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Pentafluorophenylimido Alkylidene Complexes of Molybdenum and Tungsten

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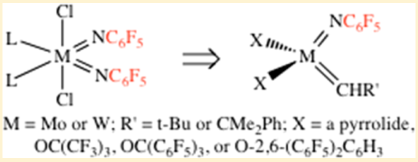
Ⓢ *Supporting Information*

ABSTRACT: Pentafluorophenylimido alkylidene complexes of molybdenum and tungsten have been prepared in good yields. Examples include $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)_2$ (Me_2Pyr = 2,5-dimethylpyrrolide), $W(NC_6F_5)(CH\text{-}t\text{-}Bu)(DME)(Pyrrolide)_2$, $Mo(NC_6F_5)(CHCMe_2Ph)[OC(CF_3)_3]_2$, $W(NC_6F_5)(CH\text{-}t\text{-}Bu)(DME)[OC(CF_3)_3]_2$, $Mo(NC_6F_5)(CHCMe_2Ph)[OC(C_6F_5)_3]_2$, $W(NC_6F_5)(CH\text{-}t\text{-}Bu)[OC(C_6F_5)_3]_2$, $Mo(NC_6F_5)(CHCMe_2Ph)(ODFT)_2$ (ODFT = O-2,6-$(C_6F_5)_2C_6H_3$), and $W(NC_6F_5)(CH\text{-}t\text{-}Bu)(ODFT)_2$. Treatment of $W(NC_6F_5)(CH\text{-}t\text{-}Bu)(DME)[OC(CF_3)_3]_2$ with ethylene led to formation of $W(NC_6F_5)(CH_2CH_2CH_2)[OC(CF_3)_3]_2$, which has a TBP structure in which the metallacyclobutane ring lies in the equatorial plane. 2,3-Dicarbomethoxynorbornadiene is polymerized by $M(NC_6F_5)(CHR')(ODFT)_2$ initiators to give *cis,isotactic*-poly(DCMNBD).



The efficiencies of molybdenum and tungsten imido alkylidene complexes, $M(NR)(CHR')(OR'')_2$[1] and, more recently, $M(NR)(CHR')(OR'')(Pyr)$ (Pyr = pyrrolide),[2] in olefin metathesis reactions depend upon many factors. One overarching factor in $M(NR)(CHR')(OR'')_2$ complexes that contributes to reactivity is the degree of electron-withdrawing ability of the OR″ ligands. For example, catalysts in which OR″ = $OCMe(CF_3)_2$ generally are much more active than those in which OR″ = $OCMe_3$. Explanations of relative *efficiencies* of olefin metathesis reactions require details such as accessibilities and relative reactivities of *syn* and *anti* alkylidene isomers, the relative stabilities of TBP or SP intermediate metallacyclobutane intermediates, and the lifetimes of alkylidene intermediates, especially methylidene complexes. However, how activities/efficiencies change when the *imido* group is electron withdrawing has not yet been explored. For this reason we have pursued the synthesis of molybdenum and tungsten pentafluorophenylimido alkylidene complexes.

$Mo(NC_6F_5)_2Cl_2(DME)$ (**1a**) has been prepared by heating a mixture of $(NH_4)_2Mo_2O_7$, NEt_3, Me_3SiCl, and $C_6F_5NH_2$ in the ratio 1:8:17:4 in DME,[3] but no dialkyl (neopentyl or neophyl) complex, a precursor to an imido alkylidene complex, was prepared. In contrast, an analogous synthesis of $W(NC_6F_5)_2Cl_2(DME)$ (**1b**) from WO_2Cl_2 has not been successful in our hands, as a consequence of a failure to convert *both* oxo ligands into imido ligands. However, **1b** has been prepared by heating WO_2Cl_2 with C_6F_5NSO under a flow of argon to give $W(NC_6F_5)_2Cl_2$ and subsequently dissolving $W(NC_6F_5)_2Cl_2$ in 1,2-dimethoxyethane.[4] In a variation of this reaction, we have found that **1b** can be prepared in 96% yield on an 18 g scale from $WO_2Cl_2(DME)$[5] and slightly more than 2 equiv of C_6F_5NSO in a mixture of refluxing DME and toluene under a flow of nitrogen (eq 1).

$$WO_2Cl_2(DME) + 2C_6F_5NSO \xrightarrow[N_2\text{purge}-2SO_2]{\text{DME/toluene reflux}} W(NC_6F_5)_2Cl_2(DME) \quad (1)$$

Traditional syntheses of $M(NR)(CHR')(OTf)_2(DME)$ (R′ = t-Bu, CMe_2Ph; M = Mo, W) compounds involve dialkylation of $M(NR)_2Cl_2(DME)$ to give $M(NR)_2(CH_2R')_2$ complexes followed by treatment of $M(NR)_2(CH_2R')_2$ with 3 equiv of triflic acid in the presence of DME. The reaction between **1a** and 2 equiv of $PhMe_2CCH_2MgCl$ in diethyl ether produced $Mo(NC_6F_5)_2(CH_2CMe_2Ph)_2$ (**2a**) as a dark oil. Approximately 1 equiv of diethyl ether remained in the mixture (according to NMR spectra), which suggests that **2a** may form an ether adduct that hinders crystallization. Therefore, *crude* **2a** was treated with 3 equiv of triflic acid to give yellow $Mo(NC_6F_5)(CHCMe_2Ph)(OTf)_2(DME)$ (**3a**) in an *overall* yield (from **1a**) of 64%. Proton and ^{19}F NMR studies of a solution of **3a** in C_6D_6 showed it initially to be an isomer that contains *trans* triflates (alkylidene $\delta(H_\alpha)$ 13.74 ppm, $\delta(C_\alpha)$ 326.6 ppm) and the required *cis* imido and alkylidene ligands. This isomer slowly is transformed into a mixture that contains ~12% of a *cis* isomer ($\delta(H_\alpha)$ 14.98 ppm, $\delta(C_\alpha)$ 336.1 ppm). Monomeric six-coordinate *trans* and *cis* bis(triflate) complexes of the type $M(NR)(CHR')(OTf)_2L_2$ have been observed in other circumstances.[1b,2] The four possible monomeric $M(NR)(CHR')(OTf)_2L_2$ structures are drawn in Figure 1, where L is a monodentate donor.

Dialkylation of $W(NC_6F_5)_2Cl_2(DME)$ with neopentylmagnesium chloride led to isolable $W(NC_6F_5)_2(CH_2CMe_3)_2$ (**2b**) in 89% yield on a 10 g scale. Treatment of **2b** with 2 equiv of triflic acid in a 5:1 mixture of diethyl ether and DME produced an 81% yield of an insoluble ivory-colored solid on a 8 g scale

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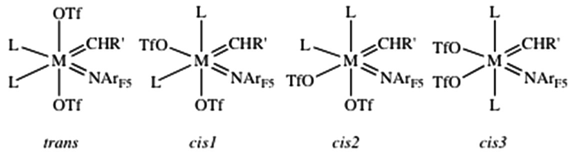
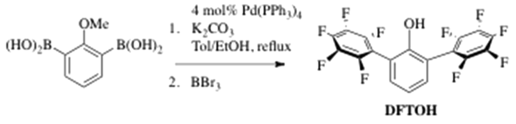


trans *cis1* *cis2* *cis3*

Figure 1. The four possible structures of $M(NC_6F_5)(CHR')(OTf)_2L_2$.

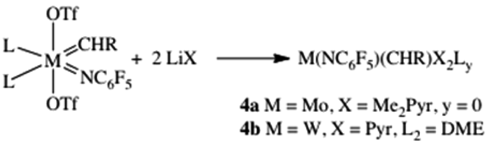
that analyzes as $W(NC_6F_5)(CH\text{-}t\text{-}Bu)(DME)(OTf)_2$ (**3b**). The solid dissolves immediately in THF to give 1 equiv of free DME and $W(NC_6F_5)(CH\text{-}t\text{-}Bu)(THF)_2(OTf)_2$ as a mixture of *trans* and *cis* isomers, according to NMR spectra. Recrystallization of **3b** from a mixture of THF and pentane gave yellow crystals whose proton NMR spectrum and elemental analysis are consistent with the formula $W(NC_6F_5)(CH\text{-}t\text{-}Bu)(DME)_{0.5}(THF)(OTf)_2$. We propose that the insoluble solid is the *cis3*, and necessarily *polymeric*, form of $W(NC_6F_5)(CH\text{-}t\text{-}Bu)(OTf)_2(DME)$: i.e., $\{W(NC_6F_5)(CH\text{-}t\text{-}Bu)(\mu\text{-}DME)(OTf)_2\}_x$ (**3b**). We ascribe this unusual circumstance to the relatively high electrophilicity of the metal in **3b** and, of course, precipitation of **3b**, which greatly aids its rapid isolation in high purity in a matter of minutes. We cannot explain at this stage why we have not been able to prepare a neophyl analogue of **2b**.

Our interest in sterically demanding electron-withdrawing alkoxides or phenoxides drew us to $HOC(C_6F_5)_3$, which we prepared in 92% yield from perfluorobenzophenone and LiC_6F_5 in diethyl ether; it has been synthesized previously,[6] although to our knowledge it has never been employed as a ligand in a transition-metal complex. On the other hand, $2,6\text{-}(C_6F_5)_2C_6H_3OH$ (DFTOH), prepared as shown in eq 2, is a new sterically demanding terphenol. The DFTO anion is a relatively electron-withdrawing variation of $2,6\text{-}(Mes)_2C_6H_3O$ (HMTO; Mes = mesityl) and $2,6\text{-}(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3O$ (HIPTO), which have proven so useful for the synthesis of *Z*-selective metathesis catalysts.[7]



(2)

Treatment of **3a** with 2 equiv of $LiMe_2Pyr$ at −30 °C in toluene gave the bis(dimethylpyrrolide) complex $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)_2$ (**4a**) as essentially the only product in 89% yield (eq 3; only one bis(triflate) isomer is shown).



(3)

Analytically pure dark red-orange **4a** could be obtained in 53% isolated yield from pentane. NMR spectra of **4a** are temperature dependent, with broad pyrrolide resonances at room temperature as a consequence of interconversion of η^1- and η^5-pyrrolides on the NMR time scale.[8] A similar reaction between **3b** and 2 equiv of LiPyr gives **4b** (eq 3) in 71% yield; NMR data for **4b** are consistent with its structure being analogous to that of $W(NAr)(CHCMe_2Ph)(Pyr)_2(DME)$.[9] Synthetic details for all compounds given in Table 1 can be found in the Supporting Information.

Table 1. Compounds and Yields

	yield (%)
$Mo(NC_6F_5)(CHCMe_2Ph)(OTf)_2(DME)$ (**3a**)	64
$Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)_2$ (**4a**)	89
$Mo(NC_6F_5)(CHCMe_2Ph)[OC(CF_3)_3]_2$ (**5a**)	69
$Mo(NC_6F_5)(CHCMe_2Ph)[OC(C_6F_5)_3]_2$ (**6a**)	92
$Mo(NC_6F_5)(CHCMe_2Ph)(ODFT)_2$ (**7a**)	84
$W(NC_6F_5)_2Cl_2(DME)$ (**1b**)	96
$W(NC_6F_5)_2(CH_2\text{-}t\text{-}Bu)_2$ (**2b**)	89
$[W(NC_6F_5)(CH\text{-}t\text{-}Bu)(\mu\text{-}DME)(OTf)_2]_x$ (**3b**)	81
$W(NC_6F_5)(CH\text{-}t\text{-}Bu)(DME)(Pyr)_2$ (**4b**)	71
$W(NC_6F_5)(CH\text{-}t\text{-}Bu)(DME)[OC(CF_3)_3]_2$ (**5b**)	86
$W(NC_6F_5)(CH\text{-}t\text{-}Bu)[OC(C_6F_5)_3]_2$ (**6b**)	78
$W(NC_6F_5)(CH\text{-}t\text{-}Bu)(ODFT)_2$ (**7b**)	66
$W(NC_6F_5)(CH_2CH_2CH_2)[OC(CF_3)_3]_2$ (**8b**)	92

Bis(alkoxides) were prepared from the bis(triflates) in a manner analogous to that shown in eq 3. These include $Mo(NC_6F_5)(CHCMe_2Ph)[OC(CF_3)_3]_2$ (**5a**), $W(NC_6F_5)(CH\text{-}t\text{-}Bu)(DME)[OC(CF_3)_3]_2$ (**5b**), $Mo(NC_6F_5)(CHCMe_2Ph)[OC(C_6F_5)_3]_2$ (**6a**), $W(NC_6F_5)(CH\text{-}t\text{-}Bu)[OC(C_6F_5)_3]_2$ (**6b**), $Mo(NC_6F_5)(CHCMe_2Ph)(ODFT)_2$ (**7a**), and $W(NC_6F_5)(CH\text{-}t\text{-}Bu)(ODFT)_2$ (**7b**).

A drawing of the structure of **6a**, as determined in an X-ray study, is shown in Figure 2. The neophylidene is in the *syn* conformation, as expected. Bond distances and angles are not unusual.

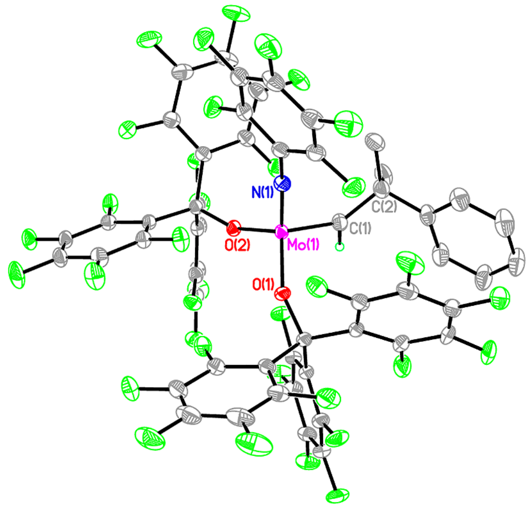


Figure 2. Thermal ellipsoid drawing (50% probability) of **6a**. Atoms for the minor component of the disorder have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)−N(1) = 1.7172(16), Mo(1)−O(1) = 1.9022(13), Mo(1)−O(2) = 1.9212(11), Mo(1)−C(1) = 1.896(2); Mo(1)−O(2)−C(41) = 152.85(12), Mo(1)−O(1)−C(21) = 153.24(12), Mo(1)−N(1)−C(11) = 168.31(15), Mo(1)−C(1)−C(2) = 142.98(15).

The structure of **7a** (Figure 3) is more interesting. A relatively small Mo(1)−O(1)−C(21) angle of 130.32(6)° and a N(1)−Mo(1)−C(1)−C(2) dihedral angle of 13.5° (with C(2) tipped back in the view in Figure 3) seem to result from steric interactions that can be traced to the two pentafluorophenyl rings in the ODFT ligand that contains O(2). Examination of the fluorine NMR spectrum of **7a** at −80 °C suggests that in the ODFT ligands the *ortho* fluorines (8), the *meta* fluorines (8), and the *para* fluorines (4) are all

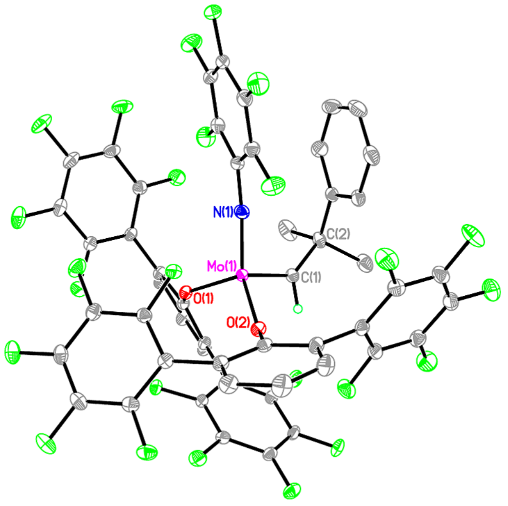


Figure 3. Thermal ellipsoid drawing (50% probability) of **7a**. Selected bond lengths (Å) and angles (deg): Mo(1)−N(1) = 1.7316(10), Mo(1)−O(1) = 1.9403(8), Mo(1)−O(2) = 1.9250(8), Mo(1)−C(1) = 1.8840(11); Mo(1)−O(2)−C(41) = 146.97(7), Mo(1)−O(1)−C(21) = 130.32(6), Mo(1)−N(1)−C(11) = 169.18(9), Mo(1)−C(1)−C(2) = 138.20(9).

inequivalent on the NMR time scale, consistent with the structure shown in Figure 3. At room temperature and up to 100 °C one *para*, two *meta*, and two *ortho* fluorine resonances are found, consistent with equilibration of the two DFTO ligands, slow rotation on the NMR time scale of the pentafluorophenyl rings about the C−C bond to the central phenyl ring, as one might expect, and free rotation about the Mo−O bonds.

Treatment of a sample of **5b** in pentane with ethylene (1 atm) led to white **8b** (92%) after 1 day. A ^{13}C-labeled version was also prepared. All NMR data are consistent with **8b** being a TBP metallacyclobutane complex that contains an equatorial metallacyclobutane ring. An X-ray study (Figure 4) showed **8b** to have a structure analogous to other TBP bis(alkoxide) imido complexes of tungsten[10] with a relatively short W(1)−C(2) distance (2.349(2) Å) and characteristic angles within the ring (C(1)−W(1)−C(3) = 84.09(10)°, C(1)−C(2)−C(3) = 118.10(18)°, W(1)−C(1)−C(2) = 79.25(13)°, W(1)−C(3)−C(2) = 78.55(13)°). An intermediate TBP metallacycle that contains a *tert*-butyl group in the *α* position could be observed in NMR spectra but could not be isolated in pure form. Compound **8b** is unstable in the absence of ethylene at 100 °C but is relatively stable at room temperature.

Several of the new Mo and W imido alkylidene complexes were screened for alkane metathesis activity.[11] Table 2 shows the total product obtained in our standard screening procedure (see the Supporting Information for details). The pentafluorophenyl complexes are poor catalysts compared to those containing the 2,6-diisopropylphenyl ligand.[11b] It should be noted that the products formed (as given in Table 2) with $W(NAr)(CHCMe_2Ph)[OC(CF_3)_3]_2$ or $W(NAr)(CHCMe_2Ph)(OSiPh_3)_2$ as a catalyst differ in quantity from the published amounts,[11b] as a consequence of the slightly different procedures employed in the work reported here. For example, products employing $W(NAr)(CHCMe_2Ph)[OC(CF_3)_3]_2$ were found at a concentration of 2760 mM (vs 2260 mM measured here).

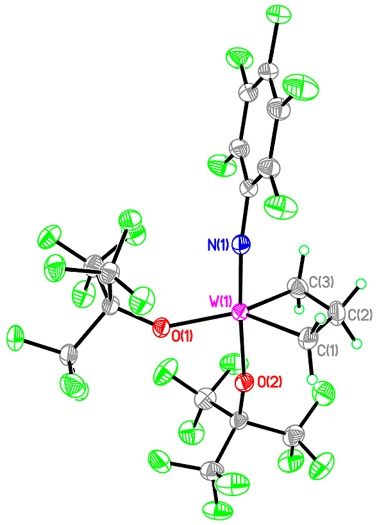


Figure 4. Thermal ellipsoid drawing (50% probability) of **8b**. Atoms for the minor component of the disorder have been omitted for clarity. Selected bond lengths (Å) and angles (deg): W(1)−N(1) = 1.7502(18), W(1)−O(1) = 1.9514(14), W(1)−O(2) = 1.9785(15), W(1)−C(1) = 2.041(2), W(1)−C(2) = 2.349(2), W(1)−C(3) = 2.065(2), C(1)−C(2) = 1.604(4), C(2)−C(3) = 1.603(4); N(1)−W(1)−O(2) = 173.79(7), W(1)−O(1)−C(17) = 142.79(13), W(1)−O(2)−C(21) = 163.19(14).

Table 2. Total Product Concentration in the Metathesis of Octane[a]

	concn (mM)
$Mo(NC_6F_5)(CHCMe_2Ph)[OC(CF_3)_3]_2$ (**5a**)	120
$W(NC_6F_5)(CH\text{-}t\text{-}Bu)[OC(C_6F_5)_3]_2$ (**6b**)	0
$Mo(NC_6F_5)(CHCMe_2Ph)(ODFT)_2$ (**7a**)	0
$W(NC_6F_5)(CH\text{-}t\text{-}Bu)(ODFT)_2$ (**7b**)	40
$W(NC_6F_5)(CH_2CH_2CH_2)[OC(CF_3)_3]_2$ (**8b**)	60
$W(NAr)(CHCMe_2Ph)[OC(CF_3)_3]_2$[b]	2260
$W(NAr)(CHCMe_2Ph)(OSiPh_3)_2$[b]	2770

[a] Conditions: 125 °C, 4 days in J. Young tubes, 16 mM metathesis catalyst, 10 mM $(POCOP)Ir(C_2H_4)$, 28.8 mM mesitylene (internal standard). See the Supporting Information for details. [b] Ar = 2,6-diisopropylphenyl.

Although the apparent thermal instability of pentafluorophenylimido complexes limits their use for alkane metathesis reactions (necessarily at relatively high temperatures), we have found other unusual olefin metathesis activity at room temperature. For example, 100 equiv of 2,3-dicarbomethoxynorbornadiene (DCMNBD) is polymerized by **7a** or **7b** to give poly(DCMNBD) with a structure that is >99% *cis,isotactic*, behavior that has been matched by biphenolate and binaphtholate imido alkylidene initiators but not bis(alkoxide) complexes that contain achiral alkoxides.[12] DCMNBD is polymerized by **6a** to give 90% *cis* polymer which is not highly tactic, while DCMNBD fails to react with **8b**; apparently ethylene is not lost readily from the metallacyclobutane ring under these conditions. We will be elaborating on the fundamental properties of pentafluorophenylimido alkylidene complexes as well as their utility in ROMP and other olefin metathesis reactions in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, and CIF files giving experimental details for the synthesis of all compounds and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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