Synthesis of Molybdenum Perfluorophenylimido 2-Adamantylidene Complexes

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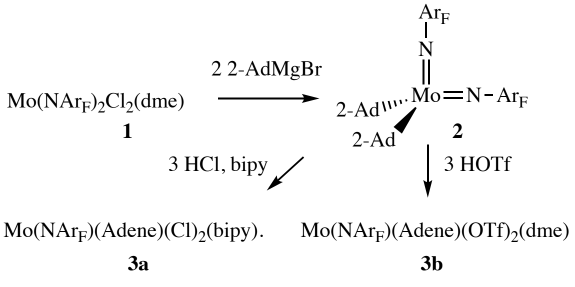
ABSTRACT: Addition of 2-adamantylMgBr in diethyl ether to $Mo(NAr_F)_2(Cl)_2(DME)$ ($Ar_F = C_6F_5$) gave $Mo(NAr_F)_2(Ad)_2$ (**2**, Ad = 2-adamantyl, DME = 1,2-dimethoxyethane). Addition of HCl and bipy to **2** gave $Mo(NAr_F)(Adene)Cl_2(bipy)$ (**3a**, Adene = 2-adamantylidene) while addition of triflic acid to **2** in the presence of DME gave $Mo(NAr_F)(Adene)(OTf)_2(DME)$ (**3b**). Compound **3b** proved to be more useful for preparing $Mo(NAr_F)(Adene)(OR_{F9})_2$ (**4**), $Mo(NAr_F)(Adene)(OR_{F9})_2(THF)$ (**4(THF)**), $Mo(NAr_F)(Adene)(OR_{F9})_2(Piv)$ (**4(Piv)**; Piv = pivalonitrile), $Mo(NAr_F)(Adene)(OTf)(OHMT)(THF)$ (**5(THF)**; OHMT = O-2,6-Mesityl$_2C_6H_3$), $Mo(NAr_F)(Adene)(OTf)(OHMT)(Piv)$ (**5(Piv)**), $Mo(NAr_F)(Adene)(OHMT)(Pyr)(Piv)$ (**6(Piv)**; Pyr = pyrrolide), and $Mo(NAr_F)(Adene)(Me_2Pyr)_2$ (**7**; Me_2Pyr = 2,5-dimethylpyrrolide). X-ray structural studies of nine Adene compounds show that the Adene ligand is distorted by a C-H_β agostic interaction, relatively little in 18e **3a** and **3b** and most significantly in 14e **4**. Preliminary studies show that compounds **4**-**7** are initiators for homocoupling of 1-decene and polymerization of cyclooctene and 5,6-dicarbomethoxynorbornadiene.

In spite of extensive studies of high oxidation state Mo=CHR and W=CHR complexes and their role in olefin metathesis reactions,[1] very little is known about the synthesis and metathesis chemistry of analogous M=CRR' complexes where both R and R' are aryl or alkyl groups. The absence of an α proton in M=CRR' complexes eliminates any possibility of forming a Mo or W alkylidyne complex[2] through loss of that proton. Therefore, new chemistry can be expected such as Mo or W analogs of rare tantalum bisalkylidene complexes[3] instead of the preferred Mo(C-*t*-Bu)(CH_2-*t*-Bu) or W(C-*t*-Bu)(CH_2-*t*-Bu) isomer.[4] Disubstituted alkylidenes also must be formed as intermediates in rare metathesis reactions that yield tetrasubstituted olefins,[5] a reaction that is likely to require more active catalysts than employed so far. Finally, an abstractable alkylidene α proton may be involved in bimolecular decomposition of high oxidation state M=CHR complexes. We found strong β agostic interactions in the methyl group in the first structurally-characterized Mo=CMePh complexes.[6] Therefore, we turned to synthesizing and studying Mo(Adene)[7] (Adene = 2-adamantylidene) complexes where a potential β hydride rearrangement of the alkylidene to an olefin is not possible. Few 2-adamantylidene complexes of any metal had been published[8] and no d^0 2-adamantylidene complexes were known prior to our report last year[7] of Mo imido Adene complexes in which the imido substituent is 2,6-diisopropylphenyl or *t*-butyl. Because the nature of the imido group in imido alkylidene complexes that have proven most useful in applications of metathesis chemistry to organic chemistry are those that contain the small and electron-withdrawing NC_6F_5 (Ar_F) ligand,[9] we felt compelled to extend the synthesis of molybdenum Adene complexes to Mo complexes in which the imido group is perfluorophenyl.

Alkylation of $Mo(NAr_F)_2(Cl)_2(DME)$ (**1**) with AdMgBr (Ad = 2-adamantyl) in ether[10] gave $Mo(NAr_F)_2(Ad)_2$ (**2**) as a bright red-orange crystalline solid. Addition of three equivalents of HCl to $Mo(NAr_F)_2(Ad)_2$ followed by 2,2'-bipyridyl gave $Mo(NAr_F)(Adene)(bipy)Cl_2$ (**3a**), while addition of three equivalents of triflic acid to **2** in the presence of DME gave $Mo(NAr_F)(Adene)(OTf)_2(DME)$ (**3b**) as a yellow-orange solid (Scheme 1). NMR spectra of **3a** and **3b** suggest that both **3a** and **3b** are mixtures of two isomers. Imido neopentylidene or neophylidene bistriflate or dichloride complexes of this general type are often a mixture of *cis* and *trans* dichloride or bistriflate isomers in which imido and alkylidene ligands *cis* to each other.[1]

An X-ray structural study of **3a** (Fig 1) shows it to be the isomer that contains *cis* chlorides that are *cis* to the imido group, while the structure of **3b** (Fig 2) contains *cis* triflates that are *cis* to the adamantylidene. Some structural and NMR data are listed in Table 1. The Mo=C bonds are longer in **3a** and **3b** compared to other compounds prepared here that contain less than 18e (**4** – **6**). The small difference between the two Mo-Cα–C$_\beta$ angles in the alkylidene suggest that the CH$_\beta$ agostic interaction is essentially nonexistent in these two complexes, consistent with the 18e count. Other bond distances and angles are unexceptional.

Scheme 1. Syntheses of 3a and 3b.



Compounds **4-7** (Scheme 2) can be synthesized most conveniently from **3b**. Compound **4** is the only 14e complex in the group; it has the shortest Mo=C bond and the strongest CH_β agostic interaction, as judged by the difference in the two Mo-C_α-C_β(angles (32°), consistent with its 14e count and the presence of relatively electron-withdrawing OR_{F9} ($OC(CF_3)_3$) and NAr_F ligands. THF and pivalonitrile (Piv) adducts of **4** were readily prepared and structurally characterized. Both adducts are essentially square pyramids with the adamantylidene in the axial position and τ values[11] of 0.16 and 0.20 (see Fig 4 for **4(THF)** and the SI for **4(Piv)**. One triflate in **3b** can be replaced selectively with OHMT (O-2,6-$Mesityl_2C_6H_3$) to give **5(THF)** (see SI) or **5(Piv)** (Fig 5); these complexes too are close to square pyramids, according to the τ values (0.16 to 0.21, respectively), and have the adamantylidene in the axial position. The second triflate in **5(Piv)** can be replaced by a pyrrolide ligand to give a MAP complex (monoaryloxide pyrrolide) as a pivalonitrile adduct. Monoaryloxide pyrrolide complexes have been found to initiate some surprising metathesis reactions in the last several years, including those that contain a labile pivalonitrile ligand.[9,12]

Scheme 2. Syntheses of 4, 4(THF), 4(Piv), 5(THF), 5(Piv), 6(Piv) and 7.

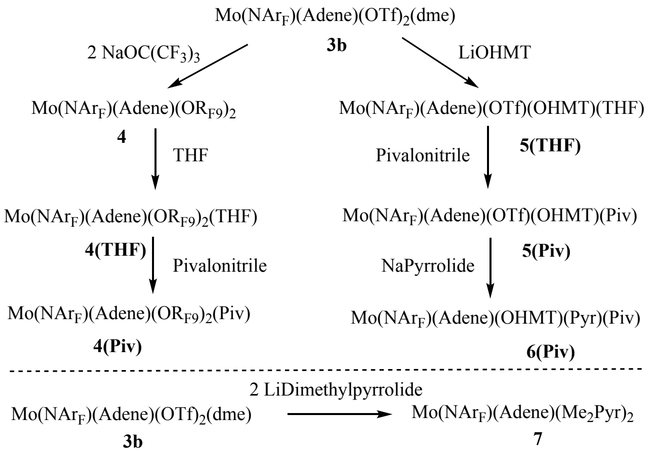


Table 1. Comparisons of structural and NMR data

Cmpd	Mo=C (Å)	τ	ΔMo-C_α-C_β(°)	δC_α (ppm)[b]
3a[a]	1.953(5)	-	0.95	354.61
3b[a]	1.9418(16)	-	2.39	367.13
4	1.860(4)	-	31.98	317.94
4(THF)	1.905(5)	0.16	24.82	325.55
4(Piv)	1.8939(18)	0.20	19.93	341.68
5(THF)	1.913(2)	0.16	10.66	352.41
5(Piv)	1.904(6)	0.21	10.51	362.63
6(Piv)	1.9052(17)	0.23	10.65	341.81
7	1.9748(19)	-	10.62	339.40

[a] Distances and angles for one of two crystallographically distinct molecules in the asymmetric unit. [b] Chemical shift of the alkylidene alpha carbon atom in the ^{13}C NMR spectrum.

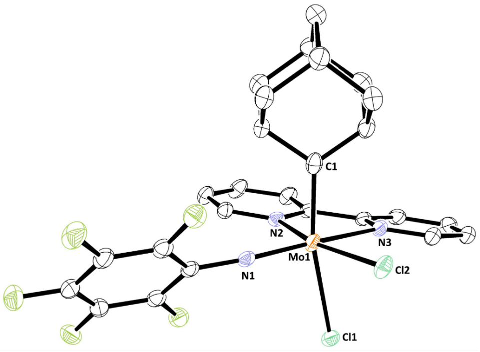


Figure 1. The structure of one isomer of **3a.**

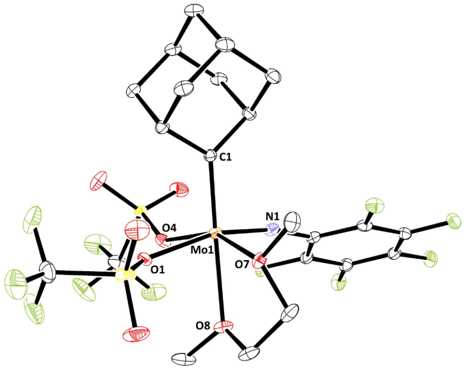


Figure 2. The structure of one isomer of **3b**.

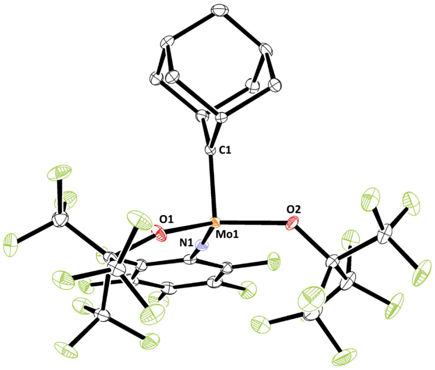


Figure 3. The structure of **4.**

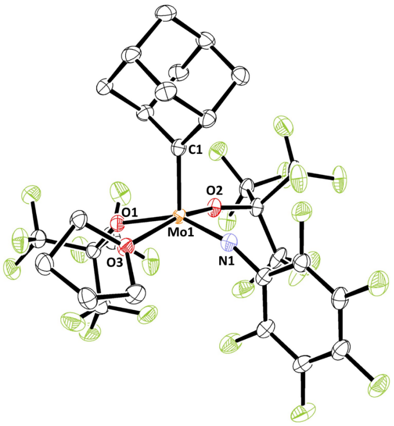


Figure 4. The structure of **4(THF).**

Bispyrrolides are useful precursors to a variety of derivatives through protonation of one or both pyrrolide ligands.[1b] The bisdimethylpyrrolide (**7**) can be prepared readily from **3b**. Its structure (Figure 7) is typical of a variety of imido bisdimethylpyrrolide complexes[13] in that one pyrrolide is bound in an η^1 fashion and the other in an η^5 fashion to give a complex with an 18e count. Its M=C bond is marginally longer than those in **3a** and **3b**. NMR spectra of **7** in CD_2Cl_2 show that η^1 and η^5 pyrrolides interconvert readily on the ^1H NMR time scale at 22 °C, but interconversion is slow at -30 ° (see SI).

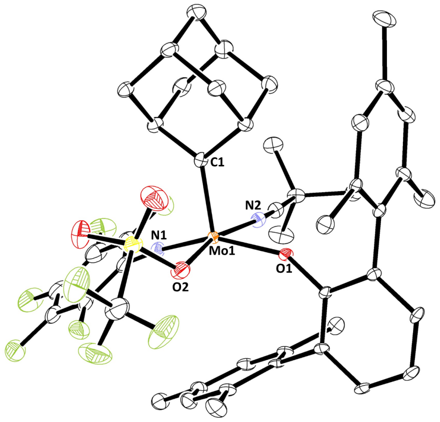


Figure 5. The structure of **5(Piv).**

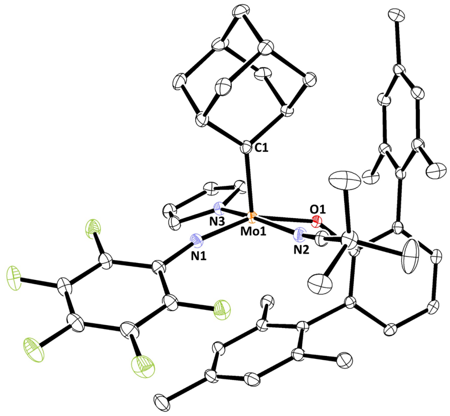


Figure 6. The structure of **6(Piv)**.

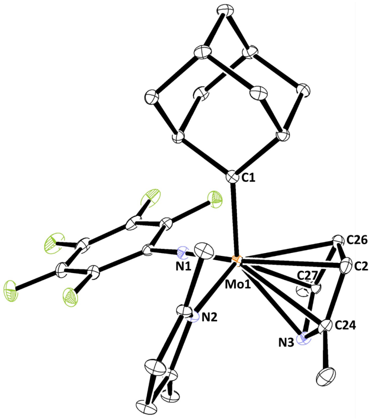


Figure 7. The structure of **7**.

It is obviously important to show that 2-adamantylidene complexes readily initiate typical metathesis reactions. Compounds **4**, **5**, **6** and **7** initiate the homocoupling of 1-decene to a mixture of *Z* and *E*-9-octadecene (~1:4) in an open vial in the glovebox at a catalyst loading of 1% (see SI for details). The differences in the rates for **4**, **4(THF)**, and **4(Piv)** are negligible, which suggests that both THF and pivalonitrile are readily lost from **4(THF)**, and **4(Piv)**. (Decompositions of intermediate alkylidenes limit conversion to 80-95% in 24 h.) They also ring-open cyclooctene in <15 minutes at 22 °C (2% loading). Finally, they polymerize 2,3-dicarbomethoxynorbornadiene (DCMNBD) at 1 mol% catalyst loading in 15 min (95-99 % conversion). The most selective is **6(Piv)** which gives >99% *cis,syndiotactic*-polyDCMNBD, a selectivity that is a feature typical only of monoaryloxide pyrrolide (MAP) ROMP initiators.[14]

We conclude that high oxidation state Mo pentafluorophenylimido 2-adamantylidene complexes are readily prepared through α hydrogen abstraction reactions analogous to those reported for Mo 2,6-diisopropylphenylimido and t-butylimido Adene complexes.[7] The chemistry of Adene complexes may be more robust and give higher yields relative to M=CHR complexes because no α hydrogen is present in the alkylidene and because the significant steric bulk of the 2-adamantylidene ligand may hinder bimolecular decomposition through coupling of 2-adamantylidenes. The fact that 2-adamantylidene complexes are competent metathesis initiators for selected reactions suggests that THF and pivalonitrile are lost readily in these initiators, perhaps in part as a consequence of the steric demands of the 2-adamantylidene ligand. We look forward to more synthetic, mechanistic, reactivity, and catalytic studies that involve 2-adamantylidene and other disubstituted alkylidene complexes.

ASSOCIATED CONTENT

Synthesis details and NMR data, metathesis details for all compounds, and X-ray studies for **3a**, **3b**, **4**, **4(THF)**, **4(Piv)**, **5(THF)**, **5(Piv)**, **6(Piv)**, and **7**.

Accession Codes

CCDC 2038749-2038754 and 2047399-2047401 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

BP performed all synthetic work while CT performed all X-ray structural studies.

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Notes

The authors declare no competing financial interest.

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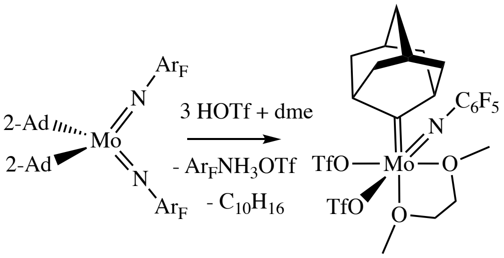

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