Classifying and understanding the reactivities of Mo based alkyne metathesis catalysts from $^95\text{Mo}$ NMR chemical shift descriptors

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ABSTRACT: The most active alkyne metathesis catalysts rely on well-defined Mo alkylidyne, $X_3\text{Mo}≡\text{CR}$ ($X = \text{OR}$), in particular the recently developed canopy catalyst family bearing silanolate ligand sets. Recent efforts to understand catalyst reactivity patterns have shown that NMR chemical shifts are powerful descriptors, though previous studies have mostly focused on ligand-based NMR descriptors. Here, we show in the context of alkyne metathesis that $^95\text{Mo}$ chemical shift tensors encode detailed information on the electronic structure of potent catalysts. Analysis by first principles calculations of $^95\text{Mo}$ chemical shift tensors extracted from solid-state $^95\text{Mo}$ NMR spectra show a direct link of chemical shift values with the energies of the HOMO and LUMO, two molecular orbitals involved in the key [2+2]-cycloaddition step, thus linking $^95\text{Mo}$ chemical shifts to reactivity. In particular, the $^95\text{Mo}$ chemical shifts are driven by ligand electronegativity ($\sigma$-donation) and electron delocalization through Mo-O $\pi$-interactions, thus explaining the unique reactivity of the silanolate canopy catalysts. These results further motivate exploration of transition-metal NMR signatures and their relations to electronic structure and reactivity.

Molybdenum is a transition metal element used in numerous catalytic processes in natural and industrial settings; the selective oxidation of hydrocarbons\textsuperscript{1–3} and the reduction of $\text{N}_2$ to ammonia\textsuperscript{4,5} are two illustrative examples. Mo also catalyzes the redox neutral and atom-economical alkene and alkyne metathesis reactions, which have found applications in organic synthesis thanks to the development of highly active and robust catalysts.\textsuperscript{6–10} Alkyne metathesis in particular has seen major recent progress with the introduction of metal alkylidyne catalysts bearing tripodal silanolate ligands (‘canopy catalysts’).\textsuperscript{11–16} Despite significant synthetic advances, there is a growing need for and interest in spectroscopic descriptors that provide information about electronic structure and relate to catalytic performances.

In this context, nuclear magnetic resonance (NMR) spectroscopy has emerged as a powerful tool for establishing the molecular origins of reactivity.\textsuperscript{17–19} Natural localized molecular orbital (NLMO) analysis of NMR parameters such as chemical shift or electric field gradient (efg) tensors can provide a link between experimentally accessible observables and reactivity. This link arises from the direct relation of these tensors to frontier molecular orbitals and electron distributions.\textsuperscript{20–22} Orbital analyses of NMR parameters have elucidated reactivity patterns of organometallic and coordination compounds in stoichiometric and catalytic reactions by providing detailed information about metal–ligand binding,\textsuperscript{23} focusing mostly on NMR signatures of nuclei in ligands bound to metal sites.\textsuperscript{24–28} A relevant example is the analysis of Mo alkylidyne $X_3\text{Mo}≡\text{CR}$ with $X = \text{alkoxide}$ or silanolate ligands, where the
\(^{13}\)C chemical shielding of the alkylidyne carbon can be related to the energy of the vacant \(\pi^*\)(M≡C) orbital as modulated by the monoanionic X ligands.\(^{12,29}\) Direct analysis of catalytic centers through NMR of metal nuclei such as \(^{95}\)Mo is an appealing and potentially more powerful alternative. The high potential resolution of this approach is manifested by the extraordinarily large \(^{95}\)Mo chemical shift range, known to span >5500 ppm\(^{30,31}\) compared to \(~300\) ppm for typical \(^{13}\)C chemical shifts. However, the origins of \(^{95}\)Mo NMR signatures and their relations to structure and reactivity remain mostly unexplored,\(^{32,33}\) due to the low intrinsic signal sensitivities and the complex lineshapes in solid-state NMR, which arise from the low gyromagnetic ratio and quadrupolar nature \((I = 5/2)\) of the \(^{95}\)Mo nucleus. Recent \(^{95}\)Mo NMR studies of Mo alkylidyne catalysts in solution\(^{12}\) indicate that more complex information is encoded in \(^{95}\)Mo chemical shifts compared to \(^{13}\)C. For instance, while a weak global correlation can be seen between \(^{95}\)Mo and \(^{13}\)C isotropic chemical shifts \((\delta_{iso})\) of the alkylidyne carbon (Figure 1a), complexes bearing different types of monoanionic ligands, e.g. silanolate vs. (fluoro)alkoxide, seem to belong to different catalyst classes. To understand these \(^{95}\)Mo NMR signatures requires clarifying the relations of molecular geometry, electronic structure, and NMR parameters.

To this end, we measured and analyzed the solid-state \(^{95}\)Mo NMR spectra of a series of Mo alkylidyne complexes bearing the same alkylidyne group but different ancillary ligands, including two tripodal silanolates, a related monodentate triphenylsilylanolate, and four tert-butoxides with varying degrees of ligand fluorination (Figure 1b). See Supporting Information (SI) Section S1 for synthetic details and Section S2 for characterization of the complexes. Though solid-state \(^{95}\)Mo NMR spectra are more challenging to access than solution NMR data, they encode information that is otherwise averaged by dynamics, namely the anisotropic chemical shift and electric field gradient \((efg)\) tensors and their relative orientations. Here, experimental measurements, first-principles calculations, and orbital analyses show that the \(^{95}\)Mo chemical shift tensors arise directly from the HOMO and LUMO energies of the complexes, providing a link to molecular reactivity and a probe of Mo-O \(\pi\) interactions that modulate HOMO energies and, correspondingly, reactivity.

The principal components of the \(^{95}\)Mo chemical shift tensors of each complex were extracted from experimental solid-state \(^{95}\)Mo NMR spectra measured at 100 K and different magic angle spinning (MAS) rates, as shown in Figure 1c for complex iF3 and for all complexes in SI Section S3. We found that the \(^{95}\)Mo \(\delta_{iso}\) are slightly but significantly different in the solid state compared to in solution, particularly for the silanolate complexes, indicating the substantial influences of dynamic and/or conformational effects (vide infra).\(^{34}\) The solid-state \(^{95}\)Mo \(\delta_{iso}\) are correlated (SI Section S3, Figures S43-S44) with the \(^{13}\)C \(\delta_{iso}\) values, but one can readily distinguish the (fluoro)alkoxide series from the silanolate series as the latter exhibit \(^{95}\)Mo chemical shifts significantly more deshielded than expected based on their \(^{13}\)C chemical shifts. The \(^{95}\)Mo quadrupolar coupling constants \((C_Q)\) were also estimated to be between 2.0 and 4.5 MHz, typically significantly lower that the values calculated from first principles (SI Table S4.1), likely due to dynamic effects, present even under the low temperature measurement conditions.\(^{35}\)

The \(^{95}\)Mo chemical shift tensors are nearly axially symmetric for all alkylidyne complexes \((\eta_{CSA} \text{ between 0.0 and 0.3})\), in relation to their almost \(C_3v\) symmetry. Density functional theory (DFT) was then employed to understand the origin and orientations of the tensor components. NMR chemical shielding tensors were calculated for all studied compounds and show good overall agreement with experimental data (SI Section S4). The \(^{95}\)Mo chemical
shift/shielding tensors of the complexes all have similar orientations (SI Section S4.3), with $\delta_{11}$ and $\delta_{22}$ perpendicular to the Mo≡C bond and $\delta_{33}$ parallel to this bond; hence, we define the perpendicular and parallel components of the chemical shift tensor as $\delta_\perp = (\delta_{11} + \delta_{22})/2$ and $\delta_\parallel = \delta_{33}$ (Figure 1c, insert). Notably, the particularly deshielded $^{95}$Mo $\delta_{\text{iso}}$ values of the silanolate compounds are primarily driven by their highly deshielded $\delta_\perp$ components (Figure 1d).

We next investigated the origin of the $^{95}$Mo $\delta_\perp$ and $\delta_\parallel$ components and their relation to electronic structure using Natural Chemical Shift (NCS) analysis for model complexes bearing truncated ligands for computational simplicity, (RO)$_3$MoC(Ar), with RO = CH$_3$O, SiH$_3$O, or CF$_3$O (SI Section S4.4). For all models, while the shielded $^{95}$Mo $\delta_\parallel$ components originate from coupling of filled Mo(4p) and $\sigma$(Mo-O) with vacant $\sigma^*$(Mo-O), the deshielded $^{95}$Mo $\delta_\perp$ components that drive the isotropic chemical shift originate from coupling of filled high lying $\pi$(Mo≡C) with low-lying empty d orbitals ($d_{xy}$ / $d_{x^2-y^2}$) involved in the $\sigma^*$(Mo-O) (Figure 2a,b SI Section S4.4). These coupled orbitals are different from those relevant to the $^{13}$C NMR chemical shift tensors of the alkylidyne carbon, which arise from

Figure 1. (a) Solution $^{95}$Mo and $^{13}$C $\delta_{\text{iso}}$ for a series of Mo alkylidyenes, including some bearing different alkylidyne substituents (unlabeled points). See SI Section S2 for details. (b) Mo alkylidyenes studied in this work. (c) Example experimental (black) and simulated (red) solid-state $^{95}$Mo NMR spectra of 1F$_3$ acquired at 100 K, 14.1 T, and different MAS rates. (d) Solid-state $^{95}$Mo $\delta_{\text{iso}}$, $\delta_\perp$, and $\delta_\parallel$ values for each complex extracted from solid-state $^{95}$Mo NMR spectra (SI Section S3)
coupling of occupied $\sigma$(Mo-C), $\sigma$(C-C), and $\pi$(Mo≡C) with vacant $\pi^*$(Mo≡C) and $\sigma^*$(Mo-C) (Figure 2c).\textsuperscript{29} Notably, the orbitals that contribute to $^{95}$Mo $\delta_\perp$ correspond to the HOMO and LUMO of the Mo alkylidynes (Figure 2d, SI Section S4.5), which are involved in the key steps of the alkyne metathesis reaction, e.g. alkyne coordination, [2+2]-cycloaddition (Figure 2e), and cycloreversion.

The trends in HOMO and LUMO energies (Figure 2f) parallel the trends observed in $^{95}$Mo NMR signatures for the small and larger (full ligand set) complexes. Both HOMO and LUMO energies of the (fluoro)alkoxide series, as well as HOMO-LUMO gap (SI Section S4.5) show a clear decrease with increasing ligand fluorination, consistent with their chemical shift trend. Complexes $^{1}$F$_0$ and $^{1}$F$_9$ show a close match in HOMO and LUMO energies with these of the CH$_3$O and CF$_3$O small models, respectively, while the small silanolate model SiH$_3$O falls in between $^{1}$F$_3$ and $^{1}$F$_6$, consistent with its expected $\sigma$-donation ability (electronegativity), which indicates that $\sigma$-donation effects drive the trends observed for these compounds. In contrast, the silanolate complexes $^{2}$Ph, $^{3}$Ph, and $^{3}$Et show distinct features: while their LUMO energies lie between those of $^{1}$F$_0$ and $^{1}$F$_3$, their HOMO energies are higher than any of the (fluoro)alkoxides, thus explaining their highly deshielded $^{95}$Mo chemical shifts. Note also that this electronic structure provides an overall better match with the energies of 1-phenyl-1-propyne as a model alkyne substrate, which would favor [2+2]-cycloaddition reactions. While the nature of the LUMO and its energies clearly parallel what is expected from the relative $\sigma$-donation abilities of the different anionic ligands, the high HOMO energy of the silanolate complexes likely originates from additional effects; namely, the silanolate ligands favor overlap of oxygen p and Mo d orbitals and enable electron delocalization across the aromatic ligand substituents ($\pi$-effect). This is consistent with the nature of the orbitals involved in the HOMO, which include significant contributions of the lone pairs of the O atoms of the anionic ligands (Figure 2d). The consequently lower HOMO-LUMO gap is manifested in more deshielded $^{95}$Mo chemical shifts and can be connected to the unique reactivity patterns of these compounds due to the better match between HOMO-LUMO positions of the alkylidyne and alkyne molecule.

Another manifestation of metal-ligand $\pi$ interactions for the silanolate complexes is the very different charges calculated at the Mo centers (1.42-1.46), compared to the (fluoro)alkoxides (1.28-1.31) (SI Section S4.6), even though the silanolate ligands of $^{2}$, $^{3}$Ph, and $^{3}$Et are expected to be similar in electron-withdrawing character ($\sigma$-donor strength) to the $^{1}$F$_3$ or $^{1}$F$_6$ fluoroalkoxides.\textsuperscript{29,37} This difference of calculated charges is consistent with the larger $^{95}$Mo $C_\perp$ values of the silanolate compounds compared to $^{1}$F$_0$, $^{1}$F$_3$, and $^{1}$F$_6$ (SI Tables S3.1 and S4.1), indicating the importance of factors beyond the $\sigma$-donor strength of the anionic X ligand. In fact, the influence of $\pi$-donation on $^{95}$Mo NMR parameters is quite significant (SI Section S4.7): changing the Mo-O-Si bond angle for a small (H$_3$SiO)$_3$MoC(Ar) model results in a linear deshielding of $\delta_\perp$ of approximately 5 ppm per degree, consistent with strong dependencies on geometry dependent metal-ligand $\pi$-interactions. For model structures (MenPh$_3$-$n$SiO)$_3$MoC(Ar) (n=0-3), the $^{95}$Mo $\delta_\perp$ increases linearly with the number of phenyl substituents from 785 to 950 ppm indicating the significant influence of the ligand $\pi$ system, which could be modulated by intramolecular dispersion interactions that were recently evidenced by UV-visible spectroscopy.\textsuperscript{13} Both these examples highlight the utility of $^{95}$Mo chemical shifts as a highly resolved probe of electron delocalization through the ligand $\pi$ system due to their direct dependence on the energy of the Mo≡C $\pi$ bond and the Mo d orbitals.
Overall, these analyses explain the observed differences between $^{13}$C and $^{95}$Mo NMR shift trends: despite the similar orientations of the $^{13}$C and $^{95}$Mo chemical shift tensors (Figure 2b,c), $^{13}$C NMR chemical shifts only indirectly probe the $\sigma$-donation of the anionic ligands, while $^{95}$Mo NMR chemical shifts directly relate to the $\pi$(Mo≡C) and low-lying $d_{xy}$ and $d_{x^2-y^2}$ orbitals involved in the key [2+2]-cycloaddition for alkyne metathesis. These orbitals correspond to the HOMO and the LUMO, thus explaining the greater sensitivity of $^{95}$Mo NMR towards subtle differences in electronic structure. In particular, the $^{95}$Mo $\delta_\perp$ component is greatly sensitive to the ligand-metal $\pi$-interactions, which modulate the energy of the HOMO. This effect is particularly pronounced for the silanolate complexes. Overall, $^{95}$Mo chemical shift analysis highlights and enables to distinguish the unique electronic structure of silanolate canopy catalysts and further supports the role of $\pi$-interactions in controlling the reactivity of these catalysts.\textsuperscript{13,16} Notably, the $^{95}$Mo $\delta_\perp$ of the highest-performing catalysts (1\textsubscript{F6}, 2\textsubscript{Ph}, 3\textsubscript{Ph}, and 3\textsubscript{Et}) are in the 800-1000 ppm range, suggesting that this chemical shift reflects optimal electronic structure for catalytic activity, e.g. best match of HOMO and LUMOs of alkylidyne and alkyne substrate. We also want to note that, while solution $^{95}$Mo chemical shifts represent dynamic averages, complicating their relation to structural features or reactivity due to the fluxionality of the Mo-O-Si bonds, solid-state NMR has the advantage of enabling extraction and analysis of the full anisotropic chemical shift tensor. This study motivates further exploration of NMR analyses of transition metal nuclei, which likely provide more direct links to the metal-based frontier molecular orbitals responsible for reactivity.

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Figure 2. (a) Relation of chemical shift and frontier molecular orbitals through the Ramsey formalism.\textsuperscript{36} Primary orbital couplings that drive (b) $^{95}$Mo and (c) $^{13}$C chemical shift tensors. (d) MO diagram showing the primary transitions probed by $^{13}$C and $^{95}$Mo NMR. The HOMO and LUMO of 3\textsubscript{Et} are shown for comparison. (e) Key orbital interactions involved in the [2+2]-cycloaddition reaction for alkyne metathesis. (f) Calculated HOMO and LUMO energies of each complex (squares: fluoroalkoxides; circles: silanlates) compared to those of 1-phenyl-1-propyne (dotted lines) as a prototypical alkyne.
Supporting Information
Experimental section, solution NMR characterization of all compounds, additional solid-state NMR and DFT results, and Cartesian coordinates of all calculated structures.

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Author Contributions
Z.J.B and C.C. conceptualized the study, designed the methodology, and analyzed the results. J.H. and A.F. developed and synthesized the Mo alkylidyne. Z.J.B. measured and analyzed the solid-state NMR spectra. Z.J.B. and L.L. conducted the DFT analyses. Z.J.B., L.L., and C.C. co-wrote the manuscript. All authors discussed the results and commented on the manuscript during its preparation.

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