

Synthesis of Ether-Functionalized and Sterically Demanding Molybdenum Alkylidyne Complexes

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Supporting Information

ABSTRACT: The synthesis of ether-functionalized molybdenum benzylidyne complexes $[ArC \equiv Mo\{OC(CF_3), Me\}_3]$ (6, Ar = para-methoxyphenyl; 7, Ar = 2,4,6-trimethoxyphenyl) and of the sterically demanding benzylidyne complex $[\{2,4,6-(i-\Pr)_3C_6H_2\}C \equiv Mo\{OC(CF_3)_2Me\}_3]$ are presented, together with their spectroscopic characterization, molecular structures, and catalytic activity in alkyne metathesis. Complexes 6 and 7 feature intermolecular contacts between the para-methoxy group and the molybdenum center that give rise to 1D-polymeric structures in the solid state. The preparation of other functionalized alkylidyne complexes, $[ArC \equiv Mo\{OC(CF_3)_2Me\}_3]$ (Ar = 2-(*i*-PrO)C₆H₄, 8-MeO-Naph, 2,6-(*i*-Pr)₂C₆H₃), was also attempted, but only the acyl precursors $[ArC(=O)Mo(CO)_5]^-$ could be isolated. The synthesis of the



molybdenum acyl complexes was challenging, and appropriate alternative protocols were developed.

■ INTRODUCTION

Since the discovery of the disproportionation of acetylenes 50 years ago,¹ great progress has been achieved in the development of efficient, well-defined catalysts (and precursors) for the alkyne metathesis reaction.² The most prominent examples essentially comprise high oxidation state tungsten- and molybdenum-based alkylidyne complexes of the Schrock type^{2a,3} bearing alkoxide⁴ (e.g., fluorinated alkoxides,⁵ silanolates,⁶ and multidentate ligands),^{2d,7} amido⁸ or iminato ligands,^{5d,6c,9} among others, and combinations thereof. The synthesis of these complexes initially followed two dominant strategies: (i) The cross-metathesis of binuclear complexes of the type $[(RO)_3W \equiv W(OR)_3]^{10}$ with alkynes $(R'C \equiv CR')$ to give 2 equiv of the corresponding alkylidyne complex $[R'C \equiv$ $W(OR)_3$, and (ii) the so-called "high-oxidation-state" route, ^{5c,11} starting from WCl₆ or MoO₂Cl₂ to afford, in several steps, neopentylidyne complexes such as [Me₃CC=M- $(dme)_n (OR)_3$ (M = Mo, W; dme = 1,2-dimethoxyethane; n = 0, 1) via the versatile precursor mer-[Me₃CC \equiv M- $(Cl)_3(dme)$]. A major improvement was the development of the "low-oxidation-state" route^{2c,9c,12} (Scheme 1), which for both tungsten and molybdenum provides access to mer- $[R'C \equiv M(Br)_3(dme)]$ (M = Mo, W) in two main steps starting from the metal hexacarbonyls. Because of higher atom economy, more convenient operability, and less restricted access to other alkylidyne ligands (R'C \equiv), this synthetic strategy is certainly superior; it has found extensive applications in the preparation of several new alkylidyne complexes that are suitable alkyne metathesis promoters, reaching in some cases high performance and outstanding functional group compatibility. Very recently, a new crossmetathesis protocol has been reported for the synthesis of Scheme 1. Application of the Low-Oxidation-State Route for the Synthesis of Molybdenum Alkylidyne Complexes^a

^{*a*}DME = 1,2-dimethoxyethane.

selectively functionalized molybdenum alkylidynes.¹³ This methodology takes advantage of versatile benzylidyne-transfer reagents derived from 1-phenyl-3,3,3-trifluoropropyne¹³ $(ArC \equiv CCF_3)$ or phenyl(trimethylsilyl)ethyne¹⁴ (ArC = CSiMe₃), which react with $[EtC \equiv Mo(dme)(OR)_3]$ (R = $C(CF_3)_2Me$ to give the corresponding $[ArC \equiv Mo(dme)_2]$ (OR)₃] complexes and the highly volatile 1,1,1-trifluoro-2pentyne or 1-(trimethylsilyl)-1-butyne, respectively. However, the alkyne reagents are not always readily accessible.

Some recent examples of homogeneous catalysts are highlighted in Figure 1 and comprise (i) the highly active alkylidyne complex $[t-BuC \equiv W(Im^{t-Bu}N) \{OC(CF_3)_2Me\}_2]$ (1, Im^{t-Bu}N = 1,3-di-*tert*-butylimidazolin-2-iminato)^{5d} supported by an asymmetric push-pull ligand environment; (ii) the triphenylsiloxy-based complex $[{4-(MeO)C_6H_4}C \equiv Mo (OSiPh_3)_3]$ (2), ^{6a} which has been extensively used in natural product synthesis; ¹⁵ (iii) the trialkoxysiloxy-substituted tung-

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Figure 1. Selection of carefully designed alkyne metathesis catalysts.

sten alkylidyne [PhC \equiv W{OSi(O-*t*-Bu)₃}₃] (3),^{6b} which emerged as a versatile catalyst able to metathesize not only acetylenes but also conjugated 1,3-diynes;¹⁶ (iv) the chelate complex 4^{7a} (and derivatives),¹⁷ largely employed in polymer¹⁸ and supramolecular chemistry;¹⁹ and (v) the most active catalyst so far in alkyne metathesis,²⁰ the 2,4,6-trimethylbenzylidyne complex [MesC \equiv Mo{OC(CF₃)₂Me}₃] (5),²¹ which performs efficiently even in terminal alkyne metathesis.^{20–22} Moreover, 5 and related complexes are also excellent initiators in ring-opening alkyne metathesis polymerization (ROAMP).^{13,23}

In spite of these significant developments in catalyst and ligand design, the applicability and the potential of the alkyne metathesis reaction is limited to some extent by the air sensitivity of the catalysts. Nevertheless, there are a few reported strategies that circumvent this shortcoming. Mortreux-type catalyst systems,²⁴ although quite obsolete and illdefined, are robust and user-friendly and exhibit catalytic activity under noninert conditions,²⁵ but at the expense of efficiency and functional group compatibility. In this context, a major milestone was reached in 2010 with the first benchstable precatalysts,^{6a} chelated derivatives of the molybdenum complex 2 (and its benzylidyne congener)²⁶ that act as reservoirs of the active species.^{2b} Accordingly, the increase in coordination number at the metal center by chelation of a nucleophilic ligand such as 1,10-phenanthroline (occupation of free coordination sites) results in air-stable complexes, which upon dissociation assisted by more electrophilic metal salts (such as MnCl₂ and ZnCl₂) at elevated temperatures liberate the active catalysts (Scheme 2).

Inspired by this previous work, we planned various strategies to improve the robustness and user-friendliness of the alkylidyne complexes. The activation of air-stable precatalysts





^{*a*}Conditions (a): $MnCl_2$ or $ZnCl_2$, toluene, 80-100 °C; abbreviations: phen = 1,10-phenanthroline.

(Scheme 2) requires a non-negligible additional step, namely, dissociation of the chelating ligand. One possibility to overcome this drawback consists in increasing the coordination number through formation of intra- or intermolecular interactions without the need for additional ligands. This can be accomplished if proper functional groups are installed at selected positions in the already existing ligand environment, including the alkylidyne moiety. These functionalities should have the ability, at least in the solid state, to promote a chelating binding mode or engage in weak covalent interactions with a neighboring molecule. For example, molybdenum complexes of the types 6-8 (Figure 2a) can



Figure 2. (a) Ether-substituted benzylidyne complexes showing proposed intermolecular coordination (complexes 6 and 7). (b) Proposed intramolecular stabilization of the MCBD complex. (c) Initiation step of the alkyne metathesis after addition of a typical substrate such as $RC \equiv CMe$ (R = alkyl, aryl). [Mo] = [Mo{OC-(CF₃)₂Me}₃].

potentially form inter- (6, 7) or intramolecular (7, 8) interactions between the ether substituents at the alkylidyne moiety and the metal center. Obviously, because of the linearity of the Mo \equiv C-Ar units, chelation in complexes 7 and 8 is not possible. Instead, stabilization of the metal-lacyclobutadiene (MCBD) structures formed by addition of an alkyne to the alkylidyne complex, e.g., 2-butyne to 8 (see Figure 2b), is envisaged, the structure of which resembles the robust and well-established Hoveyda-Grubbs catalysts^{14,27} for olefin metathesis. Since 8 and the corresponding MCBD complex are in equilibrium in solution, the release of 2-butyne

Scheme 3. Overview of All Complexes Prepared and Discussed in This Work Including the Modified Synthetic Protocol for Acyl Complexes Li[13], Li[17], and Li[19]



to activate the catalyst should be driven by its adsorption in molecular sieves or by distillation under reduced pressure. Although a decrease in the catalytic performance can be anticipated, the strength (or weakness) of these interactions is crucial to avoid complete suppression of the activity, perhaps in solution or at elevated reaction temperatures. In particular, if the substituents at the alkylidyne moiety are involved in this process, then substitution of the alkylidyne in the initiation step of the alkyne metathesis reaction (Figure 2c), which is expected to proceed at slow rates, would liberate the binding site and generate the catalytically active species, so that complete conversion would presumably be reached, as usual, within a few minutes. It should be mentioned here that a similar strategy (albeit with different intentions) has been applied by Fischer and co-workers,²⁸ in which the addition of functionalized ynamines to a molybdenum alkylidyne catalyst generates MCBD complexes stabilized intramolecularly by secondary metal binding sites, thus irreversibly deactivating the catalytically active center. This approach grants control over the termination of living ring-opening alkyne metathesis polymerizations and gives access to telechelic polymers.²⁸

Alternatively, an increase in the steric bulk at the metal center can hinder undesirable decomposition reactions and enhance the stability of the complex toward air or moisture. We have already explored this concept by replacement of the phenyl group of the alkylidyne moiety by the sterically more demanding 2,4,6-trimethylphenyl (mesityl, Mes) substituent in complexes of the type $[MesC \equiv M(X)(Y)_2]$ (M = Mo, W; X = $Im^{t-\hat{B}u}N, Y = OC(CF_3)_2Me \text{ or } X = Y = OC(CF_3)_2Me$ (5, M = Mo), $OC(CF_3)_3$, $OSi(O-t-Bu)_3$; $Im^{t-Bu}N = 1,3$ -di-tert-butylimidazolin-2-iminato).^{6c} Whereas the molybdenum complexes were not air-stable, some of the tungsten analogs, namely $[MesC \equiv W(Im^{t-Bu}N) \{OC(CF_3)_2Me\}_2]$ and $[MesC \equiv W \{OSi (O-t-Bu)_3$], proved sufficiently robust to be handled in air for at least 2 or 3 h without perceptible loss of their catalytic performance. The question addressed in the present work is whether even more crowded alkylidyne complexes bearing isopropyl or tert-butyl groups (i.e., 2,6-disubstituted or 2,4,6trisubstituted benzylidynes, *vide* infra) can improve the stability of the precatalysts in comparison with their less encumbered congeners.

In principle, all envisaged complexes are accessible from the Schrock carbyne complexes mer-[ArC \equiv Mo(Br)₃(dme)], which in turn can be conveniently prepared, as mentioned above, through the low-oxidation-state route (Scheme 1) from the corresponding lithium aryls (LiAr) and [Mo(CO)₆]. In most cases, however, the preparation of these precursors proved challenging; therefore, it was crucial to review the established synthetic protocols and develop alternative strategies, which will be discussed throughout this work.

RESULTS AND DISCUSSION

We initially attempted the synthesis of complexes of the type **6–8**, containing *para*-methoxyphenyl, 2,4,6-trimethoxyphenyl or *ortho*-isopropoxyphenyl in place of the aryl (Ar) moiety. In *para*-substituted arylalkylidyne **6**, intermolecular interactions are intended to stabilize the alkylidyne complex, whereas *ortho*-substitution in **8** aims at the stabilization of the MCBD through intramolecular coordination (Figure 2b). In the intermediate case (7), both strategies apply because of substitution at both *ortho*- and *para*-positions. As for the second concept outlined in the introduction, the synthesis of bulky alkylidyne complexes is discussed in a separate section. Finally, preliminary catalytic studies with the new alkylidyne complexes are presented at the end of this contribution.

Synthesis of (para-Methoxybenzylidyne)molybdenum Complexes. Aiming at the preparation of complex 6, the para-anisole moiety was selected based on the established use of 2, for which a multi-gram-scale synthesis has been reported.²⁶ In addition, closely related complexes to 6 such as $[\{4-(MeO)C_6H_4\}C\equiv Mo(L)\{OC(CF_3)_2Me\}_3]$ (L = DME or N-heterocyclic carbene) have been successfully prepared and tested as alkyne metathesis initiators.^{13,2} However, these complexes are not suitable for our purpose, as the free binding site is already blocked by the additional coordinating ligand (L). In contrast, mesityl complex 5 is obtained without coordinating solvent via the low-oxidationstate route with $[Me_4N][MesC(=O)Mo(CO)_5]$, $[Me_4N][9]$, and mer-[MesC=Mo(Br)₃(dme)] (10) as key intermediates (see Scheme 3). Therefore, we aimed at the synthesis of DMEfree alkylidyne complex 6, which can be accomplished in an analogous fashion by reacting mer-[{4-(MeO)C₆H₄}C=Mo- $(Br)_3(dme)$ ²⁶ (11) with 3 equiv of K[OC(CF₃)₂Me] in THF (Scheme 3). Although already reported by Fürstner et al.,²⁶ the preparation of 11 following the low-oxidation-state route deserves some attention here, especially with regard to its precursor $[Me_4N][\{4-(MeO)C_6H_4\}C(=O)Mo(CO)_5],$ [Me₄N][12]. Starting with 4-methoxyphenyl lithium and $[Mo(CO)_6]$, acyl complex $[Me_4N][12]$ is obtained in a twostep synthesis (Scheme 3), in which the intermediate lithium salt Li[12] is not isolated. Fürstner and co-workers found by NMR spectroscopy that two isomers of [Me₄N][12] were present in solution in an approximately 9:1 ratio, but no discussion of the nature and origin of the minor isomer was presented. Moreover, the reported NMR resonances are inconsistent with two configurational isomers of the same compound (for example, only one downfield signal at $\delta_{\rm C}$ = 294.5 ppm is listed for the alkylidene carbon atom) and can be better explained if the minor constituent is in fact a degradation product (presumably the decarbonylated derivative analogous to 15 and 18, vide infra). In contrast to this

observation, our NMR spectroscopic analyses (see Figures S20a,b) showed one signal set, indicating the presence of only one species in solution. In addition, the purity of the compound was verified by elemental analysis (which is missing in the original publication; for experimental details, see Supporting Information p S3), and since its solid-state structure has not been reported to date, we attempted to grow single crystals. Orange crystals were obtained from a concentrated dichloromethane solution at -30 °C, and the crystal structure of compound [Me₄N][12] was established by X-ray diffraction analysis (Figure 3); it crystallizes in the



Figure 3. Molecular structure of the anion of $[Me_4N][12]$ with thermal displacement parameters drawn at the 50% probability level. For selected bond lengths and angles, see Figure S2.

monoclinic space group $P2_1/n$. The molybdenum atom resides in a distorted octahedral environment and is coordinated to five carbonyl ligands (average Mo–C bond distances of 2.0391(18) Å and C–O distances of 1.142(2) Å) and to the alkylidene carbon atom with a significantly elongated Mo–C bond length of 2.2907(18) Å (Table 1). Indeed, this distance is

Table 1. Comparison of the Mo-C(O)Ar Bond in the Acyl Complexes Reported in This Work

compound	Mo-C [Å]
[Me ₄ N][9]	$2.268(4)^{a}$
[Me ₄ N][12]	2.2907(18)
$[\text{Li}(13) \cdot \text{Et}_2 O]_2$	2.2470(13)
$[\text{Li}(13) \cdot \text{thf}]_2$	2.251(2)
[Li(14)·Et ₂ O] ₂ , polymorph A	2.196(3)
[Li(14)·Et ₂ O] ₂ , polymorph B	2.183(2)
$[\text{Li}(19)\cdot(\text{thf})_3]$	2.2467(19)
$[\mathrm{Li}_4(25)_4 \cdot (\mathrm{Et}_2\mathrm{O})_2]$	$2.238(2)^{a}$
$[Me_4N][{2,6-(i-Pr)_2Ph}C(=O)Mo(CO)_5]$	2.2819(14)
Average value.	

comparable to the longest Mo–C distance of 2.293(2) Å³⁰ found in complexes of the type $[(R)C(=O)Mo(CO)_5]$.³¹ We have also determined the structure of analogous mesityl complex $[Me_4N][9]$ and present this in Figure S1; it features an Mo–C bond length of 2.268(4) Å (Table 1).

To complete the synthesis of the alkylidyne complex 6, reaction of the tribrominated precursor 11 with K[OC- $(CF_3)_2Me$] in THF, followed by extraction with *n*-pentane, delivered a pale brown solid in good yields. As shown by NMR spectroscopy (Figures S22a-c) and elemental analysis, the isolated product was the THF solvate of the expected (*p*-methoxybenzylidyne)molybdenum complex, [6(thf)]. Storing of a concentrated *n*-pentane solution at low temperature afforded yellow crystals, which were analyzed by X-ray diffraction, but the structure could not be refined satisfactorily because of twinning and severe disorder. However, the data

(see structure in Figure S3) qualitatively confirmed the presence of one THF molecule *trans* to the alkylidyne group. In order to obtain better crystals of [6(thf)], recrystallization was attempted from a cold solution of [6(thf)] in *n*-pentane, to which a drop of THF was added. In addition to the known yellow crystals, red crystals were obtained and subjected to X-ray diffraction analysis. The molecular structure (Figure 4)



Figure 4. Molecular structure of $cis,mer-[6(thf)_2]$ with thermal displacement parameters drawn at the 50% probability level. Only one position of the disordered THF molecule (at OS) is shown; hydrogen atoms are omitted for clarity. For selected bond lengths and angles, see Figure S4.

shows *cis,mer*-[**6**(thf)₂], in which two THF molecules are coordinated to parent compound **6**. The compound crystallizes in the monoclinic space group $P2_1/n$ and the molybdenum atom resides in a distorted octahedral environment (the bond angles around the metal center are in the range of 150.80–177.79° (*trans*) and 76.51–102.47° (*cis*)). Furthermore, the Mo–C1 triple bond length (1.757(2) Å) is comparable to those of similar molybdenum alkylidyne complexes.³¹

In contrast to the closely related DME derivative [{4- $(MeO)C_6H_4$ C \equiv Mo $(dme){OC(CF_3)_2Me}_3$ (vide supra), which was prepared in diethyl ether²⁹ or toluene,¹³ the reaction of 11 and $K[OC(CF_3)_2Me]$ in THF afforded THF complex [6(thf)] (Scheme 3). This distinction is crucial, considering that, as reported previously,²¹ THF is much more easily removed than DME to generate the solvent-free alkylidyne complex (cf. 5, Scheme 3). Indeed, recrystallization of [6(thf)] from a cold mixture of toluene and *n*-pentane or, alternatively, repeated dissolution of [6(thf)] in toluene followed by evaporation of the solvent at 50 °C and crystallization from n-pentane afforded the desired THF-free complex 6 in moderate yields. The NMR spectra of 6 (Figures S23a-c) show significant differences in comparison with the spectra of [6(thf)]. For instance, the methyl groups of the alkoxide ligands are found at $\delta_{\rm H}$ = 1.68 ppm in the former compound and are more deshielded ($\delta_{\rm H}$ = 1.84 ppm) in the latter. Similarly, an increase of the resonances for the aryl protons ($\delta_{\rm H}$ = 6.41 ppm and $\delta_{\rm H}$ = 7.04 ppm for 6) is observed for [6(thf)] ($\delta_{\rm H}$ = 6.44 ppm and $\delta_{\rm H}$ = 7.16 ppm). In the ¹⁹F NMR spectrum, the fluorine atoms give rise to a single peak, which is slightly shifted from $\delta_{\rm F} = -77.81$ ppm in [6(thf)] to $\delta_{\rm F}$ = -77.92 ppm in the THF-free complex. Furthermore, the ¹³C NMR signals of the ortho and meta positions at the aromatic ring resonate at $\delta_{\rm C}$ = 113.8 ppm and $\delta_{\rm C}$ = 132.6 ppm in [6(thf)], whereas they appear at $\delta_{\rm C}$ = 114.1 and $\delta_{\rm C}$ = 131.9 ppm in 6. Finally, the alkylidyne carbon atom is shifted downfield for 6 ($\delta_{\rm C}$ = 299.2 ppm) compared to its THF solvate ($\delta_{\rm C}$ = 294.3 ppm).

The structure of 6 (Figure 5) was confirmed by X-ray diffraction analysis of pale yellow, platy crystals; it crystallizes



Figure 5. Molecular structure of one of the two independent monomers of 6 with thermal displacement parameters drawn at the 50% probability level. A second independent molecule in the asymmetric unit, a disordered $C(CF_3)_2Me$ group (at O3), and hydrogen atoms are omitted for clarity. Relevant parts of neighboring molecules are indicated using paler colors. For selected bond lengths and angles, see Figure S5a.

in the noncentrosymmetric monoclinic space group $P2_1$ with two independent molecules in the asymmetric unit. Each molecule is connected to its neighbor through the paramethoxy group at the alkylidyne moiety, forming zigzag polymeric chains (cf. Figure S5b) with bridging angles Mo2… O1-C5, 128.67(16)° and Mo1...O5#-C25#, 118.41(16)° (operator x - 1, y, z - 1). The overall chain direction is parallel to [101]. The geometry around the pentacoordinated molybdenum atom is trigonal-bipyramidal ($\tau_5 = 0.94$ and 1.03 for the two independent molecules),³² with an axial angle of 174.28(10)° (C1-Mo1···O5#) and 179.44(11)° (C21-Mo2···O1) and equatorial mean angles of 114.72(10) and 115.39(9)°. The alkylidyne bond distances of 1.750(3) Å (Mo-C1) and 1.753(3) Å (Mo2-C21) are in the expected range for alkylidyne molybdenum complexes,³¹ whereas the intermolecular contacts of 2.7241(19) Å (Mo1···O5#) and 2.4723(19) Å (Mo2…O1) are clearly below the sum of the van der Waals radii of molybdenum and oxygen (3.65 Å),³³ although much longer than the covalent Mo-O bonds (1.896(2)-1.9052(19) Å and 1.905(2)-1.908(2) Å), indicating the weak character of the interactions.

Synthesis of a (2,4,6-Trimethoxybenzylidyne)molybdenum Complex. Complex 7 was prepared following the low-oxidation-state route (see Scheme 3). However, the synthesis of this *ortho-* and *para*-methoxy-substituted benzylidyne complex was unusually challenging, and the protocol was adapted to accomplish this goal. First, the synthesis of $[Me_4N][\{2,4,6-(MeO)_3C_6H_2\}C(=O)Mo(CO)_5]$ ($[Me_4N]-$ [13]) starting from 2,4,6-trimethoxyphenyl lithium and $[Mo(CO)_6]$ in diethyl ether, followed by salt metathesis with $[Me_4N]Br$ in degassed water, afforded a pale yellow solid,



Figure 6. (a) Molecular structure of $[\text{Li}(13)\cdot\text{Et}_2O]_2$ with thermal displacement parameters drawn at the 50% probability level. The second molecule in the inversion-symmetric dimer (except for atoms labeled with #) and hydrogen atoms are omitted for clarity. (b) Molecular structure of one polymorph (A) of $[\text{Li}(14)\cdot\text{Et}_2O]_2$ with thermal displacement parameters drawn at the 50% probability level. The second molecule in the inversion-symmetric dimer (except for atoms labeled with #) and hydrogen atoms are omitted for clarity. (c) Molecular structure of $[\text{Li}(15)\cdot(\text{Et}_2O)_2]_n$ with thermal displacement parameters drawn at the 50% probability level. Contacts to the next units of the polymeric structure are indicated by dashed bonds. Hydrogen atoms and one position of the disordered ethyl group at O10 are omitted for clarity. For selected bond lengths and angles, see Figures S6–S8.





which was assumed to contain molybdenum species 13 and, as judged by NMR spectroscopy (see Figures S25a-d), significant amounts of 1,3,5-trimethoxybenzene and [Mo- $(CO)_6$] that increased with time. In addition, not all the expected signals for [Me₄N][13] were observable; the signal of the acyl carbon atom (ArC(=O)Mo), usually found at $\delta_{\rm C}$ > 300 ppm, was missing in the ${}^{13}C{}^{1}H$ NMR spectrum. These findings suggested the formation of the decarbonylated species $[Me_4N][{2,4,6-(MeO)_3C_6H_2}Mo(CO)_5], [Me_4N][15]$ (see Scheme 3, bottom left), a hypothesis that was confirmed later by solid-state structural analysis (vide infra). Presuming that the desired compound is unstable in water, the isolation of the intermediate lithium complex $Li[{2,4,6-(MeO)_3C_6H_2}C (=O)Mo(CO)_{5}$ (Li[13]) was attempted, which resulted in a mixture of Li[13], its decarbonylated counterpart (Li[{2,4,6- $(MeO)_{3}C_{6}H_{2}Mo(CO)_{5}$, Li[15]), and minor amounts of 1,3,5-trimethoxybenzene, as revealed by NMR spectroscopy (see Figures S26a,b). Fortunately, our efforts to separate the complexes through fractional crystallization yielded several vellow-orange crystals from an Et_2O/n -hexane solution at -40 °C. Interestingly, inspection under the microscope revealed three different types of crystals. In all three cases single crystals suitable for X-ray diffraction analysis were available and the determined molecular structures are presented in Figure 6. Remarkably, the structures unfold the mechanism of the CO deinsertion (Scheme 4) and show three species involved in this reaction: (i) desired complex Li[13], (ii) aryl complex Li[15], and (iii) intermediate species $Li[{2,4,6-(MeO)_3C_6H_2}]C(=$ $OMo(CO)_4$ (Li[14]), in which a CO ligand has been released but the carbonyl group in the acyl moiety has not yet been deinserted. In the latter structure, the vacant coordination site arising at the metal center is occupied by a chelating methoxy group of the aryl unit, giving additional stability to the unsaturated tetracarbonyl complex.

Compound Li[13] crystallizes as pale yellow prisms in the triclinic space group $P\overline{1}$ as the diethyl ether solvate and is composed of centrosymmetric dimers of the type [Li(13)]. $Et_2O]_2$ in which the lithium atoms bridge the two halves of the molecule. The molybdenum atom resides in a distorted orthogonal environment with average angles of $173.51(6)^{\circ}$ (trans) and 90.07(6)° (cis). The Mo-C1 distance of 2.2470(13) Å (Table 1) is particularly long and characteristic of a Mo-C single bond, underlining the acyl character of the substituent (Ar-C(=O)-Mo) rather than a carbene structure (Ar-C(O)=Mo). The lithium cation is tetracoordinated by the carbonyl group of the acyl moieties (O1 and O1#, operator 1 - x, 1 - y, 1 - z), one *ortho*-methoxy group of the aromatic ring (O2) and one diethyl ether molecule. Calculation of the structural index parameter $\tau_4 = (360 - \alpha - \beta)/141 =$ $0.80(19)^{34}$ indicates a distorted trigonal pyramidal geometry at

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the lithium atom, in which the apex (O1) is tilted away from O10 $(O1 \cdots Li - O10, 107.27(13))$.

The highly air-sensitive, yellow-orange dichroic crystals of complex Li[14] are triclinic with space group $P\overline{1}$ and, as observed for Li[13], reveal a dimeric structure of its diethyl ether solvate ($[Li(14) \cdot Et_2O]_2$) symmetrically bridged by two tetracoordinated lithium atoms (to O1, O1#, O4#, and one solvent molecule, operator 1 - x, 1 - y, 1 - z), which adopt a distorted trigonal pyramidal geometry $(\tau_4 = 0.80(4))^{34}$ with the apex (O1#) tilted away from O9 (O1#...Li-O9, $110.3(3)^{\circ}$). The molybdenum atom resides in a distorted orthogonal environment with bond angles in the range of 168.81-174.59° (trans) and 72.97-102.15° (cis) and mean angles of $171.09(14)^{\circ}$ (*trans*) and $90.12(12)^{\circ}$ (*cis*). Notably, as observed for a similar structure,³⁵ the C1-Mo-O2 angle is particularly acute $(72.97(9)^\circ)$ because of the chelating nature of the acyl ligand, which forms a five-membered ring upon coordination of one methoxy group (through O2) to the metal center. This ring is almost planar, but exhibits a slight envelope conformation in which the Mo atom lies 0.40 Å out of the plane of the other four atoms. The Mo-C1 bond of 2.196(3) Å is 5.1(4) pm shorter than that in complex Li[13] (Table 1), but is still in the range of a single bond. Interestingly, successive experiments reproduced the concomitant crystallization of the different species and on one occasion also produced orange crystals of a second polymorph (B) of Li[14], which crystallized in the monoclinic space group $P2_1/n$ (see Table S9 and Figure S9). The coordination geometry and structural parameters are very similar to those discussed for polymorph A.

Finally, aryl complex Li[15] crystallizes in the monoclinic space group $P2_1/n$ as a diethyl ether disolvate, forming highly air-sensitive, blade-shaped, colorless crystals. In the crystal structure, the complex is a 1D-coordination polymer [Li(15)· (Et₂O)₂]_n organized in chains parallel to the *b* axis (cf. Figure S8b), in which the lithium cations bridge the molybdenum fragments at O2 and O4, the *para*-methoxy substituent of the aryl ring and the carbonyl ligand coordinated *trans* to this ring, respectively. The hexacoordinated molybdenum core resides in an orthogonal environment (average angles: 177.92(8)° (*trans*) and 90.00(8)° (*cis*)), whereas the four-coordinate geometry around the lithium atom is close to tetrahedral ($\tau_4 =$ 0.90(3)),³⁴ with a particularly wide angle of 124.89(19)° for O9–Li–O10. The Mo–C_{Ar} distance (2.312(2) Å) is indicative of a single bond.

Carbonyl deinsertions are a classical type of organometallic reaction and have already been described for Fischer carbene complexes of chromium,³⁶ molybdenum³⁵ and tungsten,³ which led to the formation of carbene(tetracarbonyl) chelate complexes similar to Li[14]. In order to obtain some kinetic information on the decarbonylation of Li[13], the reaction progress was monitored by NMR spectroscopy. Assuming that the concentration of intermediate Li[14] is negligible (it is not observed in the NMR spectra) and the CO deinsertion accordingly occurs rapidly to give Li[15], the loss of CO in Li[13] must be the rate-determining step, and its consumption can be followed. The natural logarithm of the peak integral (ln $A_{\text{Li}[13]}$) against reaction time shows a linear dependence (Figure S39), which suggests that the rate law is first-order in 13 (r = k[13]; k, first-order rate constant). The observed rate constant can be derived from the slope of the regression line and has a value of $k_{293} = 1.26(6) \ 10^{-6} \ s^{-1}$, which corresponds to a half-life of $t_{1/2} = 6.4(3)$ days and a free activation energy of $\Delta G^{\ddagger} = 25.51(19) \text{ kcal mol}^{-1} (106.7(8) \text{ kJ mol}^{-1}) \text{ at } T = 293 \text{ K.}$

In view of these results, we tried to circumvent the decarbonylation problem. On the basis of the calculated halflife, the deinsertion process can be assumed to be very slow in solution at ambient temperature, which does not explain the observed mixtures of complexes. Hence, the deinsertion reaction must be accelerated during isolation of the product, probably because of removal of the solvent under dynamic vacuum, which promotes the release of carbon monoxide and governs the outcome of the reaction. For this reason, we decided to avoid the solvent evaporation step and explored new conditions to isolate the acyl complex. Accordingly, we isolated the complex from the reaction mixture by precipitation with *n*-hexane (Scheme 3), giving Li[13] as a yellow powder in moderate yields, the purity and homogeneity of which was confirmed by NMR spectroscopy (Figures S27a,b) and elemental analysis and powder X-ray diffraction (Figure S10b). It should be mentioned here that the solvent choice (diethyl ether, tetrahydrofuran, and *n*-hexane) and ratio (8:1:14) were critical to avoid the precipitation of byproducts or unreacted $[Mo(CO)_6]$. The latter is moderately soluble in all three solvents, so small amounts remain in solution after precipitation. In addition, large block-shaped crystals of the THF solvate $[Li(13) \cdot thf]_2$ precipitated from the filtrate and were analyzed by X-ray diffraction (Figure S10a); structural parameters are similar to those discussed for $[Li(13) \cdot Et_2O]_2$.

Subsequently, the alkylidyne complex mer-[{2,4,6- $(MeO)_{3}C_{6}H_{2}C \equiv Mo(Br)_{3}(dme)$ (16) was prepared directly from Li[13] (Scheme 3) to avoid decarbonylation during the classical salt metathesis step with [Me₄N]Br. Thus, oxidation to the alkylidyne complex was accomplished by treatment with oxalyl bromide and bromine at -80 °C, although the reaction did not proceed as cleanly as usual, and removal of some unidentified impurities was unsuccessful (see Figures S28a-c). Nevertheless, a crude product containing indeterminate amounts of 16 was obtained in moderate yields and was used without further purification in the next step. Fortunately, the reaction of crude 16 with three equivalents of K[OC- $(CF_3)_2$ Me] in THF (Scheme 3), followed by extraction with *n*hexane and recrystallization from *n*-pentane, afforded yelloworange dichroic plates of pure [7(thf)], as determined by X-ray diffraction analysis (Figure 7). The compound crystallizes in the triclinic space group P1 with two independent molecules in the asymmetric unit; these differ in the orientation of the ligand at O4 but are otherwise similar. The molybdenum atoms are pentacoordinated and reside in a distorted trigonalbipyramidal geometry, as indicated by the structural index parameters $\tau_5 = 0.89$ and $\tau_5' = 0.82$.³² The alkoxide ligands occupy the equatorial positions, whereas the THF molecule is attached trans to the alkylidyne group with axial angles of 174.63(7)° (C1–Mo–O7) and 173.55(7)° (C1′–Mo′–O7′). The Mo-O distances in the alkoxide ligands range from 1.9005(13) Å to 1.9226(13) Å, which is commonly found for covalent bonds; in contrast, the THF molecule is weakly coordinated, as can be concluded by the considerably longer Mo-O bond lengths of 2.4256(13) Å (Mo-O7) and 2.4007(13) Å (Mo'-O7').

In addition, the structure of the compound was confirmed by NMR spectroscopy. The experimental elemental composition, however, indicated a partial loss of THF (\sim 0.5 equiv, probably because of the thorough drying of the sample), which supports the assumption that the THF is weakly coordinated.



Figure 7. Molecular structure of [7(thf)] with thermal displacement parameters drawn at the 50% probability level. Only one independent molecule is shown; all hydrogen atoms are omitted for clarity. For selected bond lengths and angles, see Figure S11.

As expected, a subtle but nontrivial modification of the workup (extraction of the product with *n*-pentane, then evaporation of the solvent at 50 °C followed by several cycles of dissolution/ evaporation) afforded THF-free complex 7 in modest yields. As discussed above for the para-anisole analogs, compounds [7(thf)] and 7 can be distinguished by NMR spectroscopy (Figures S29a-c and S30a-c). For example, a decrease of all 1 H shifts (1.87, 3.14, 3.18, 5.64 ppm) can be observed for the latter compared to its THF counterpart (1.94, 3.17, 3.21, 5.66 ppm). Moreover, in the ¹⁹F NMR spectrum, the fluorine resonance for 7 (-78.1 ppm) is slightly high-field-shifted in comparison to that for [7(thf)] (-77.9 ppm). The most relevant differences in the ¹³C NMR spectrum are found for the signals of the alkoxide ligands (18.0, 84.8, and 123.9 ppm for [7(thf)] vs 18.2, 84.5, and 123.6 ppm for 7) and the alkylidyne carbon atom, which resonates at 292.6 ppm in [7(thf)] and at a lower field in 7 (296.73 ppm).

Single crystals of 7 were obtained from a cold *n*-pentane solution at -35 °C, which allowed confirmation of the structure (Figure 8a) by X-ray diffraction analysis. The yelloworange dichroic prisms crystallize in the monoclinic space group $P2_1/n$. Analogous to 6, the complex is a 1Dcoordination polymer in the solid state (Figures 8b and S12b), in which the para-substituent of the alkylidyne moiety is connected via the n glide plane to the molybdenum atom of the neighboring molecule, forming zigzag chains with a bridging angle of 124.16(12)° (C5-O2…Mo#) and overall direction parallel to [101]. The molybdenum center features a nearly ideal trigonal-bipyramidal geometry ($\tau_5 = 0.97$),³² wherein the fluorinated ligands occupy the equatorial positions but are slightly tilted out of the plane toward O2#. The molybdenum-carbon triple bond of 1.758(2) Å is in the expected range for alkylidyne complexes and the axial angle C1-Mo···O2# between the alkylidyne and the para-methoxy group of the next molecule is nearly linear $(177.66(7)^\circ)$. This intermolecular contact is characterized again by an elongated Mo…O2# bond of 2.5664(15) Å, which confirms the weak nature of the interaction. Interestingly, the unprecedented

Article



C9%

a)

Figure 8. (a) Molecular structure of 7 with thermal displacement parameters drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Contacts to neighboring molecules are shown using paler colors. For selected bond lengths and angles, see Figure S12a. (b) Representation as a wireframe model of a polymer string of 7 seen along the a axis.

formation of these alkylidyne-based, single-chain coordination polymers is not affected by the ortho-substitution at the benzylidyne ring, but depends strongly on the nature of the ancillary ligands. Hence, such intermolecular contacts are not observed, for example, in complex 2^{26} , which bears triphenylsilanolate ligands, certainly more sterically demanding than the fluorinated alkoxides. Unfortunately, as will be discussed in the last section, the bridging of single molecules in the solid state by the ether functional group did not lead to any significant enhancement of the stability toward air or moisture.

The question remains whether the ether functionalities at the ortho positions could promote the stabilization of the MCBD generated upon addition of a small alkyne to molybdenum alkylidyne 7. In our hands, the only presumably identified products after reacting 7 with 3-hexyne were the propylidyne complex $[EtC \equiv Mo\{OC(CF_3)_2Me\}_3]$ and the mixed acetylene (ArC=CEt) formed by cross metathesis. Crystallization attempts of the same reaction applying lowtemperature conditions (as described for recently isolated MCBD complexes)^{5e,38} afforded no crystals of the desired MCBD complex. These unsuccessful attempts underline the fact that the MCBD intermediates in the alkyne metathesis catalytic cycle, formed by [2 + 2] cycloaddition of an alkyne with an alkylidyne complex, feature a low energy barrier,⁵ which makes it extremely difficult to kinetically trap and isolate the MCBD species. This is particularly true if the complexes perform as highly active catalysts, such as 5 and similar molybdenum alkylidynes bearing the hexafluorinated alkoxides.

2-Isopropoxybenzoyl and 8-Methoxynaphthoyl Complexes. In spite of the unsuccessful stabilization of the MCBD species involving the ortho-substituted benzylidyne molybdenum complex 7, we focused on the preparation of the envisaged isopropoxy-functionalized benzylidyne complex 8 (see Figure 2). As usual, the synthetic pathway began with the reaction of 2-isopropoxyphenyl lithium (generated in situ by metal-halogen exchange of 2-bromo-1-isopropoxybenzene and *n*-butyl lithium at -20 °C) with $[Mo(CO)_6]$ in diethyl ether to furnish the anionic benzovl complex Li[{2-(i- $PrOC_6H_4$ C(=O)Mo(CO)₅], Li[17], which was converted to $[Me_4N][17]$ via salt metathesis in degassed water. However, the ¹H NMR spectrum (Figure S31a) revealed two sets of resonances for the isopropyl moiety and for the aromatic protons, again suggesting (cf. [Me₄N][13], vide supra) the presence of two molybdenum species in solution. Accordingly, the signal duplication was also observed in the ${}^{13}C{}^{1}H$ NMR spectrum (Figure S31b), except for the most low-field-shifted signal at about $\delta_{\rm C}$ = 303 ppm, which correlates with the acyl carbon atom (ArC(=O)Mo). Colorless prisms precipitated from the NMR solution and their molecular structure was established by X-ray diffraction analysis, confirming the nature of the second component in the mixture, the anionic arylpentacarbonylmolybdenum complex [Me₄N][{2-(*i*-PrO)- C_6H_4 }Mo(CO)₅] ([Me₄N][18], Figure 9). As discussed above



Figure 9. Molecular structure of one anion of $[Me_4N]$ [18] with thermal displacement parameters drawn at the 50% probability level. The second independent anion in the asymmetric unit and the two cations ($[Me_4N]^+$) are omitted. For selected bond lengths and angles, see Figure S13.

for 13, acyl complex 17 underwent a decarbonylation process, in which the released CO ligand was replaced by the deinserted carbonyl group of the acyl unit to give 18. Compound $[Me_4N][18]$ crystallizes with two independent molecules per unit cell in the monoclinic, noncentrosymmetric space group *P*2₁ and adopts essentially an octahedral geometry around the zero-valent molybdenum atom (average angles for each independent molecule, respectively: *trans*, 176.2(4) and 172.8(5)°; *cis*, 90.0(4) and 90.1(5)°). The Mo–C_{Ar} bond lengths of 2.275(9) and 2.299(9) Å, slightly shorter than that of complex 15, are indicative of a Mo–C single bond and are in the expected range for aryl polycarbonyl molybdenum complexes³¹ (cf. structure of $[(C_6F_5)Mo(CO)_5]^{-}$).³⁹

Because of similar properties of both compounds, their separation failed. Moreover, we realized that the decarbonylation already takes place (at least partially) during the first step of the reaction, as revealed by an NMR sample of intermediate Li[17], which presented the characteristic pattern with duplicated resonances besides, again, the downfield signal in the carbon NMR spectrum. Instead, the expedient protocol modifications introduced into the synthesis of Li[13], involving its precipitation with *n*-hexane (Scheme 3), were applied successfully in the isolation of Li[17] in pure form (see Figures S33a,b and the Experimental Section for details). Indeed, the precipitation approach gives access to functionalized acyl complexes (Fischer carbene precursors) for which suitable synthetic strategies were missing. To illustrate the applicability of the method, the synthesis of the unreported $Li[(8-MeO-Naph)C(=O)Mo(CO)_5]$ (Li[19], Naph = 1naphthyl; for details, see Scheme 3, Supporting Information p S4, and Figures S34 and S35) was achieved in good yield upon treatment of $[Mo(CO)_6]$ with 8-methoxynaphthyl lithium in diethyl ether and precipitation with *n*-hexane. The molecular structure was additionally determined by X-ray diffraction analysis of pale yellow acicular single crystals of $[\text{Li}(19)\cdot(\text{thf})_3]$ (Figure S14), confirming the formation of the acyl complex, with structural parameters similar to those found for Li[13] (Table 1).

Notwithstanding, the present approach faces some limitations. For example, in an attempt to improve the synthesis of the *p*-anisole derivative presented above, benzylidyne complex **11**, the isolation of acyl precursor Li[**12**] proved to be more difficult than expected (characterization of the complex was only possible in solution by NMR spectroscopy; for details, see **Supporting Information p S4**). Thus, direct oxidation omitting salt metathesis to access **11** was not considered further, and it was obtained as described above.²⁶ In addition, it has to be noted that this procedure is only straightforward if the lithium aryl compounds are available as pure substances. Otherwise, the use of, e.g., *n*-BuLi or *t*-BuLi to generate the lithium organyl in situ can yield LiBr as a byproduct, which could interfere in the isolation of the acyl complex by coprecipitation.

Finally, with acyl complexes Li[17] and Li[19] in hand, the preparation of the alkylidyne complexes [ArC=Mo- $(Br)_3(dme)$] (Ar = 2-(*i*-PrO)C₆H₄ (**20**), 8-MeO-Naph (**21**)) via treatment with oxalyl bromide and bromine in the presence of DME at subambient temperatures was attempted (Scheme 5). We were surprised to find that the reaction repeatedly resulted in a mixture of decomposition products,⁴⁰ suggesting that the introduced substituents may be incompatible with the conditions of the low-oxidation-state route. We anticipate at this point that the cross-metathesis approach using benzylidyne-transfer reagents (ArC=CCF₃ or ArC=CSiMe₃),^{13,14} as mentioned in the introduction, may be a suitable alternative to generate the projected alkylidynes [ArC=Mo{OC- $(CF_3)_2Me_3]$ (Ar = 2-(*i*-PrO)C₆H₄ (8), 8-MeO-Naph (22)), although in such case the removal of DME may be problematic.

Bulky Benzylidyne Molybdenum Complexes. The second strategy to improve the stability of the alkylidyne complexes consists in increasing the steric bulk of the benzylidyne moiety. Hence, we attempted first the preparation of the (2,4,6-triisopropyl)benzylidyne complex [ArC \equiv Mo-{OC(CF₃)₂Me}₃] (Ar = (2,4,6-triisopropyl)phenyl, 23) from the corresponding tribromide species *mer*-[ArC \equiv Mo-(Br)₃(dme)] (24), which in turn can be synthesized from [Mo(CO)₆] and (2,4,6-triisopropyl)phenyl lithium via the low-oxidation-state route (Scheme 3). Our precipitation approach, however, was not employed here because of

Scheme 5. Attempted Synthesis of Alkylidyne Complexes 8 and 20–22



difficulties in the isolation of the lithium organyl, and instead, the acyl complex $[Me_4N][(ArC(=O)Mo(CO)_5], [Me_4N]-$ [25], was obtained in rather low yields after salt metathesis in deoxygenated water (for details, see Supporting Information p S5). Because of the low yields, we explored again the possibility of isolating lithium derivative Li[25]; therefore, the following changes were introduced in the workup procedure. Combination of $[Mo(CO)_6]$ and in situ generated (2,4,6-triisopropyl)phenyl lithium followed by solvent removal under reduced pressure yielded a mixture of acyl complex Li^[25] and lithium bromide; this mixture was subsequently extracted with dichloromethane to remove the inorganic salt. Precipitation of the extract with *n*-pentane afforded the desired product in acceptable yields, which was then successfully oxidized using standard conditions to give complex 24 in excellent yields. In the final step, bromide exchange with $K[OC(CF_3)_2Me]$ in THF, followed by exhaustive drying at slightly elevated temperatures and extraction with *n*-pentane, produced desired alkylidyne complex 23 after recrystallization in dichloromethane at low temperatures. Characterization by means of NMR spectroscopy (Figures S38a-c) confirmed the structure of the complex; for example, the ¹H NMR spectrum displays the expected doublets (1.20, 1.25 ppm) and septets (2.98, 3.86 ppm) for the isopropyl groups at the para and ortho positions of the aryl moiety, respectively. In addition, the singlet at 1.86 ppm attributable to the methyl groups of the alkoxide ligands integrates to nine protons, whereas the resonance for the aromatic protons appears at 6.96 ppm. In the ¹³C{¹H} NMR spectrum the isopropyl substituents give rise to four signals at 23.9, 24.7, 30.7, and 34.8 ppm, whereas the four expected resonances for the aryl ring are found in the aromatic region (121.5, 141.4, 152.8, and 153.4 ppm). Furthermore, the carbon atoms in the alkoxide ligands are observed as a singlet (CH₃, 19.3 ppm), a quartet (CF₃, 123.3 ppm), and a poorly resolved septet (quaternary C, 83.8 ppm). Finally, the most downfield shift (320.2 ppm) can be assigned to the alkylidyne carbon atom. Naturally, the fluorine NMR spectrum consists of only one singlet at -78.2 ppm.

The solid-state structures of alkylidyne complex **23** and its precursors **24** and Li[**25**] were additionally determined by Xray diffraction analysis. Acyl species Li[**25**] crystallizes from an *n*-pentane solution in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ and consists of tetramers of diethyl ether hemisolvate $[Li_4(25)_4 \cdot (Et_2O)_2]$ (Figure 10). The molecule has



Figure 10. (a) Molecular structure of one Li(**25**) unit of $[Li_4(25)_4: (Et_2O)_2]$ with thermal displacement parameters drawn at the 50% probability level. Neighboring atoms of other units are included using paler colors. Hydrogen atoms are omitted for clarity. (b) Representation of the tetrameric structure as a wireframe model. For selected bond lengths and angles, see Figure S15a.

approximate- C_2 symmetry along the *b* axis (see Figure S15b for details) and can be divided virtually into two halves. Hence, considering only one half of the molecule, two Li(25) fragments are bridged by both lithium cations through the oxygen atoms at the acyl groups forming a pair, $Li_2(25)_2 \cdot Et_2O$. The second pair, rotated 180° around the pseudo- C_2 axis, is joined to the first through interactions of one carbonyl ligand at each molybdenum core with the inner lithium atom of the other pair. This arrangement results in a [5.5.5.]paddlane-like structure, in which the four O-C-Mo-C-O bridges intersect at the interior lithium cations (Li1 and Li3). These tetracoordinated atoms are best described as distorted tetrahedral (Li1, $\tau_4 = 0.877(3)$; Li3, $\tau_4 = 0.899(3)$),³⁴ whereas the outer lithium ions (Li2 and Li4) display a distorted trigonal planar or Y-shaped geometry with the smallest O-Li-O bond angle approximately equal to 90°. The molybdenum centers show essentially octahedral geometries, and the Mo-C(=O)bond lengths (2.231(2)-2.245(2) Å, Table 1) and the Mo-CO distances (1.981(2)-2.098(3) Å) are all in the expected range.

Brown-orange dichroic needles of 24 were grown from dichloromethane/*n*-pentane solution at -30 °C and the molecular structure is illustrated in Figure 11. The compound



Figure 11. Molecular structure of **24** with thermal displacement parameters drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. For selected bond lengths and angles, see Figure S16.

crystallizes in the monoclinic space group $P2_1/n$ and shows, as expected, the structure of the *mer*-isomer, in which the hexacoordinated molybdenum complex exhibits a distorted octahedral geometry (angles: *trans*, 178.6(3)–164.169(19)°; *cis*, 72.86(12)–97.11(14)°) in which the Mo atom lies 0.26 Å out of the plane of Br1, Br2, Br3, and O2 in the direction of C1. Thus, the bromide ligands are arranged in a T-shape around the metal center; the two oxygen atoms of the DME molecule are chemically inequivalent and force a particularly acute angle O1–Mo–O2 of 72.86(12)° by chelation. The alkylidyne bond (Mo–C1, 1.740(4) Å) is unremarkable and forms a virtually linear angle of 178.6(3)° with the aryl moiety.

Finally, yellow crystals of **23** were grown from *n*-pentane solution at -30 °C, and the molecular structure is presented in Figure 12. The complex crystallizes in the monoclinic space group $P2_1/n$ and features a distorted tetrahedral geometry ($\tau_4 = 0.9338(9)$),³⁴ in which the molybdenum atom is coordinated by the three fluorinated alkoxide ligands and the benzylidyne unit with typical Mo–O bond distances (1.8892(14)–1.9237(14) Å) and a Mo–C1 bond length in the expected



Figure 12. Molecular structure of **23** with thermal displacement parameters drawn at the 50% probability level. Only one position of the disordered isopropyl group (at C7) is shown; hydrogen atoms are omitted for clarity. For selected bond lengths and angles, see Figure S17.

range (1.745(2) Å). The Mo-C1-C2 bond angle of $174.41(15)^{\circ}$ deviates slightly from linearity.

Our efforts to prepare further bulky derivatives of the benzylidyne complex failed for various reasons. For example, the synthesis of the 2,6-diisopropylphenyl analog was prevented by unselective lithiation and miserable yields of the benzoyl precursor $[Me_4N][\{2,6-(i-Pr)_2C_6H_3\}C(=O)Mo(CO)_5]$ (for further details, see Supporting Information p S6), for which solely the molecular structure could be established by X-ray diffraction analysis (Figure S18). The attempted preparation of the even more sterically hindered tris(*tert*-butyl)benzoyl complex $[Li][\{2,4,6-(t-Bu)_3C_6H_2\}C(=O)Mo(CO)_5]$ unexpectedly produced the already known η^6 -(1,3,5-tri-*tert*-butylbenzene)tricarbonylmolybdenum(0) complex⁴¹ as revealed by comparison of the cell parameters of single crystals obtained at -35 °C from a CH₂Cl₂/*n*-pentane solution of the product.

Activity in Alkyne Metathesis. Both complexes [6(thf)]and 6 and complex 7 are excellent initiators of the alkyne metathesis reaction and achieve 90, 94, or 90% conversion, respectively, of our standard substrate^{9c} BnO(CH₂)₂C \equiv CMe (26a) into BnO(CH₂)₂C \equiv C(CH₂)₂OBn (27) in 10 min (Figure 13) with a catalyst loading of 1 mol % (not optimized;



Figure 13. GC conversion—time plot of **26a** (0.25 mmol) into **27** in toluene (0.2 M) with 1 mol % catalyst loading in the presence of molecular sieves 5 Å (250 mg) and *n*-decane (0.25 mmol) as internal standard. The inset shows an expansion of the diagram for clarity.

 $\text{TOF}_{10 \text{ min}} ([6(\text{thf})]) = 9.0 \text{ min}^{-1}, \text{TOF}_{10 \text{ min}} (6) = 9.4 \text{ min}^{-1}, \text{TOF}_{10 \text{ min}} (7) = 9.0 \text{ min}^{-1})$ in the presence of molecular sieves. The presence of the attached THF molecule does not interfere significantly with the catalytic performance, suggesting that THF is displaced easily by the alkyne substrate. In the same way, it is reasonable to affirm that the intermolecular coordination in 6 and 7 disappears upon dissolution or alkyne binding. Related to this phenomenon, weak coordination of

heteroatoms (such as in Ph₃SiOH or CH₃CN) to the molybdenum atom in alkylidyne complexes has been briefly discussed,^{26,29} focusing on the geometrical implications and how this circumstance affects the binding of the alkyne substrate. To test our hypothesis that intermolecular contacts can increase the stability of the complexes, at least in the solid state, a sample of 7 was exposed for 1 h to air before the catalytic test was repeated (for details, see Supporting Information p S7). Unfortunately, the results fell short of our expectations, as the metathesis conversion decreased dramatically, and after 1 h only a marginal conversion of 4% was determined by gas chromatography. Finally, the ability of complex 23 to promote alkyne cross-metathesis was tested in the conversion of both the internal alkyne 26a and the terminal alkyne BnO(CH₂)₂C=CH (26b) into 27 applying standard conditions (for details, see Supporting Information p S7). Even though the activity (97 or 92% conversion after 10 min, respectively) was indeed comparable with that of 5^{21} 6, or 7, the bulky benzylidyne presented no signs of air stability, and after exposure of the complex to air for just 10 min, the conversion was negligible.

CONCLUSIONS

The portfolio of molybdenum alkylidyne complexes bearing fluorinated alkoxides has been extended by the installation of ether substituents or sterically demanding isopropyl groups on the benzylidyne moiety, a strategy that may contribute to increasing the air stability of the complexes. While the synthesis of complexes 6, 7, and 23 was successful, the preparation of other benzylidyne derivatives (8, 22) was not feasible under the applied conditions. However, after the established synthetic protocol was deliberately modified, it was possible to isolate and characterize the corresponding acyl precursors. The principal problem was the undesired deinsertion of the carbonyl fragment at the acyl moiety. Thus, the lithium acyl complexes were isolated directly by precipitation, before salt metathesis in water, to avoid decarbonylation during the solvent evaporation step, giving a more straightforward access to acylpentacarbonylmolybdenum complexes featuring challenging functional groups.

Remarkably, complexes 6 and 7 feature in the solid state a polymeric structure, in which the methoxy group at the *para*position is bridged to the neighboring molecule forming zigzag chains. This is, to the best of our knowledge, the first example of an intermolecular coordination involving metal alkylidynes. Unfortunately, neither the presence of intermolecular contacts in the solid state nor the increase of the steric bulk in 23 positively affected the stability of the complexes. Whether more Lewis basic functionalities such as amines or phosphines may be more successful in fulfilling this challenge is currently under investigation in our group.

EXPERIMENTAL SECTION

General Considerations. All operations were performed under an atmosphere of dry argon using Schlenk and vacuum techniques. Solvents (except THF) were purified and dried by an MBraun GmbH solvent purification system and degassed by argon-bubbling for at least 15 min prior to use. THF and deuterated solvents were dried by conventional methods⁴² and stored under argon over molecular sieves. Celite diatomaceous earth (D.E.) was stored at least 3 days in an oven at 120 °C.

Starting Materials. Compounds 11,²⁶ 26a,^{9c} and 26b²¹ were synthesized according to the literature. The syntheses of K[OC- $(CF_3)_2Me$], 8-methoxynaphthyl lithium and 4-methoxyphenyl lithium

are described in Supporting Information pp S3-S6. All other reagents were obtained commercially. Bromine (Acros), 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (Apollo Scientific), 2-bromo-1,3-diisopropylbenzene (Sigma-Aldrich), 2-bromo-1,3,5-triisopropylbenzene (Sigma-Aldrich), *n*-butyl lithium (Acros), *t*-butyl lithium (Sigma-Aldrich), 2-isopropoxyphenyl bromide (TCI), molybdenum hexacarbonyl (ABCR), 1,3,5-trimethoxybenzene (Acros), 1-methoxynaphthalene (TCI), and oxalyl bromide (Sigma-Aldrich) were used without further purification. Bromanisole (Fluka) was distilled under reduced pressure (68 °C/5.2 mbar) before use. n-Decane (Alfa Aesar) and 1,2-dimethoxyethane (Alfa Aesar) were dried over Na/benzophenone and stored under argon over molecular sieves. The molecular sieve 5 Å MS (powder < 50 μ m, Sigma-Aldrich) for metathesis reactions was dried for 24 h at 180 °C under vacuum prior to use. Potassium hydride dispersion in mineral oil (30%, Acros) was washed several times with *n*-hexane on a frit and dried under vacuum before use.

Equipment. Gas chromatography (GC) was executed on a Hewlett-Packard 5890 SERIES II using a DB5-HT column (l = 30 m, d = 0.25 mm) and FID detection (310 °C). The sample (1 μ L) was injected at 250 °C with a split/splitless ratio of 1:10 and heated in the column from 50 to 300 °C with a heating rate of 10 °C min⁻¹. For calibration, *n*-decane was used as an internal standard. Elemental analyses (C, H, N) were determined by combustion and gas chromatographic analysis on a VarioMICRO Tube instrument equipped with WLD and IR detectors.

NMR Spectroscopy. NMR spectra were recorded on Bruker DPX 200, AV II 300, AV III HD 300, AV III 400, AV III HD 500, or AV II 600 spectrometers. Chemical shifts (δ) are reported in ppm (parts per million) and are referenced relative to internal TMS (tetramethylsilane, $\delta_{\rm H}$ 0.00 ppm), to residual solvent ¹H signals (C₆D₆, $\delta_{\rm H}$ 7.16; THF- d_8 , $\delta_{\rm H}$ 1.72; CD₂Cl₂, $\delta_{\rm H}$ 5.32; toluene- d_8 , $\delta_{\rm H}$ 2.08), to the 13 C resonance of the solvents (C_6D_6 , δ_C 128.06; THF- d_8 , δ_C 25.31; CD_2Cl_2 , δ_C 53.84; toluene- d_8 , δ_C 20.43) or to virtual internal $CFCl_3$ (the observation frequencies of a dilute solution of CFCl₃ in the deuterated solvents were determined earlier). The number of protons (n) for a given resonance is indicated by nH. All ${}^{13}C$ and ${}^{19}F$ NMR spectra are proton-decoupled, and the number of protons attached to each carbon atom was determined by ¹³C-DEPT135 experiments. If required, then signals were assigned by 2D H,H-COSY, H,H-NOESY, H,H-ROESY, H,C-HSQC, and H,C-HMBC NMR experiments. The following abbreviations are used for spin multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet; app, apparent; br, broad.

X-ray Diffraction Studies. Single crystals were examined and mounted in perfluorinated inert oil and transferred to the cold gas stream of the diffractometer. Data were recorded on an Oxford Diffraction Nova A diffractometer, using mirror-focused Cu K α radiation (compounds [6(thf)], 7, [7(thf)], [Me₄N][12], [Li(13). thf]₂, [Li(14)·Et₂O]₂ (polymorphs A and B), [Li(15)·(Et₂O)₂]_n, [Me₄N][18], 23, 24, [Me₄N][$\{2,6-(i-Pr)_2C_6H_3\}C(=O)Mo(CO)_5$]. CH_2Cl_2 , and $Li[O \equiv MoBr{OC(CF_3)_2Me}_3] \cdot (thf)_2$) or an Oxford Diffraction Xcalibur E diffractometer using graphite-monochromated Mo K α radiation (compounds 6, *cis,mer*-[6(thf)₂], [Me₄N][9], $[\text{Li}(13)\cdot\text{Et}_2\text{O}]_2$, $[\text{Li}(19)\cdot(\text{thf})_3]$, and $[\text{Li}_4(25)_4\cdot(\text{Et}_2\text{O})_2]$). Absorption corrections were performed on the basis of multiscans. All structures were solved by direct methods (SHELXS-97) and refined anisotropically by full-matrix least-squares procedures on F^2 using the SHELXL-97 program.⁴³ Hydrogen atoms were included as idealized methyl groups allowed to rotate but not tip (all methyls with the exception of disordered methyl groups in 6 and $[\text{Li}(15) \cdot (\text{Et}_2 \text{O})_2]_n)$ or placed geometrically and allowed to ride on their attached carbon atoms (all other H atoms). Numerical details are summarized in Tables S1-S19. For special features and exceptions, see Supporting Information pp S8-S34. The program Diamond⁴⁴ was used for graphical representations.

Experimental Procedures. Preparation of Tris((1,1,1,3,3,3-hexafluoro-2-methyl-2-propanyl)oxy)(4-methoxybenzylidyne)-(tetrahydrofuran)molybdenum(VI), [6(thf)]. A solution of K[OC-(CF₃)₂Me] (0.66 g, 3.00 mmol, 3 equiv) in THF (7 mL) was added to a stirred solution of**11**(0.54 g, 1.00 mmol) in THF (3 mL), and

the reddish brown mixture was stirred overnight at ambient temperature. The volatiles were removed under reduced pressure, and the brown residue was dried under dynamic vacuum. It was then extracted repeatedly with n-pentane (total amount 10 mL), filtered through D.E., and the frit was washed with more n-pentane to give a yellow filtrate. The solvent was removed under high vacuum and the product was isolated as a pale brown solid in 70% yield (0.58 g, 0.70 mmol). Crystallization attempts from concentrated n-pentane solutions at -35 °C afforded yellow crystals of [6(thf)], but the structure could not be refined satisfactorily (for details, see Figure S3). Single crystals of $[6(thf)_2]$ were obtained from a concentrated *n*pentane/THF (~20:1) solution of [6(thf)] at -35 °C. Elemental analysis. Found: C, 34.62; H, 3.04. Calcd for C24H24F18MoO5: C, 34.71; H, 2.91%. NMR spectroscopy. δ_H (C₆D₆, 300.1 MHz, 297 K) 1.38 (m, 4H, THF), 1.83 (s, 9H, $3 \times C(CH_3)(CF_3)_2$), 3.17 (s, 3H, OCH₃), 3.82 (m, 4H, THF), 6.44 (d, 2H, ${}^{3}J_{HH} = 8.9$ Hz, 2 × Ar–H), 7.16 (d, 2H, ${}^{3}J_{HH} = 8.9$ Hz, 2 × Ar-H) (Figure S22a); $\delta_{\rm F}$ (C₆D₆) 188.3 MHz, 300 K) -77.81 (CF₃) (Figure S22b); $\delta_{\rm C}$ (C₆D₆, 75.5 MHz, 299 K) 19.4 (C(CH₃)(CF₃)₂), 25.5 (THF), 54.9 (OCH₃), 68.6 (THF), 84.7 (sep, ${}^{2}J_{CF} = 29$ Hz, $C(CH_{3})(CF_{3})_{2}$), 113.8 (m-CH), 124.1 (q, ${}^{1}J_{CF} = 288$ Hz, CF₃), 132.6 (o-CH), 139.2 (i-C_q), 160.7 (p- C_q), 294.4 (C=Mo) (Figure S22c).

Preparation of Tris((1,1,1,3,3,3-hexafluoro-2-methyl-2propanyl)oxy)(4-methoxybenzylidyne)molybdenum(VI), 6. A solution of [6(thf)] (47 mg, 57 μ mol) in toluene (1 mL) and *n*-pentane (1 mL) was stored for 5 days at -35 °C. From that solution pale brown crystals precipitated, which were suitable for X-ray diffraction analysis. After decantation and drying under dynamic vacuum the product was isolated in 43% yield (20 mg, 26 µmol). Alternatively, [6(thf)] can be repeatedly dissolved in toluene and the solvent subsequently evaporated at 50 °C to obtain THF-free complex 6. Elemental analysis. Found: C, 31.70; H, 1.86. Calcd for $C_{20}H_{16}F_{18}MoO_4$: C, 31.68; H, 2.13%. NMR spectroscopy. δ_H $(C_6D_{61} 300.1 \text{ MHz}, 298 \text{ K}) 1.68 (s, 9H, 3 \times C(CH_3)(CF_3)_2), 3.16$ (s, 3H, OCH₃), 6.41 (d, 2H, ${}^{3}J_{HH} = 9.0$ Hz, 2 × Ar–H), 7.04 (d, 2H, ${}^{3}J_{\text{HH}} = 9.0 \text{ Hz}, 2 \times \text{Ar}-H)$ (Figure S23a); δ_{F} (C₆D₆, 188.3 MHz, 300 K) -77.92 (CF₃) (Figure S23b); $\delta_{\rm C}$ (C₆D₆, 75.5 MHz, 299 K) 19.6 (C(CH₃)(CF₃)₂), 55.2 (OCH₃), 84.6 (sep, ²J_{CF} = 29 Hz, C(CH₃)- $(CF_3)_2$, 114.1 (*m*-CH), 123.5 (q, ${}^{1}J_{CF} = 288$ Hz, CF_3), 131.9 (*o*-CH),

139.3 $(i-C_q)$, 161.1 $(p-C_q)$, 299.2 $(C \equiv Mo)$ (Figure S23c). Preparation of 2,4,6-Trimethoxyphenyl Lithium. A published procedure⁴⁵ was modified as follows. In a 100 mL Schlenk tube, n-BuLi (1.6 M in hexanes, 20 mL, 32.0 mmol, 1.01 equiv) was added to a stirred solution of 1,3,5-trimethoxybenzene (5.35 g, 31.8 mmol, 1.0 equiv) in diethyl ether (12 mL). A reflux condenser was attached, and the reaction mixture was refluxed at 40 °C for 2.5 h, inducing the rapid formation of a white precipitate. The mixture was allowed to cool down and then stirred overnight at ambient temperature. The white solid was collected on a frit, washed with *n*-hexane $(3 \times 5 \text{ mL})$, and dried under high vacuum. Yield: 93% (5.13 g, 29.5 mmol). Elemental analysis. Found: C, 62.06; H, 6.61. Calcd for C₉H₁₁LiO₃: C, 62.08; H, 6.37%. NMR spectroscopy. $\delta_{\rm H}$ (THF- $d_{\rm 8}$, 300.1 MHz, 297 K) 3.68 (s, 3H, p-OCH₃), 3.69 (s, 6H, 2 × o-OCH₃), 5.98 (s, 2H, $2 \times m$ -H) (Figure S24a); $\delta_{\rm C}$ (THF- d_{8} , 75.5 MHz, 298 K) 54.2 (o-OCH₃), 54.8 (p-OCH₃), 90.2 (m-CH), 136.0 (i-C_a), 161.3 (p- $C_q OCH_3$), 169.8 (*o*- $C_q OCH_3$) (Figure S24b).

¹Preparation of Lithium (2,4,6-Trimethoxybenzoyl)pentacarbonylmolybdate(0), Li[13]. A suspension of 2,4,6-trimethoxyphenyl lithium (1.60 g, 9.20 mmol, 1.0 equiv) in diethyl ether (15 mL) was added to a 250 mL Schlenk flask charged with a suspension of $[Mo(CO)_6]$ (2.43 g, 9.20 mmol, 1.0 equiv) in diethyl ether (25 mL), and residual 2,4,6-trimethoxyphenyl lithium in the first flask was rinsed with THF (2 × 2.5 mL) and added to the reaction flask. The mixture immediately turned yellow, and stirring for 15 min at ambient temperature resulted in a clear orange solution. Then, *n*hexane (70 mL) was added, precipitating a yellow powder that remained in suspension, and a gluey dark orange solid that stuck to the walls of the flask. The suspension was immediately filtered before the yellow powder started to settle; the yellow solid was then dried on the frit under dynamic vacuum to give 1.16 g of the title compound. A second crop of product precipitated from the filtrate as large blockshaped orange crystals (0.91 g). Total yield: 44% (2.07 g, 4.06 mmol). Elemental analysis. Found: C, 44.45; H, 4.07. Calcd for $C_{19}H_{19}LiMoO_{10}$: C, 44.72; H, 3.75%. NMR spectroscopy. $\delta_{\rm H}$ (THF- $d_{\rm s}$, 200.1 MHz, 300 K) 1.73 (m, THF), 3.57 (m, THF), 3.62 (s, 6H, 2 × o-OCH₃), 3.67 (s, 3H, p-OCH₃), 6.01 (s, 2H, 2 × m-H), (Figure S27a); $\delta_{\rm C}$ (THF- $d_{\rm s}$, 75.5 MHz, 299 K) 26.4 (THF), 55.1 (o-OCH₃), 55.3 (p-OCH₃), 68.2 (THF), 91.0 (m-CH), 134.5 (*i*- $C_{\rm q}$), 153.4 (o- $C_{\rm q}$ O), 159.8 (p- $C_{\rm q}$ O), 211.0 (*cis*-CO), 218.6 (*trans*-CO), 313.9 (Ar–C=O) (Figure S27b).

Preparation of Tris(bromido)(1,2-dimethoxyethane- κ^2 O,O')-(2,4,6-trimethoxybenzylidyne)molybdenum(VI), 16. To a stirred and precooled (-80 °C) suspension of Li[13.thf] (1.16 g, 2.27 mmol) in dichloromethane (30 mL) was added a precooled $(-80 \degree C)$ solution of oxalyl bromide (0.59 g, 2.72 mmol, 1.2 equiv) in dichloromethane (5 mL). The brown mixture was allowed to warm up gradually to -20 °C (the cooling bath was not removed) during which time the color darkened slightly and evolution of gas was observed. The mixture was cooled back to -80 °C and filtered at this temperature through D.E. on a jacketed frit to separate the precipitated LiBr. Then, 1,2-dimethoxyethane (2.35 mL, 2.04 g, 22.60 mmol, 10.0 equiv) was added to the stirred filtrate at -70 °C, followed by slow addition of a precooled (-70 °C) solution of bromine (0.12 mL, 0.37 g, 2.31 mmol, 1.02 equiv) in dichloromethane (5 mL). The resulting orange-brown solution was allowed to warm up gradually to approximately 15 °C, and the volatiles were removed under high vacuum. The deep brown residue was dissolved in dichloromethane (10 mL), and after addition of n-pentane (45 mL), a brown solid precipitated. The mother liquor was decanted off and the solid dried under high vacuum to give 16 as a crude product as judged by NMR spectroscopy (any attempts to recrystallize or further purify the compound resulted in additional decomposition). Yield (crude product): 73% (996 mg, 1.65 mmol). NMR spectroscopy. $\delta_{\rm H}$ (CD₂Cl₂, 300.1 MHz, 297 K) 3.48 (br s, DME), 3.65 (br s, DME), 3.82 (br s, DME), 3.87 (s, 3H, p-OCH₃), 3.91 (s, 6H, $2 \times o$ -OCH₃), 3.97 (br s, DME), 6.03 (s, 2H, $2 \times m$ -H) (Figure S28a); $\delta_{\rm C}$ (CD₂Cl₂, 75.5 MHz, 299 K) 56.0 (p-OCH₃), 56.2 (o-OCH₃), 60.0 (DME-CH₃), 70.0 (DME-CH₂), 73.4 (DME-CH₃), 78.6 (DME-CH₂), 88.9 (*m*-CH), 117.1 (*i*-C_a), 165.1 (*p*-C_aO), 168.4 (*o*-C_aO), 331.4 (C≡Mo) (Figure S28b).

Preparation of Tris((1,1,1,3,3,3-hexafluoro-2-methyl-2propanyl)oxy)(tetrahydrofuran)(2,4,6-trimethoxybenzylidyne)molybdenum(VI), [7(thf)]. To a stirred solution of K[OC(CF_3)₂Me] (132 mg, 600 μ mol, 3.3 equiv) in THF (1.5 mL) was added the crude molybdenum complex 16 (111 mg, 183 μ mol) in portions through a funnel, and the funnel was rinsed with THF (2 \times 0.5 mL). The mixture immediately turned deep brown and was stirred for 16 h at ambient temperature. The volatiles were removed under vacuum, and the deep brown residue was dried for 1 h at 50 °C under dynamic vacuum. The residue was extracted several times with n-hexane, filtered through D.E., and the frit was washed with more *n*-hexane, leaving a black residue and a yellow filtrate. Removal of the solvent under high vacuum afforded the title compound as a yellow solid in 62% yield (101 mg, 113 μ mol). Single crystals suitable for X-ray diffraction analysis were obtained by storing a concentrated *n*-pentane solution at -30 °C. Elemental analysis. Found: C, 33.52; H, 2.81. Calcd for $C_{26}H_{28}F_{18}MoO_7\!\!:$ C, 35.07; H, 3.17%. Combustion analysis repeatedly produced low carbon and hydrogen values, which we ascribe to partial loss of THF. NMR spectroscopy. $\delta_{\rm H}$ (C₆D₆, 300.1 MHz, 297 K) 1.43 (m, THF), 1.94 (s, 9H, $3 \times C(CH_3)(CF_3)_2)$, 3.17 $(s, 6H, 2 \times o-OCH_3)$, 3.21 $(s, 3H, p-OCH_3)$, 3.86 (m, THF), 5.66 $(s, 6H, 2 \times o-OCH_3)$, 3.21 $(s, 3H, p-OCH_3)$, 3.86 (m, THF), 5.66 $(s, 6H, 2 \times o-OCH_3)$, 3.21 $(s, 3H, p-OCH_3)$, 3.86 (m, THF), 5.66 $(s, 6H, 2 \times o-OCH_3)$, 3.21 $(s, 3H, p-OCH_3)$, 3.86 (m, THF), 5.66 $(s, 6H, 2 \times o-OCH_3)$, 3.21 $(s, 2H, p-OCH_3)$, 3.86 (m, THF), 5.66 $(s, 6H, 2 \times o-OCH_3)$, 3.21 $(s, 2H, p-OCH_3)$, 3.86 (m, THF), 5.66 $(s, 6H, 2 \times o-OCH_3)$, 3.86 (m, THF), 5.66 $(s, 6H, 2 \times o-OCH_3)$, 5.66 (s, 6H2H, 2 × m-H) (Figure S29a); $\delta_{\rm F}$ (C₆D₆, 188.3 MHz, 300 K) -77.9 (CF₃) (Figure S29b); $\delta_{\rm C}$ (C₆D₆, 75.5 MHz, 298 K) 18.0 (C(CH₃)(CF₃)₂), 25.6 (THF), 54.4 (*o*-OCH₃), 55.0 (*p*-OCH₃), $\begin{array}{l} (1.1)$

²Preparation of Tris((1,1,1,3,3,3-hexafluoro-2-methyl-2-propanyl)oxy)(2,4,6-trimethoxybenzylidyne)molybdenum(VI),**7** $. K-<math>[OC(CF_3)_2Me]$ (228 mg, 1035 µmol, 0.97 equiv) was dissolved in

THF (3 mL) and added to a stirred solution of crude 16 (216 mg, 357 μ mol) in THF (1 mL), which immediately turned dark brown. The mixture was stirred overnight at ambient temperature. The volatiles were removed under vacuum, and the brown residue was dried for 90 min at 50 °C under dynamic vacuum. It was then extracted several times with n-pentane, filtered through D.E., and the frit was washed with more *n*-pentane, leaving a black residue and a yellow filtrate. The solvent was removed under high vacuum, and the residue was dried for 90 min at 40 °C under dynamic vacuum. n-Pentane (5 mL) was added and then removed quickly at 40 °C twice. After additional drying for 15 min at 40 °C under dynamic vacuum, the product was isolated as a brown solid in 36% yield (101 mg, 123 μ mol). Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated *n*-pentane solution at -30 °C. Elemental analysis. Found: C, 32.29; H, 2.29. Calcd for $C_{22}H_{20}F_{18}MoO_6$: C, 32.29; H, 2.46%. NMR spectroscopy. δ_{H} $(C_6D_{61} 600.1 \text{ MHz}, 303 \text{ K}) 1.87 (s, 9H, 3 \times C(CH_3)(CF_3)_2), 3.14$ (s, 6H, $2 \times o$ -OCH₃), 3.18 (s, 3H, p-OCH₃), 5.64 (s, 2H, $2 \times m$ -H) (Figure S30a); $\delta_{\rm F}$ (C₆D₆, 470.7 MHz, 298 K) -78.14 (CF₃) (Figure S30b); δ_C (C₆D₆, 150.9 MHz, 303 K) 18.19 (C(CH₃)(CF₃)₂), 54.54 $(o-OCH_3)$, 55.01 $(p-OCH_3)$, 84.52 (sep, ${}^2J_{CF} = 30.1$ Hz, $C(CH_3)$ - $(CF_3)_2$), 89.75 (*m*-CH), 120.35 (*i*-C_q), 123.62 (q, ¹J_{CF} = 286.5 Hz, CF₃), 163.02 (*o*-C_qO), 163.19 (*p*-C_qO), 296.73 (C \equiv Mo) (Figure S30c).

Preparation of 2-Isopropoxyphenyl Lithium. A solution of n-BuLi (1.6 M in hexanes, 8.88 mL, 14.2 mmol, 1.0 equiv) was added to a stirred solution of 2-isopropoxyphenyl bromide (3.06 g, 14.2 mmol) in diethyl ether (20 mL) at ambient temperature, which resulted in the formation of a white precipitate. The mixture was stirred at ambient temperature for 12 h, then cooled in an ice bath, the solid collected by filtration, washed with *n*-hexane (5×20 mL), and dried under high vacuum to give the title compound as a white solid. Yield: 87% (1.76 g, 12.4 mmol). NMR spectroscopy. $\delta_{\rm H}$ (THF- $d_{\rm 8}$, 600.1 MHz, 303 K) 1.25 (d, 6H, ${}^{3}J_{HH} = 6.1$ Hz, 2 × CH₃), 4.50 (sep, 1H, ${}^{3}J_{\rm HH} = 6.1$ Hz, OCH), 6.55 (app d, 1H, ${}^{3,\rm app}J_{\rm HH} = 8.0$ Hz, Ar-H), 6.66 (app tm, 1H, ${}^{3,app}J_{HH} = 6.7$ Hz, Ar–H), 6.84 (app tm, 1H, ${}^{3,app}J_{HH} =$ 7.6 Hz, Ar–H), 7.70 (app dd, 1H, ${}^{3,app}J_{HH} = 6.3$ Hz, ${}^{4,app}J_{HH} = 1.7$ Hz, Ar-H) (Figure S32a); $\delta_{\rm C}$ (THF- d_8 , 150.9 MHz, 303 K) 22.78 (2 × CH₃), 69.49 (OCH), 109.94 (Ar-CH), 121.36 (Ar-CH), 125.19 (br, $\nu_{1/2} = 19.5$ Hz, Ar–CH), 143.21 (Ar–CH), 167.82 (C_aO), 169.2 (br, $\nu_{1/2} = 113$ Hz, C_q Li) (Figure S32b).

Preparation of Lithium (2-Isopropoxybenzoyl)pentacarbonylmolybdate(0), Li[17]. A 250 mL Schlenk flask was charged with $[Mo(CO)_6]$ (3.70 g, 14.0 mmol), 2-isopropoxyphenyl lithium (2.00 g, 14.1 mmol, 1.01 equiv), and diethyl ether (15 mL), and the yellow suspension was stirred for 2 h at ambient temperature. After addition of diethyl ether (20 mL) and n-hexane (40 mL) a brown precipitate began to deposit from solution. The mixture was placed in an ice bath (0 °C) for 2 h to facilitate complete precipitation of the product. The supernatant was decanted, and the residue was washed with *n*-hexane $(3 \times 10 \text{ mL})$ and dried under dynamic vacuum to give a dark yellow solid. A second crop of product was obtained after the mother liquor had stood for several hours. Total yield: 87% (1.93 g, 12.1 mmol). Elemental analysis. Found: C, 44.31; H, 2.95. Calcd for C₁₅H₁₁LiMoO₇: C, 44.36; H, 2.73%. NMR spectroscopy. $\delta_{\rm H}$ (THF- d_8 , 399.8 MHz, 298 K) 1.29 (d, 2 × 3H, $^3J_{\rm HH}$ = 6.1 Hz, 2 × CH_3), 4.53 (sep, 1H, ${}^{3}J_{HH}$ = 6.1 Hz, OCH), 6.62–6.65 (m, 1H, 6-H), 6.73-6.79 (m, 2H, 3-H, 5-H), 6.91-6.96 (m, 1H, 4-H) (Figure S33a); $\delta_{\rm C}$ (THF- d_8 , 100.5 MHz, 299 K) 22.4 (2 × CH₃), 70.0 (OCH), 113.5 (3-CH), 120.3 (5-CH), 122.1 (6-CH), 126.5 (4-CH), 150.1 (2- C_q O), 154.1 (*i*- C_q), 210.9 (4 × *cis*-CO), 218.2 (*trans*-CO), 316.3 (Ar-C=O) (Figure S33b).



Preparation of Lithium (2,4,6-Triisopropylbenzoyl)pentacarbonylmolybdate(0), Li[25]. A solution of 1-bromo-2,4,6triisopropylbenzene (3.0 mL, 12.0 mmol) in diethyl ether (30 mL) was treated with t-BuLi (1.7 M in pentane, 14 mL, 24 mmol, 2 equiv) at -30 °C. After stirring at low temperature for 2 h, the solution was transferred to a precooled (0 °C) suspension of $[Mo(CO)_6]$ (3.17 g, 12.00 mmol) in diethyl ether (20 mL), and the reaction mixture was stirred at ambient temperature for 2 h. The solvent was removed under reduced pressure, and the residue was dried for several hours under high vacuum. The yellow solid was dissolved in dichloromethane (100 mL) and filtered through a small pad of D.E. to remove LiBr. The orange filtrate was concentrated to 20 mL, and the product was precipitated with *n*-pentane (80 mL) to give $Li[25 \cdot Et_2O]$ as an intensely yellow solid. Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated *n*-pentane solution at -35°C. Yield: 52% (3.42 g, 6.24 mmol). Elemental analysis. Found: C, 53.53; H, 5.47. Calcd for C₉₂H₁₁₂Li₄Mo₄O₂₆: C, 54.02; H, 5.52%. Although the carbon content is outside the range viewed as establishing analytical purity, it is provided to illustrate the best values obtained to date. NMR spectroscopy. $\delta_{\rm H}$ (CD₂Cl₂, 300.1 MHz, 300 K) 1.05 (d, 2 × 3H, ${}^{3}J_{HH}$ = 6.8 Hz, p-CH(CH₃)₂), 1.12 (t, 2 × 3H, ${}^{3}J_{HH}$ = 7.0 Hz, Et₂O-CH₃), 1.20 (d, 2 × 3H, ${}^{3}J_{HH}$ = 6.8 Hz, 2 × o-CHCH₃), 1.33 (d, 2 × 3H, ${}^{3}J_{HH} = 6.8$ Hz, 2 × o-CHCH₃), 2.82 (sep, 1H, ${}^{3}J_{HH} = 6.8$ Hz, *p*-CH), 3.12 (sep, 2 × 1H, ${}^{3}J_{HH} = 6.6$ Hz, 2 × o-CH), 3.43 (m, $2 \times 2H$, Et₂O-CH₂), 6.93 (m, 2H, m-H) (Figure S36a); $\delta_{\rm C}$ (CD₂Cl₂, 75.5 MHz, 300 K) 14.4 (Et₂O-CH₃), 23.2 (2 × CH_3), 24.2 (2 × CH_3), 26.6 (2 × CH_3), 28.9 (o-CH), 34.5 (p-CH), 65.7 (Et₂O-CH₂), 121.6 (m-CH), 139.2 (o-C_a), 147.5 (p-C_a), 155.7 $(i-C_q)$, 209.5 (4 × *cis*-CO) (Figure S36b).

Preparation of Tris(bromido)(1,2-dimethoxyethane- κ^2 0,0')-(2,4,6-triisopropylbenzylidyne)molybdenum(VI), 24. A precooled (-80 °C) solution of oxalyl bromide (0.9 mL, 1.37 g, 6.26 mmol, \sim 1.2 equiv) in dichloromethane (20 mL) was added dropwise to a precooled (-80 °C) solution of Li[25·Et₂O] (2.90 g, 5.28 mmol) in dichloromethane (100 mL). After stirring for 2 h at -80 °C, the reaction mixture was slowly warmed to -35 °C and then instantly cooled back to -80 °C. The suspension was filtered through D.E. in a jacketed frit at low temperature (-80 °C) and then treated with 1,2dimethoxyethane (5.5 mL, 4.76 g, 52.8 mmol, 10 equiv) followed by addition of a precooled (-80 °C) solution of bromine (0.27 mL, 0.84 g, 5.28 mmol, 1 equiv) in dichloromethane (40 mL). The resulting red-brown solution was allowed to warm up and stirred for 12 h at ambient temperature. The volatiles were evaporated under reduced pressure and the resulting brown residue was dissolved in dichloromethane (7 mL) and precipitated with n-pentane (100 mL) three times. The brown solid thus obtained was separated from the supernatant by decantation and dried under high vacuum. Yield: 87% (2.96 g, 4.62 mmol). Single crystals suitable for X-ray diffraction analysis were obtained from a dichloromethane/n-pentane solution at -35 °C. Elemental analysis. Found: C, 38.02; H, 5.29. Calcd for C₂₀H₃₃Br₃MoO₂: C, 37.47; H, 5.19%. Although the carbon content is outside the range viewed as establishing analytical purity, it is provided to illustrate the best values obtained to date. NMR spectroscopy. $\delta_{\rm H}$ (CD_2Cl_2, 600.1 MHz, 303 K) 1.22 (d, 2 \times 3H, ${}^{3}J_{\rm HH}$ = 6.9 Hz, p-CH(CH₃)₂), 1.37 (d, 4 × 3H, ${}^{3}J_{\rm HH}$ = 6.8 Hz, 2 × o- $CH(CH_3)_2$), 2.98 (sep, 1H, ${}^{3}J_{HH}$ = 6.9 Hz, p-CH), 3.86 (br s, 3H, DME-CH₃), 3.93 (br s, 3H, DME-CH₃), 3.99-4.07 (br m, $2 \times 2H$, $2 \times DME-CH_2$, 4.76 (sep, $2 \times 1H$, ${}^{3}J_{HH} = 6.8$ Hz, $2 \times o$ -CH), 7.11 (s, 2 × 1H, 2 × *m*-H) (Figure S37a); $\delta_{\rm C}$ (CD₂Cl₂, 150.9 MHz, 303 K) 24.29 (p-CH(CH₃)₂), 26.02 (o-CH(CH₃)₂), 30.41 (o-CH), 34.47 (p-CH), 60.37 (DME-CH₃), 69.96 (DME-CH₂), 73.29 (DME-CH₃), 78.70 (DME-CH₂), 120.60 (m-CH), 136.85 (i-C_a), 154.15 (p-C_a), 157.12 (o- C_q), 339.81 (C \equiv Mo) (Figure S37b).

Preparation of tris((1,1,1,3,3,3-hexafluoro-2-methyl-2propanyl)oxy)(2,4,6-triisopropylbenzylidyne)molybdenum(VI), **23**. A solution of K[OC(CF₃)₂Me] (628 mg, 2.85 mmol, 3.2 equiv) in THF (25 mL) was treated with a suspension of benzylidyne complex **24** (579 mg, 0.90 mmol) in THF (10 mL). After stirring the reaction mixture at ambient temperature for 24 h the solvent was evaporated at 50 °C under reduced pressure. The residue was extracted with *n*- pentane $(7 \times 7 \text{ mL})$ and filtered through a small pad of D.E. to give a vellow filtrate. The solvent was evaporated under reduced pressure, and the residual yellow solid was dissolved in a small amount of dichloromethane. Storing the solution for several days at -80 °C gave compound 23 as yellow crystals. Yield: 34% (265 mg, 0.31 mmol). Elemental analysis. Found: C, 39.25; H, 3.97. Calcd for $C_{28}H_{32}F_{18}MoO_3$: C, 39.36; H, 3.77%. NMR spectroscopy. δ_H (CD₂Cl₂, 600.1 MHz, 303 K) 1.20 (d, 2 × 3H, ${}^{3}J_{HH}$ = 7.0 Hz, p- $CH(CH_3)_2$), 1.25 (d, 4 × 3H, $^3J_{HH}$ = 6.7 Hz, 2 × o-CH(CH₃)₂), 1.86 $(s, 3 \times 3H, 3 \times C(CH_3)(CF_3)_2)$, 2.87 (sep, 1H, ${}^{3}J_{HH} = 7.0$ Hz, p-CH), 3.86 (sep, 2×1 H, ${}^{3}J_{HH} = 6.7$ Hz, $2 \times o$ -CH), 6.96 (s, 2×1 H, 2 × *m*-H) (Figure S38a); $\delta_{\rm F}$ (CD₂Cl₂, 188.3 MHz, 298 K) -78.2 (CF₃) (Figure S38b); $\delta_{\rm C}$ (CD₂Cl₂, 150.9 MHz, 303 K) 19.26 (C(CH₃)-(CF₃)₂), 23.88 (p-CH(CH₃)₂), 24.75 (o-CH(CH₃)₂), 30.73 (o-CH), 34.75 (*p*-CH), 83.81 (sep, ${}^{2}J_{CF} = 30$ Hz, $C(CH_{3})(CF_{3})_{2}$), 121.55 (*m*-CH), 123.35 (q, ${}^{1}J_{CF} = 287$ Hz, CF₃), 141.43 (*i*-C_a), 152.82 (*p*-C_a), 153.44 (o- C_a), 320.23 ($C \equiv Mo$) (Figure S38c).

Metathesis of 5-(Benzyloxy)-2-pentyne (**26a**). A mixture of **26a**, (0.25 mmol), *n*-decane (0.25 mmol), molecular sieves (250 mg), and toluene (1.25 mL, 200 mm) was stirred for 10 min before adding the catalyst (1 mol %, 2.5 μ mol) as a solid. Aliquots (0.05 mL) for GC analysis were taken at t = 0 min (prior to addition of catalyst) and at specified time intervals (see Figure 13). The samples were filtered through a small pad of neutral alox, washed with diethyl ether (1 mL) and analyzed by GC. RT(*n*-decane) = 5.1 min, RT(**26a**) = 12.2 min, RT(**27**) = 22.5 min. To determine isolated yields, the procedure described above was repeated without *n*-decane, and the mixture was stirred for 1 h at ambient temperature, followed by filtration through neutral alox and evaporation of the solvent under reduced pressure. The crude reaction product was purified by flash chromatography on silica gel with 1:8 ethyl acetate/*n*-hexane.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00783.

Additional experimental procedures and catalytic studies, tables of crystallographic data, figures, special features, and featured structural parameters for all crystallized compounds, NMR spectra of new compounds and mixtures, and details on the decomposition study of Li[13] (PDF)

Accession Codes

CCDC 1875368–1875385 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.

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Notes

The authors declare no competing financial interest.

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