane (40 mL) yields 0.85 g (62%) of green-yellow crystals, mp 92 °C.

Method b. A suspension containing equimolar amounts of (η^5-C_5Me_5)WCl_4 (**1b**) (1.41 g, 3.1 mmol) and N-*t*-BuH_2 (**2a**) (0.22 g, 3.1 mmol) in toluene (40 mL) was treated with triethylamine (0.63 g, 6.2 mmol) at room temperature for 4 h. Once the resulting triethylammonium chloride was filtered off, all volatile compounds were removed in vacuo. The green-yellow residue was recrystallized from *n*-hexane (30 mL) to yield 0.64 g (45%) of **3e**. IR (CsI, cm^{-1}): 1272 (s), 1214 (m), 1033 (s), 806 (s), 723 (m), 615 (m), 548 (s), 371 (s), 337(s), 320 (s). MS (EI) *m/z* (%): 462 (100) [M$^+$]. Anal. Calcd for $C_{14}H_{24}Cl_2NW$: C, 36.43; H, 5.20; N, 3.04; Cl, 15.38. Found: C, 36.41; H, 5.24; N, 2.97; Cl, 15.28.

Preparation of (η^5-C_5Me_5)W(N-*i*-Pr)Cl_2 (3f). In a manner similar to that used for **3e** (method b) (η^5-C_5Me_5)WCl_4 (**1b**) (1.34 g, 2.9 mmol), *i*-PrNH_2 (**2b**) (0.17 g, 2.9 mmol), and triethylamine (0.61 g, 6.0 mmol) yield 0.58 g (45%) of **3f** as green-yellow needles, mp 117 °C. IR (CsI, cm^{-1}): 1270 (s), 1100 (w), 1077 (w), 1024 (m), 799 (s), 520 (m), 371 (m), 334 (s). MS (EI) *m/z* (%): 448 (100) [M$^+$]. Anal. Calcd for $C_{13}H_{22}Cl_2NW$: C, 34.89; H, 4.92; N, 3.13; Cl, 15.86. Found: C, 35.10; H, 4.75; N, 3.16; Cl, 15.02.

Preparation of (η^5-C_5Me_5)W(NC_6F_5)Cl_2 (3g). To a stirred suspension of (η^5-C_5Me_5)WCl_4 (**1b**) (1.01 g, 2.2 mmol) and pentafluoroaniline (**2c**) (0.40 g, 2.2 mmol) in toluene (40 mL) triethylamine (0.46 g, 4.6 mmol) was added. After the resulting solution was stirred for 12 h, the triethylammonium chloride was filtered off and the solvent was removed in vacuo to give a green solid that was recrystallized from toluene (40 mL): yield 0.88 g (70%) of **3g**; mp 185 °C. IR (CsI, cm^{-1}): 1261 (m), 1239 (s), 1160 (w), 1071 (s), 1028 (m), 992 (s), 801 (s), 434 (m), 385 (s), 346 (s), 327 (s). MS (EI) *m/z* (%): 572 (100) [M$^+$]. Anal. Calcd for $C_{16}H_{15}Cl_2F_5NW$: C, 33.62; H, 2.63; N, 2.45; Cl, 12.42. Found: C, 34.40; H, 2.99; N, 2.54; Cl, 12.98.

Preparation of (η^5-C_5Me_5)W(N-2,6-(*i*-Pr)$_2C_6H_3$)Cl_2 (3h). A stirred suspension of (η^5-C_5Me_5)WCl_4 (**1b**) (0.99 g, 2.1 mmol) in toluene (40 mL) was treated with 2,6-(*i*-Pr)$_2C_6H_3NH_2$ (**2d**) (0.38 g, 2.1 mmol) and triethylamine (0.45 g, 4.4 mmol) at room temperature. After the reaction mixture was stirred for 2 days, the triethylammonium chloride was filtered off and the volatile compounds were removed in vacuo. The resulting yellow-brown residue was recrystallized from toluene (60 mL) to yield 0.68 g (56%) dark yellow crystals of **3h**, mp 245 °C. IR (KBr, cm^{-1}): 1261 (s), 1102 (s), 1057 (m), 1032 (s), 807 (s), 766 (s), 742 (m), 537 (w). MS (EI) *m/z* (%): 566 (100) [M$^+$]. Anal. Calcd for $C_{22}H_{32}Cl_2NW$: C, 46.70; H, 5.67; N, 2.48; Cl, 12.54. Found: C, 45.89; H, 5.83; N, 2.50; Cl, 12.48.

Preparation of (η^5-C_5Me_5)W(NC_6F_5)Cl_3 (4). (η^5-C_5Me_5)W(NC_6F_5)Cl_2 (**3g**) (0.57 g, 1.0 mmol) was dissolved in toluene (30 mL). The resulting green solution was stirred for 15 min while exposed to air. During this time the color changed from green to yellow. After filtration, the solution was stored at room temperature. Over 4 days it deposited two products: one product, yellow crystals of **4,** which are characterized by X-ray crystallography; the other product, a green powder, which could not been characterized, mp 168 °C. IR (CsI, cm^{-1}): 1261 (m), 1096 (s), 1067 (s), 1022 (s), 966 (s), 897 (m), 866 (w), 800 (s), 399 (m), 382 (m), 330 (w), 306 (w). MS (EI) *m/z* (%): 572 (80) [M$^+$ − Cl], 135 (100) [C_5Me_5]. ^{1}H NMR ($CDCl_3$, TMS): 2.07 (s, 15H, C_5Me_5) ppm.

X-ray Data Collection, Structure Solution and Refinement of 3a, 3c, 3e, 4, and 5. Crystals suitable for X-ray diffraction were mounted on a glass fiber in a rapidly cooled perfluoropolyether.[16] Diffraction data were collected on a Siemens-Stoe AED2 four-circle instrument at 150(2) K (**3c**, **3e**, **4**, and **5**) and 223(2) K (**3a**), with graphite-monochromated Mo-Kα radiation, ω-2θ scans, on-line profile fitting,[17] and constant scan speed. Absorption correction based on ψ-scans was performed in the cases of **3c**, **3e**, **4**, and **5**. The structures were solved by the Patterson method SHELXS-86[18] and refined against F^2 on all data by full-matrix least-squares methods with SHELXL-93.[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

Further details of the crystal structure investigation are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB2 1EW, England, on quoting the full journal citation.

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Supporting Information Available: Full tables of crystal and refinement parameters, bond distances, bond angles, anisotropic thermal parameters and hydrogen atom positions and complete ORTEP drawings for **3a**, **3c**, **3e**, **4**, and **5** (30 pages). Ordering information is given on any current masthead page.

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