ORGANOMETALLICS

pubs.acs.org/Organometallics Article

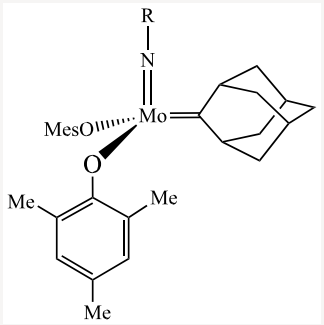
Synthesis of Molybdenum Imido 2-Adamantylidene Complexes through α Hydrogen Abstraction

Jordan W. Taylor, Richard R. Schrock,* and Charlene Tsay

Cite This: Organometallics 2020, 39, 2304−2308 Read Online

ACCESS | Metrics & More | Article Recommendations | * Supporting Information

ABSTRACT: Addition of 2-adamantylMgBr in diethyl ether to $Mo(NAr)_2(Cl)_2(DME)$ (Ar = 2,6-i-$Pr_2C_6H_3$) gave $Mo(NAr)_2(2\text{-}Ad)_2$ (2-Ad = 2-adamantyl, DME = 1,2-dimethoxyethane), from which $Mo(NAr)(Adene)(OTf)_2(DME)$ (1, Adene = 2-adamantylidene) was prepared upon addition of triflic acid. Methods analogous to those that have been successful for synthesizing neopentylidene and neophylidene complexes were used to form $Mo(NAr)(Adene)(OMes)_2$ (2; Mes = 2,4,6-trimethylphenyl), $[Mo(NAr)(Adene)(OC_6F_5)_2]_2$ (3), $Mo(NAr)(Adene)(OC_6F_5)_2(MeCN)$ (4), $Mo(NAr)(Adene)(Cl)_2(bipy)$ (5; bipy = 2,2′bipyridine), Mo(NAr)(Adene)(Cl)(OHMT) (6; OHMT = O-2,6-$Mesityl_2C_6H_3$), Mo(NAr)(Adene)(Cl)(OHMT)(t-BuCN) (6(t-BuCN)), and Mo(NAr)(Adene)(OHMT)(Pyr) (7; Pyr = pyrrolide). Analogous methods beginning with $Mo(N\text{-}t\text{-}Bu)_2(2\text{-}Ad)_2$ yielded Mo(N-t-Bu)(Adene)$(Cl)_2$(bipy) (8a), Mo(N-t-Bu)(Adene)(Cl)(OHMT)(THF) (8b), Mo(N-t-Bu)(Adene)(Cl)(OHMT)(t-BuCN) (8c), and Mo(N-t-Bu)(Adene)(OHMT)(Pyr)(THF) (8d). X-ray structural studies of 1-5, 6(t-BuCN), 7, 8a, 8c, and 8d suggest that one of the Adene β protons is engaged in an agostic interaction with the metal when the electron count is less than 18. Preliminary olefin metathesis studies confirm that Adene complexes react with cyclooctene and 1-decene in the manner expected for high-oxidation-state Mo alkylidene complexes.

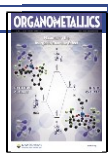


High-oxidation-state alkylidene complexes have been synthesized largely through α hydrogen abstraction reactions in d^0 transition metal complexes containing at least two alkyls that lack one or more β hydrogen atoms.[1] Neopentylidene or neophylidene complexes are most common. Some preferential abstractions of an α hydrogen instead of a β hydrogen in d^0 alkyl complexes have been observed in some Ta triamidoamine compounds.[2] However, exclusively β proton abstractions take place instead of α abstractions outside the triamidoamine environment. d^0 Alkylidenes that contain one or more β hydrogens are wellknown intermediates in olefin metathesis reactions initiated by Mo and W complexes,[1,3] and no rearrangement of an alkylidene to an olefin through a β hydride process has been documented in high-oxidation-state alkylidene complexes.

Recently we showed that disubstituted d^0 alkylidene (Mo = CMePh) complexes can be prepared in a reaction between CH_2=CMePh and Mo imido neopentylidene complexes.[4] The question therefore arose as to whether some analogous disubstituted alkylidene could be prepared through a selective α hydrogen abstraction reaction if the olefin formed through β hydrogen abstraction in that alkyl were highly disfavored. This process led us to consider preparing 2-adamantylidene[5] (Adene) complexes from 2-adamantyl (2-Ad) complexes as a consequence of the well-known resistance to formation of a C=C bond within an adamantyl cage.[6] Well-characterized 2adamantyl[7] and 2-adamantylidene[8] transition-metal complexes have been reported only relatively recently. What are proposed to be $Cr(2\text{-}Ad)_4$[9] and $Fe(2\text{-}Ad)_4$[10] have been reported, but their insolubility prevented their full characterization and confirmation.

A solution of 2-AdMgBr in diethyl ether was prepared from commercially available 2-AdZnBr and magnesium. After optimization of the literature procedures,[7] 80−90% yields of 2-adamantylmagnesium bromide (2-AdMgBr) were obtained free of 2,2′-biadamantane and adamantane. Alkylation of $Mo(NAr)_2(Cl)_2(DME)$ (Ar = 2,6-i-$Pr_2C_6H_3$) with titrated solutions of 2-AdMgBr gave $Mo(NAr)_2(2\text{-}Ad)_2$ in 75% yield as a bright red-orange pentane-soluble solid, which upon addition of triflic acid in the presence of 1,2-dimethoxyethane gave $Mo(NAr)(Adene)(OTf)_2(DME)$ (1, Adene = 2-adamantylidene) in 71% yield as a yellow-orange solid (Scheme 1). Neopentylidene or neophylidene

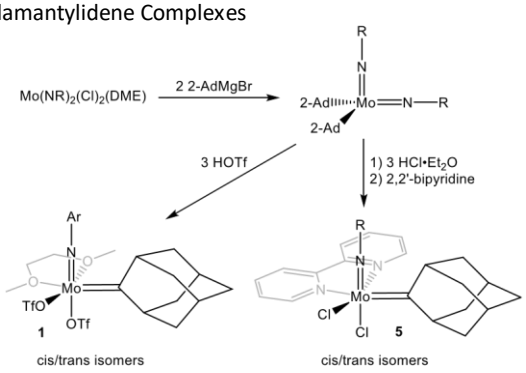
Received: April 10, 2020
Published: June 8, 2020



https://dx.doi.org/10.1021/acs.organomet.0c00244
Organometallics 2020, 39, 2304−2308

bistriflate complexes are commonly prepared in this fashion.[1] NMR spectra of 1 obtained at 22 °C revealed broadened resonances, but at −40 °C in CD_2Cl_2, resonances consistent with two isomers were present with an alkylidene resonance for the dominant isomer being observed at 365.6 ppm (Table 1); the alkylidene carbon

Scheme 1. Syntheses of Bistriflate and Dichloride Mo Adamantylidene Complexes

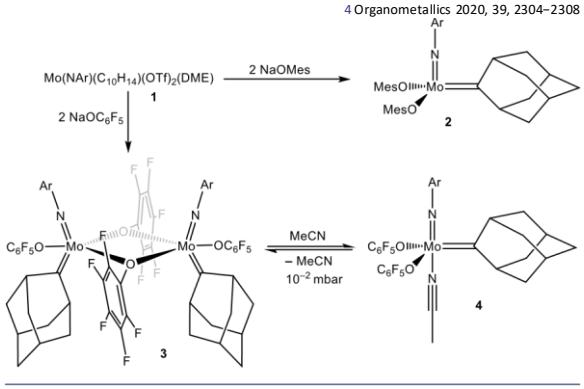


R = *tert*-butyl, 2,6-diisopropylphenyl; Ar = 2,6-diisopropylphenyl

resonance for the second isomer was not detected in this spectrum.

The X-ray structure of 1 (see SI) revealed two crystallographically distinct molecules in the asymmetric unit that are essentially equivalent with slightly different Mo−C_α distances (1.944; 1.946 Å) and M−C_α−C_β angles (125.9° and 124.3° in one; 122.6° and 126.5° in the other). The imido and alkylidene ligands are cis to one another, as always observed in imido alkylidene complexes of this type, and the triflates are also cis to one another. The (small) difference between the two M−C_α−C_β angles in the adamantylidene is consistent with no agostic CH_β interaction[11] in this 18 electron complex nor steric pressure that would result in a distortion of the alkylidene to give unequal M−C_α−C_β angles (see below).

Addition of two equivalents of NaOMes (Mes = 2,4,6trimethylphenyl) to 1 gave Mo(NAr)(Adene)$(OMes)_2$ (2) in 92% yield while addition of $NaOC_6F_5$ to 1 gave $[Mo(NAr)(Adene)(OC_6F_5)_2]_2$ (3) in 91% yield (Scheme 2). An X-ray structural study of 2 showed it to be a monomer (Figure 1), while 3 is a dimer (Figure 2) that contains bridging pentafluorophenoxides, as proposed for the analogous Mo−CMePh complex.[4] In 14e 2 and 16e 3, the two M−C_α−C_β angles differ by 26.2° and 20° (Table 1), consistent with an agostic CH_β interaction in each case. An agostic CH_β interaction alkylidene in related 14e and 16e M−CMePh complexes has been observed to give rise to Mo−C−C_{Me} and Mo−C−C_{Ph} angles in the alkylidene that differ by 30−36°.[4] The smaller difference in the M−C_α−C_β angles in 2 and 3 Scheme 2. Syntheses of 2, 3, and 4 from 1



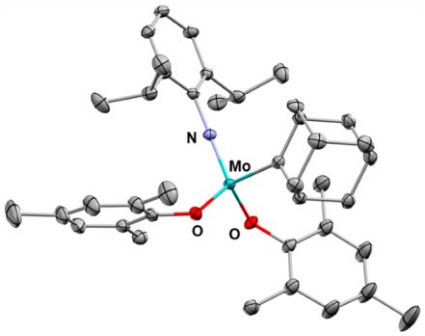


Figure 1. Thermal ellipsoid plot (50%) of 2. Unlabeled ellipsoids correspond to carbon. Solvent molecules and hydrogen atoms have been omitted for clarity.

suggests that the agostic interaction is weaker in an Adene than in a CMePh ligand.

Addition of acetonitrile to 3 gave Mo(NAr)(Adene)$(OC_6F_5)_2$(MeCN) (4), an X-ray structural study of which showed it to be the expected five-coordinate monomer (Figure 3). Acetonitrile can be readily removed from 4 in vacuo (10^{-2} mbar) in the solid state.

https://dx.doi.org/10.1021/acs.organomet.0c00244
Organometallics 2020, 39, 2304−2308

The reaction between $Mo(NAr)_2(2\text{-}Ad)_2$ and 3 equiv of HCl followed by addition of 2,2′-bipyridine gave $Mo(NAr)(Adene)(Cl)_2(bipy)$ (5) in 82% yield. NMR studies at 22 °C were consistent with fluxional behavior on the NMR time scale, although cooling samples to −40 °C resolved resonances for two isomers with alkylidene resonances at 346.3 and 338.7 ppm. The X-ray structure of 5 (see SI for figure and details) consisted of a single, cis-chloride isomer with minor differences in the M−C_α−C_β angles (Table 1), consistent with no significant agostic CH_β interaction.

Compound 5 can be converted into Mo(NAr)(Adene)(Cl)(OHMT) (6; OHMT = O-2,6-$Mesityl_2C_6H_3$), which can be isolated as a pivalonitrile adduct, Mo(NAr)(Adene)(Cl)(OHMT)(t-BuCN) (6(t-BuCN)), in 98% yield (Scheme 3). (A description of the structure of 6(t-BuCN) can be found in the SI.) Treatment of 6 with sodium pyrrolide led to formation of Mo(NAr)(Adene)(OHMT)(Pyr) (7), a structural study of which showed unequal M−C_α−C_β angles (Table 1) as found in the other complexes with formal electron counts <18e such as 2, 3, 4, and 6 (Figure 4).

Table 1. Comparisons of Bond Lengths and Angles

	M⍰C_α (Å)		M−C_α−$C_{\beta1}$ (°)		M−C_α−$C_{\beta2}$ (°)		Δ (°)		δ C_α
1[a]	1.943(2)		125.9(1)		124.3(1)		1.6		365.6[b,f]
2	1.885(2)	136.8(1)	110.6(1)	26.2	293.5				
3	1.88(1)	134(1)	114(1)	20	320.7[c]				
4	1.907(1)	135.40(1)	112.25(9)	23.2	342.4[d,f]				
5	1.995(2)	127.5(1)	122.0(1)	5.5	346.3[b,f]				
6(t-BuCN)[a]	1.890(4)		132.9(3)		114.8(3)		18.1		343.1[c]
7	1.885(3)		136.4(2)		111.6(2)		24.8		318.4
8a[a]	1.947(5)	125.6(4)	124.8(4)	0.8	336.2[e]	8c[a]	1.895(3)	133.4(2)	114.8(2)	18.6	336.0[c]

[a]Distances and angles for one of two crystallographically distinct molecules in the asymmetric unit; − 40 °C in [b]CD_2Cl_2, [c]toluene-d_8; −20 °C in [d]CD_3CN, [e]CD_2Cl_2; [f]Major isomer in solution

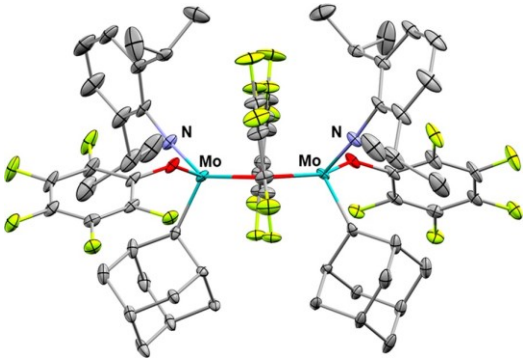


Figure 2. Thermal ellipsoid plot (30%) of 3. Unlabeled gray ellipsoids correspond to carbon, green to fluorine, and red to oxygen. Solvent molecules and hydrogen atoms have been omitted for clarity.

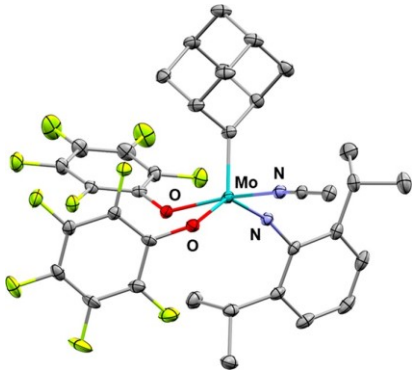


Figure 3. Thermal ellipsoid plot (30%) of 4. Unlabeled gray ellipsoids correspond to carbon and green to fluorine. Solvent molecules and hydrogen atoms have been omitted for clarity.

Scheme 3. Syntheses of 6, 6(t-BuCN), and 7

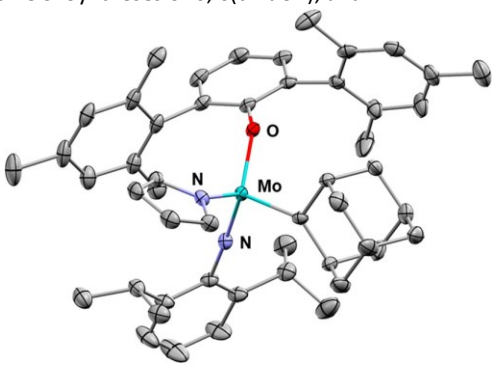


Figure 4. Thermal ellipsoid plot (30%) of 7. Unlabeled ellipsoids correspond to carbon atoms. Solvent molecules and hydrogen atoms have been omitted for clarity.

We were interested in extending imido 2-adamantylidene chemistry to complexes containing the less sterically demanding tert-butylimido ligand. Alkylation of $Mo(N\text{-}t\text{-}Bu)_2(Cl)_2(DME)$ with 2-AdMgBr gave $Mo(N\text{-}t\text{-}Bu)_2(2\text{-}Ad)_2$, which was isolated in 91% yield as a yellow crystalline solid. Methods analogous to those just described for NAr complexes led to isolation $Mo(N\text{-}t\text{-}Bu)(Adene)(Cl)_2(bipy)$ (8a) in 81% yield, Mo(N-t-Bu)(Adene)(Cl)(OHMT)(THF) (8b, 86% yield), Mo(N-t-Bu)(Adene)(Cl)(OHMT)(t-BuCN) (8c, 91% yield), and Mo(N-t-Bu)(Adene)(OHMT)(Pyr)(THF) (8d, 88% yield).

https://dx.doi.org/10.1021/acs.organomet.0c00244
Organometallics 2020, 39, 2304−2308

An X-ray structural study of 8a (see SI for details) showed the Adene ligand to be relatively undistorted (Table 1), while 8d (see SI and Figure 5) was found to have a structure

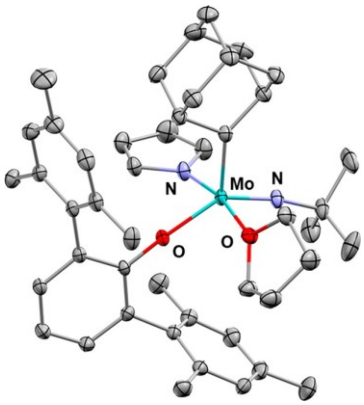
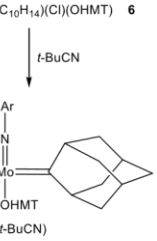


Figure 5. Thermal ellipsoid plot (50%) of 8d. Solvent molecules and hydrogen atoms have been omitted for clarity.



approximately halfway between a TBP and an SP core (τ^{12} = 0.44) and an alkylidene that is slightly distorted (Δ = 18.2°). A description of the structure of 8c can be found in the SI.

We have explored the baseline catalytic competence of Moadamantylidene complexes prepared here for the polymerization of cyclooctene and homocoupling of 1-decene (see SI for details). ROMP of cyclooctene (~20 equiv) with Mo(NAr)(Adene)(Cl)(OHMT) (6) as the initiator in C_6D_6 was essentially complete on examination by proton NMR after 20 min, while ROMP of cyclooctene with Mo(NAr)(Adene)(Cl)(OHMT)(t-BuCN) (6(t-BuCN)) and Mo(NAr)(Adene)(OHMT)(Pyr) (7) as initiators was complete within 2 h. ROMP experiments employing tert-butylimido derivatives Mo(N-t-Bu)(Adene)(Cl)(OHMT)(THF) (8b), Mo(N-t-Bu)(Adene)(Cl)(OHMT)(t-BuCN) (8c), and Mo(N-t-Bu)(Adene)(OHMT)(Pyr)(THF) (8d) were essentially complete on examination by proton NMR after 20 min with the exception of 8c, which required 2 h to go to completion. 1Decene (100 equiv) also was homocoupled by 8b, 8c, and 8d in uncapped vials (under N_2) to give a mixture of (E)- and (Z)-9-octadecene in >90% yields. The reactions initiated by 8b and 8d are fastest, being 97% and 93% complete in 20 min, respectively.

We conclude that high-oxidation-state Mo imido 2adamantylidene complexes are readily prepared through α hydrogen abstraction reactions analogous to those reported for the many neopentylidene and neophylidene complexes that have been prepared and studied[1] and that the method can be extended to t-butylimido complexes. All complexes that have <18e counts show a distorted 2-adamantylidene that is consistent with an agostic CH_β interaction. Preliminary studies show that NAr 2-adamantylidene complexes are competent metathesis initiators for selected reactions. We look forward to more extensive synthetic, mechanistic, reactivity, and catalytic studies that involve 2-adamantylidene and other disubstituted alkylidene complexes.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00244.

Synthesis details and NMR data for all compounds and details of X-ray studies (PDF)

Accession Codes

CCDC 1994554−1994562 contain the supplementary crystallographic data for this paper. These 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.

AUTHOR INFORMATION

Corresponding Author

Richard R. Schrock − Department of Chemistry, University of California at Riverside, California 92521, United States; orcid.org/0000-0001-5827-3552; Email: richard.schrock@ucr.edu

Authors

Jordan W. Taylor − Department of Chemistry, University of California at Riverside, California 92521, United States

Charlene Tsay − Department of Chemistry, University of California at Riverside, California 92521, United States Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00244

Author Contributions

J.W.T. performed all synthetic work, while C.T. performed all X-ray structural studies.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the University of California at Riverside for financial support and to the National Science Foundation for providing funds toward purchase of an X-ray diffractometer (Grant CHE 1919677).

REFERENCES

(1) (a) Schrock, R. R. Alkylidene Complexes of the Earlier Transition Metals. Braterman, P. R., Ed. Reactions of Coordinated Ligands; Plenum: New York, 1986; pp 221−283. (b) Schrock, R. R. High Oxidation State Multiple Metal-Carbon Bonds. Chem. Rev. 2002, 102, 145−180. (c) Schrock, R. R. Recent Advances in High Oxidation State Mo and W Imido Alkylidene Chemistry. Chem. Rev. 2009, 109 , 3211−3226.

(2) (a) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. Synthetic and Mechanistic Investigations of Trimethylsilyl-Substituted Triamidoamine Complexes of Tantalum that Contain Metal-Ligand Multiple Bonds. J. Am. Chem. Soc. 1996, 118 , 3643−3655. (b) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. Alkyl and Alkylidene Complexes of Tantalum that Contain a Triethylsilyl-Substituted Triamido-Amine Ligand. Organometallics 1996, 15, 2777−2783. (c) Freundlich, J.; Schrock, R. R.; Cummins, C. C.; Davis, W. M. Organometallic Complexes of Tantalum That Contain the Triamidoamine Ligand, $[(Me_3SiNCH_2CH_2)_3N]_{3-}$, Including an Ethylidene Complex Formed via a Phosphine-Catalyzed Rearrangement of an Ethylene Complex. J. Am. Chem. Soc. 1994, 116, 6476−6477.

(3) Schrock, R. R.; Hoveyda, A. H. Discovery and Development of Molybdenum and Tungsten Imido Alkylidene Complexes as Efficient Olefin Metathesis Catalysts for use in Organic Synthesis. Angew. Chem., Int. Ed. 2003, 42, 4592−4633.

(4) Taylor, J. W.; Schrock, R. R.; Tsay, C. Molybdenum Disubstituted Alkylidene Complexes. Organometallics 2020, 39 , 658−661.

(5) Rojisha, V. C.; Nijesh, K.; De, S.; Parameswaran, P. Singlet 2adamantylidene − an ambiphilic foiled carbene stabilized by hyperconjugation. Chem. Commun. 2013, 49 , 8465−8467.

(6) Fort, R. C.; Schleyer, P. V. R. Adamantane: Consequences of the Diamondoid Structure. Chem. Rev. 1964, 64, 277−300.

(7) (a) Armstrong, D.; Taullaj, F.; Singh, K.; Mirabi, F.; Lough, A. J.; Fekl, U. Adamantyl metal complexes: new routes to adamantyl anions and new transmetallations. Dalton Trans. 2017, 46, 6212−6217. (b) Taullaj, F.; Armstrong, D.; Datta, S.; Lough, A. J.; Fekl, U. 2Adamantyl Complexes of Platinum. Eur. J. Inorg. Chem. 2019, 2019 , 1288−1291.

(8) (a) Bauer, J.; Braunschweig, H.; Damme, A.; Carlos, J. O.; Jimenez-Halla; Kramer, T.; Radacki, K.; Shang, R.; Siedler, E.; Qing, Y. Metathesis Reactions of a Manganese Borylene Complex with Polar Heteroatom−Carbon Double Bonds: A Pathway to Previously Inaccessible Carbene Complexes. J. Am. Chem. Soc. 2013, 135, 8726−8734. (b) Wang, H.; Wan, Q.; Low, K.; Zhou, C.; Huang, J.; Zhang, J.; Che, C. Stable group 8 metal porphyrin mono- and bis(dialkylcarbene) complexes: synthesis, characterization, and catalytic activity. Chem. Sci. 2020, 11, 2243−2259.

(9) Bochmann, M.; Wilkinson, G.; Young, G. B. Preparation and Properties of 1-Adamantylmethyl and Adamantyl Complexes of Transition Metals. J. Chem. Soc., Dalton Trans. 1980, 1879−1887.

(10) Casitas, A.; Rees, J. A.; Goddard, R.; Bill, E.; DeBeer, S.; Fuerstner, A. Two Exceptional Homoleptic Iron(IV) Tetraalkyl Complexes. Angew. Chem., Int. Ed. 2017, 56, 10108−10113.

(11) (a) Brookhart, M.; Green, M. L. H. Carbon-HydrogenTransition Metal Bonds. J. Organomet. Chem. 1983, 250, 395−408. (b) Brookhart, M.; Green, M. L. H.; Parkin, G. Agostic interactions in transition metal compounds. Proc. Natl. Acad. Sci. U. S. A. 2007, 104, 6908−6914.

(12) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds Containing Nitrogen-Sulfur Donor Ligands: the Crystal and Molecular Structure of Aqua[1,7-Bis(N-methylbenzimidazol-2′-yl)-2,6-dithiaheptane]copper(II) Perchlorate. J. Chem. Soc., Dalton Trans. 1984, 1349−1356.

https://dx.doi.org/10.1021/acs.organomet.0c00244
Organometallics 2020, 39, 2304−2308