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Communication

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Synthesis of Molybdenum and Tungsten Alkylidene Complexes That Contain the 2,6-Bis(2,4,6-triisopropylphenyl)phenylimido (NHIPT) Ligand

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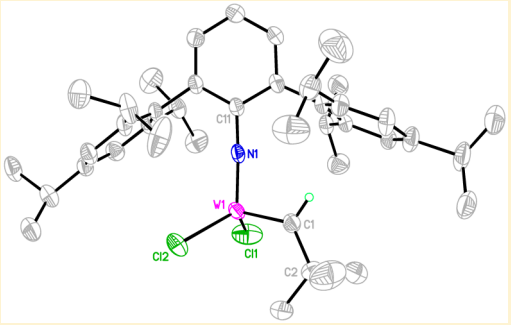
Supporting Information

ABSTRACT: Molybdenum and tungsten alkylidene complexes that contain the sterically demanding hexaisopropylterphenylimido ligand, N-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$ (NHIPT), have been prepared from Mo(N-*t*-$Bu)_2Cl_2$(1,2-dimethoxyethane) or W(N-*t*-$Bu)_2Cl_2(pyridine)_2$, employing *tert*-butylimido ligands as sacrificial proton acceptors. These complexes include M(NHIPT)(CH-*t*-Bu)Cl_2 (M = Mo, W), Mo(NHIPT)(CH-*t*-Bu)$(pyrrolide)_2$, and Mo(NHIPT)(CH-*t*-Bu)(pyrrolide)(OC_6F_5)-(CH_3CN). In all cases only anti alkylidene isomers are observed in solution, as a consequence of the steric demands of the NHIPT ligand. An X-ray structure of W(NHIPT)(CH-*t*-Bu)Cl_2 showed it to be a monomer with a disordered alkylidene that is 86% in the anti configuration and 14% in the syn configuration.



A characteristic of all 14-electron "d^0" alkylidene (M=CHR) complexes of molybdenum and tungsten is the possibility of forming two isomers: one (syn) in which R is pointed toward X (oxo or imido) and one (anti) in which R is pointed away from X (Figure 1).[1,2] The agostic interaction[3] of

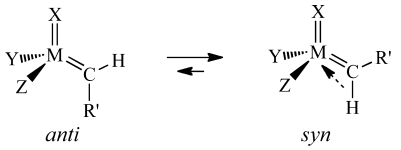


Figure 1. Anti and syn isomers where M = Mo, W, X = imido, oxo (W only), and Y and Z are the same or different monoanionic monodentate ligands.

the CH_α electrons with the metal in the syn isomer reduces the value of $^1J_{CH_\alpha}$ to 120−130 Hz in comparison to 140−150 Hz in the anti isomer, which is part of the reason the syn form is usually the more stable of the two by a few kilocalories per mole and therefore is the form observed in many circumstances. Syn and anti isomers can interconvert in the absence of an olefin at rates that vary from ~10^{-5} to ~100 s^{-1}.[4] Syn and anti isomers also are likely to have dramatically different reactivities. An untested feature of an anti alkylidene versus a syn alkylidene is the possible lower acidity of the H_α proton in the anti alkylidene and therefore a reduced tendency for it to be abstracted to form an alkylidyne ligand.[5] Abstraction of a relatively acidic α proton from an alkylidene or alkyl ligand as a consequence of a CH agostic interaction in a sterically crowded coordination sphere is the basis for forming high-oxidation-state alkylidyne and alkylidene ligands, respectively.[6]

In the last several years we have reported monoaryloxide pyrrolide (MAP) catalysts for the *Z*-selective metathesis reactions of disubstituted olefins,[7] an example being Mo(*N*-1-adamantyl)(CHCMe$_2$Ph)(Pyr)(OHIPT) (OHIPT = O-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$).[8] The theory is to limit the substitution pattern in the intermediate TBP metallacyclobutane to one in which any single substituent on a metallacycle carbon atom points away from a large axial aryloxide ligand and toward a relatively small X ligand (imido or oxo (W only); Figure 2). An "inversion" of the roles of a "large" aryloxide and a "small" imido group would be another way to limit the formation of metallacyclobutane intermediates to those with substituents all on one side and at the same time could limit formation of syn

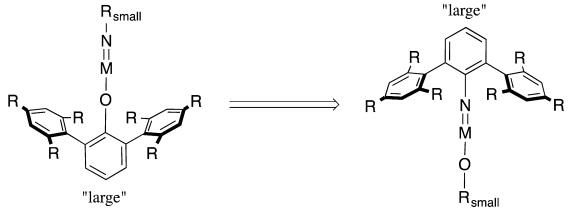


Figure 2. Exchanging the "large/small" roles of the imido and aryloxide (R = Me, *i*-Pr).

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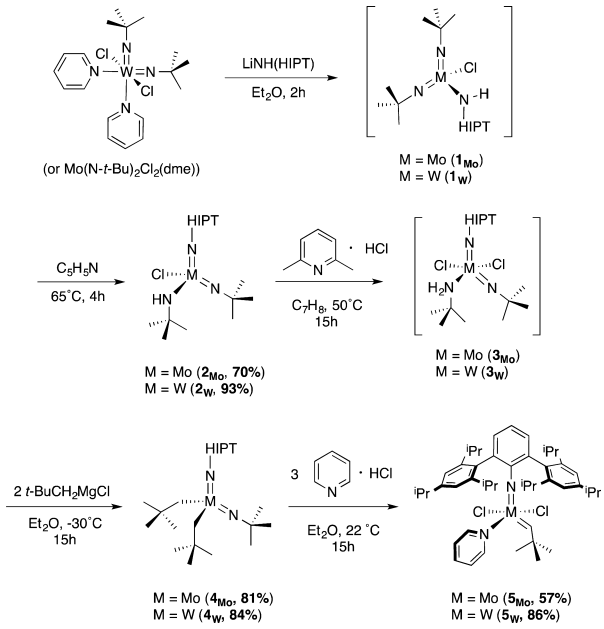
alkylidene isomers in favor of anti alkylidene isomers. Inversion of the relative steric influences became possible with the synthesis by Gavenonis and Tilley of relatively large 2,6-disubstituted anilines in which the substituents in the 2- and 6-positions are 2,4,6-trimethylphenyl (Mes) or 2,4,6-triisopropylphenyl (Trip) groups.[9]

The large size of the NHMT (hexamethylterphenylimido or N-2,6-$Mes_2C_6H_3$) ligand prevented synthesis of Mo(NHMT)$_2$(CH$_2$-*t*-Bu)$_2$ and other bisimido intermediates that are required in a traditional synthesis of an imido alkylidene complex. Therefore, an entirely new synthesis (inspired by a report by Gibson[10]) had to be devised that employed two *tert*-butylimido ligands as "sacrificial" imido groups in order to prepare Mo and W complexes that contain the NHMT ligand.[11] We found that the NHMT ligand was not sufficiently large to completely prevent formation of syn isomers in the complexes that were prepared. Therefore, we turned to the synthesis of Mo and W NHIPT complexes.

We were pleased to find that essentially the same methods employed for the synthesis of NHMT complexes are successful for the synthesis of NHIPT complexes. As shown in Scheme 1,

Scheme 1. Synthesis of the M(NHIPT)(CH-*t*-Bu)Cl$_2$(py) Complexes



Mo(N-*t*-Bu)$_2$Cl$_2$(dme)[10] and W(N-*t*-Bu)$_2$Cl$_2$py$_2$,[12] which are readily prepared on a large scale, serve as starting points. Intermediates $\mathbf{1_{Mo}}$ and $\mathbf{1_W}$ were not isolated and characterized but converted to $\mathbf{2_{Mo}}$ (70%) and $\mathbf{2_W}$ (93%) by dissolving crude $\mathbf{1_{Mo}}$ and $\mathbf{1_W}$ in pyridine and heating the mixture to 65 °C for 4 h. Pyridine-catalyzed transfer of the proton from the N(H)-HIPT to a *tert*-butylimido ligand is a key to formation of $\mathbf{2_{Mo}}$ and $\mathbf{2_W}$ in good yields (70% and 93%, respectively). The *tert*-butylamido ligand in **2** could then be protonated selectively with 2,6-lutidinium chloride to generate M(NHIPT)(N-*t*-Bu)(NH$_2$-*t*-Bu)Cl$_2$ ($\mathbf{3_{Mo}}$ and $\mathbf{3_W}$), which were alkylated (without isolation) employing 2 equiv of *t*-BuCH$_2$MgCl to give $\mathbf{4_{Mo}}$ and $\mathbf{4_W}$ in 81% and 84% yields, respectively. An X-ray structural study of $\mathbf{4_{Mo}}$ showed it to be the proposed monomeric complex (Figure 3). Bond distances and angles are not unusual. (see the Supporting Information for a full list and description).

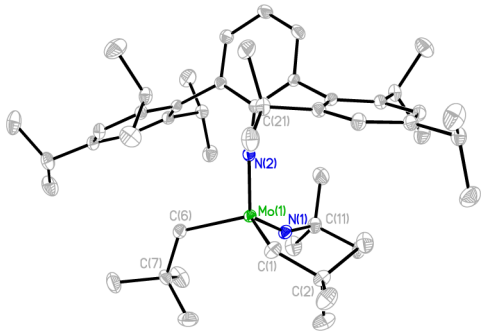


Figure 3. Thermal ellipsoid drawing (50%) of Mo(NHIPT)(N-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ ($\mathbf{4_{Mo}}$). Selected bond distances (Å) and angles (deg): Mo1−N1 = 1.7477(17), Mo1−N2 = 1.7641(17); Mo1−N1−C11 = 156.88(15), Mo1−N2−C21 = 162.53(14).

Treatment of $\mathbf{4_{Mo}}$ and $\mathbf{4_W}$ with 3 equiv of finely ground pyridinium chloride afforded the desired alkylidene complexes $\mathbf{5_{Mo}}$ and $\mathbf{5_W}$ in 57% and 86% yields, respectively. Complex $\mathbf{5_W}$ is obtained as the cis isomer shown, which is readily apparent from the presence of six different isopropyl groups in the HIPT group in the proton NMR spectrum. The alkylidene proton in $\mathbf{5_W}$ is found at 10.65 ppm with $^1J_{CH}$ = 147 Hz, a value that is characteristic of an anti alkylidene; no syn alkylidene proton resonance could be found.

Proton NMR spectra of $\mathbf{5_{Mo}}$ in C_6D_6 (Figure 4) show that two isomers are present in approximately a 1:1 ratio. One is *cis*-

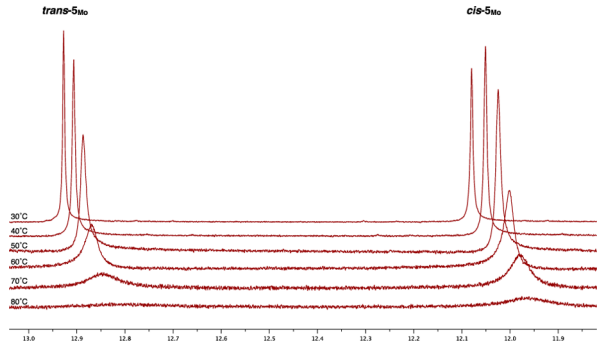


Figure 4. Variable-temperature ^{1}H NMR of $\mathbf{5_{Mo}}$ in C_6D_6.

$\mathbf{5_{Mo}}$ (analogous to *cis*-$\mathbf{5_W}$), while the second has mirror symmetry and therefore must contain trans chlorides (*trans*-$\mathbf{5_{Mo}}$). The large $^1J_{CH}$ values (148 Hz for *cis*-$\mathbf{5_{Mo}}$, 158 Hz for *trans*-$\mathbf{5_{Mo}}$) are characteristic of anti alkylidenes; again, no alkylidene resonance for a syn isomer could be found. The two alkylidene resonances broaden at temperatures up to 80 °C, consistent with interconversion of *cis*-$\mathbf{5_{Mo}}$ and *trans*-$\mathbf{5_{Mo}}$. Because the rate of interconversion of the two isomers is slower at any given temperature when pyridine is added to the sample, *cis*-$\mathbf{5_{Mo}}$ and *trans*-$\mathbf{5_{Mo}}$ must interconvert through loss of pyridine. Evidently, M(NHIPT)(py)$_2$Cl$_2$ is too crowded to form, and even five-coordinate **5** loses pyridine in solution. The main isomer of $\mathbf{5_{Mo}}$ in a proton NMR spectrum in CD_2Cl_2 is the *cis* isomer, which might be expected in view of the likely larger dipole moment for *cis*-$\mathbf{5_{Mo}}$ versus *trans*-$\mathbf{5_{Mo}}$.

Treatment of $\mathbf{5_{Mo}}$ in diethyl ether with 3 equiv of $ZnCl_2$ over 1 h resulted in the formation of Mo(NHIPT)(CHCMe$_3$)Cl$_2$

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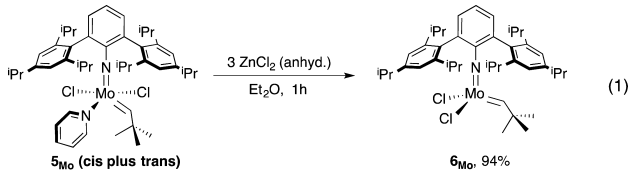
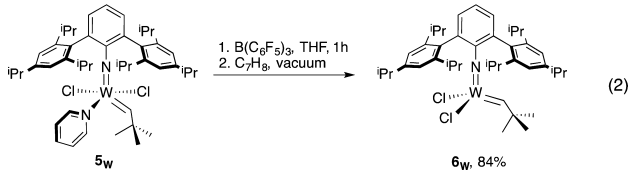
($\mathbf{6_{Mo}}$, eq 1); this reaction is successful as a consequence of the lability of pyridine in $\mathbf{5_{Mo}}$. The alkylidene in $\mathbf{6_{Mo}}$ is also an anti



(1)



(2)

isomer ($^1J_{CH}$ = 158 Hz). Treatment of $\mathbf{5_W}$ with 1 equiv of $B(C_6F_5)_3$ in THF cleanly converted $\mathbf{5_W}$ to the THF adduct of $\mathbf{6_W}$ (eq 2). The THF can be removed under vacuum after dissolution of the THF adduct in toluene to give 14-electron $\mathbf{6_W}$. A value of $^1J_{CH}$ = 155 Hz suggests that the alkylidene in $\mathbf{6_W}$ is also the anti isomer.

An X-ray crystallographic study of $\mathbf{6_W}$ was complicated by whole-molecule disorder. Two structures contribute to the disorder: *anti*-$\mathbf{6_W}$ (~86%) and *syn*-$\mathbf{6_W}$ (~14%). Drawings of *anti*-$\mathbf{6_W}$ are shown in Figure 5. The geometry at the metal is pseudotetrahedral. One of the Trip rings is positioned approximately over the alkylidene (Figure 5b). The bond lengths and angles are unexceptional for an anti alkylidene complex. The N1–W1–C1–C2 dihedral angle (177.7(7)°) is consistent with essentially no twisting (within 3σ) of the alkylidene out of the N1–W1–C1–C2 plane.

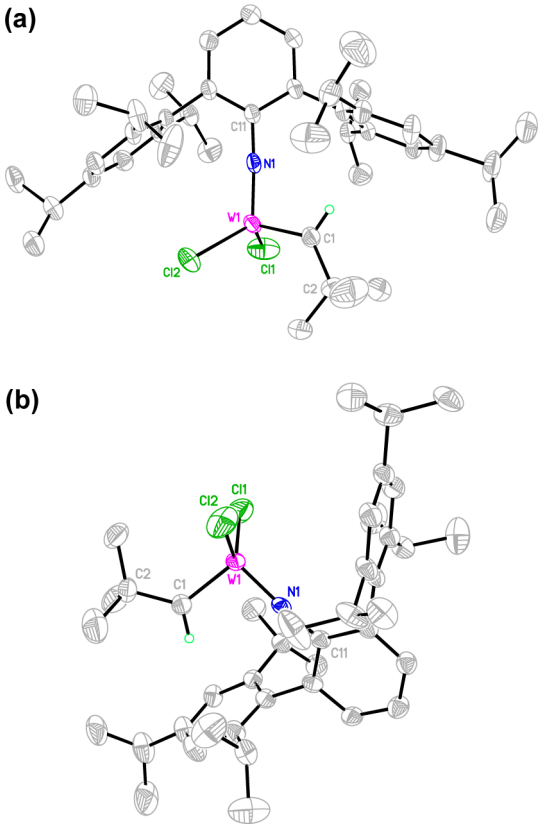


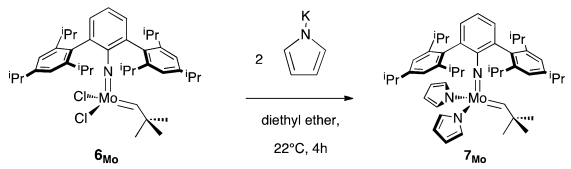
Figure 5. (a) Solid-state structure of *anti*-$\mathbf{6_W}$ and (b) solid-state structure of *anti*-$\mathbf{6_W}$ showing the position of one of the NHIPT Trip rings approximately over the *anti* alkylidene proton. Selected bond distances (Å) and angles (deg): W1–C1 1.892, W1–N1 1.702, W1–Cl1 2.274, W1–Cl2 2.272; W1–C1–C2 126.88, W1–N1–C11 178.37, N1–W1–C1 98.31.

The overall structure of *syn*-$\mathbf{6_W}$, as described in the Supporting Information, is similar to that of *anti*-$\mathbf{6_W}$, although the standard deviations for various bond lengths and angles are much larger than they are for *anti*-$\mathbf{6_W}$. The N1–W1–C1–C2 dihedral angle in *syn*-$\mathbf{6_W}$ is 17(6)°, which again suggests that within experimental error the alkylidene is not "twisted" out of the N1–W1–C1–C2 plane, in spite of the steric interaction between the *tert*-butyl group of the neopentylidene ligand and one of the Trip groups in the NHIPT ligand. Even though some *syn*-$\mathbf{6_W}$ is found in the solid state, we were unable to observe any resonances for the syn isomer in solution by proton NMR, even at −80 °C, where syn and anti interconversion is expected to be slow on the NMR time scale.[4] Because both isomers are found in the solid state, it seems likely that both are accessible in solution, although the equilibrium clearly overwhelmingly favors *anti*-$\mathbf{6_W}$.

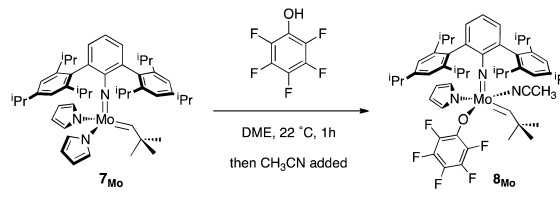
To our knowledge $\mathbf{6_W}$ and (we presume isostructural) $\mathbf{6_{Mo}}$ are the only 14-electron imido alkylidene dihalide complexes in the literature. We propose that formation of dimers or higher oligomers in which halides or imido ligands bridge between metals is not possible in $\mathbf{6_W}$ and $\mathbf{6_{Mo}}$ for steric reasons.

Complexes analogous to $\mathbf{6_W}$ and $\mathbf{6_{Mo}}$ that contain the NHMT ligand were not reported,[11] although no attempts to make them by methods analogous to or related to those shown in the equations were attempted at the time.

We were interested in preparing other M(NHIPT) complexes that contain relatively small anionic ligands: in particular, bispyrrolide and MAP species. We have shown that both can be prepared, so far with Mo. The reaction between $\mathbf{6_{Mo}}$ and potassium pyrrolide gave $\mathbf{7_{Mo}}$ (eq 3), while subsequent



(3)



(4)

treatment of $\mathbf{7_{Mo}}$ in diethyl ether at −30 °C with 1 equiv of pentafluorophenol, followed by crystallization from acetonitrile, led to Mo(NHIPT)(CH-*t*-Bu)(pyr)(OC_6F_5)(CH_3CN) ($\mathbf{8_{Mo}}$; eq 4). Proton NMR spectra of $\mathbf{8_{Mo}}$ (see the Supporting Information) suggest that the acetonitrile is dissociating on the NMR time scale, but efforts to obtain a sample completely free of acetonitrile have not yet been successful.

In summary, we have taken advantage of a synthetic route in which *tert*-butylimido ligands are employed as sacrificial proton acceptors to prepare Mo and W alkylidene complexes that contain the NHIPT imido ligand. Alkylidene NHIPT

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complexes reported here exist exclusively as anti isomers in solution, in contrast to the previously reported closely analogous M(NHMT) complexes,[11] which are mixtures of syn and anti isomers in solution. We are in the process of exploring olefin metathesis reactions with M(NHIPT) complexes. Our hope is that they will be especially stable and long-lived as a consequence of the steric protection toward bimolecular decomposition reactions afforded by the NHIPT ligand.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving experimental details for the synthesis of all compounds and crystallographic data for $\mathbf{4}_{Mo}$ and $\mathbf{6}_{W}$. 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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