ORGANOMETALLICS

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Reactivity of 1.1.1-Propellane with $(silox)_3M$ (M = Ti, V, Cr): Structures of $(silox)_3V{=}(^cC_4H_4){=}CH_2$ and $[(silox)_3Cr{-}(1.1.1\text{-}C_5H_6){-}]_2$

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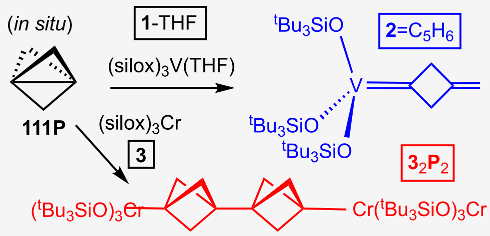
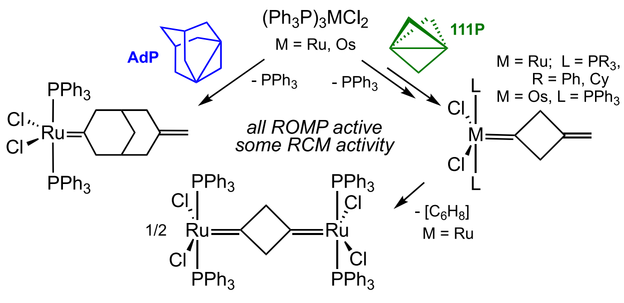
ABSTRACT: Application of the two-orbital, two-electron, four-state paradigm to 1.1.1-propellane (**111P**), which contains an unusual "inverted" central bond, suggests that an electrophilic metal center can activate it toward ring opening. Low-valent, early-metal complexes ($(silox)_3M$ (M = Ti (**1**), V (**2**) (or M = V(THF) (**2-THF**), Cr (**3**))) were employed to test this assessment with mixed results. Facile ring opening of **111P** occurs for **1**, producing known degradation products, and **2**, which generates the alkylidene $(silox)V{=}(^cC_4H_4){=}CH_2$ (**2=C_5H_6**), a species capable of catalyzing the ROMP (ring-opening metathesis polymerization) of norbornene. For **3** and **111P**, a radical-like dimerization to $[(silox)_3Cr\text{-}(1.1.1\text{-}C_5H_6){-}]_2$ (or $(silox)_3Cr(C_5H_6)_2Cr(silox)_3$ (**3_2P_2**)) effectively competes with ring opening. In conjunction with the experiments, high-level calculations provide a rationale for the trichotomy in reactivity.



INTRODUCTION

The successful implementation of 1.1.1-propellane (**111P**)[1−4] and 1,3-dehydroadamantane (**AdP**)[5] as alkylidene precursors in established Ru and Os ligand systems[6] prompted attempts to apply the method to other transition metals. As shown in Scheme 1, electrophilic ring opening of **111P** led to ROMP

Scheme 1. Ru and Os Alkylidene Complexes Derived from 1.1.1-Propellane (111P) and Dehydroadamantane (AdP)[a]



[a]ROMP and some RCM activity was noted.

(ROMP = ring-opening metathesis polymerization) and RCM (RCM = ring-closing metathesis) catalysts containing the 3-*exo*-methylenecyclobutylidene fragment: i.e., $L_2Cl_2M{=}(^cC_4H_4){=}CH_2$ (M = Ru, L = PPh_3, P^cHex_3; M = Os, L = PPh_3).[6] The alkylidene catalysts can be prepared *in situ* or via isolation and implementation. A related cyclohexylidene, $(Ph_3)_2Cl_2Ru{=}C_{10}H_{14}$, derived from **AdP** ring opening, also proved catalytically competent toward the ROMP of norbornene (NBE).

The electronic structure of 1.1.1-propellane (**111P**) provides important clues to its reactivity, while the thermochemistry of hydrogenation of its 1.60 Å bond[7] reveals a BDE of ∼59−65 kcal/mol.[8,9] Focusing on the unusual "inverted bond" connecting the bridgehead carbons, a first-order approximation using the two-orbital, two-electron, four-state paradigm originally introduced by Coulson and Fischer[10] for H_2 may be implemented. This approach has been employed in the understanding of the δ-bond[11−14] in transition-metal quadruple-bonded complexes by Gray,[11] Cotton,[12] and Nocera[13] and within these laboratories in approximating a dimolybdenum π-bond.[15] Details of this approach have been previously delineated[16] and are recapitulated in Figure S1 in the Supporting Information. Like-symmetry ground and excited states possess wave functions having ionic and covalent components, but due to a configuration interaction, one state becomes predominantly covalent and the other ionic. Typically, the ground state (GS) is covalent, but in the case of **111P**, the unusual spatial character of the orbitals suggests that the ionic contribution is crucial to its reactivity (Figure 1).

Related valence bond calculations show the covalent (∼60%) and ionic (∼40%) contributions to be similar to a normal C−C bond as in ethane, and the orbitals in **111P** are sp^x-hybridized ($x \approx 1.6$) and displaced to the periphery of the propellane cage, just as in the MO approach. The spatial nature of the orbitals suggest that a special type of "charge-shift" bonding is applicable.[17] In a nonclassical "charge-shift" bond, a

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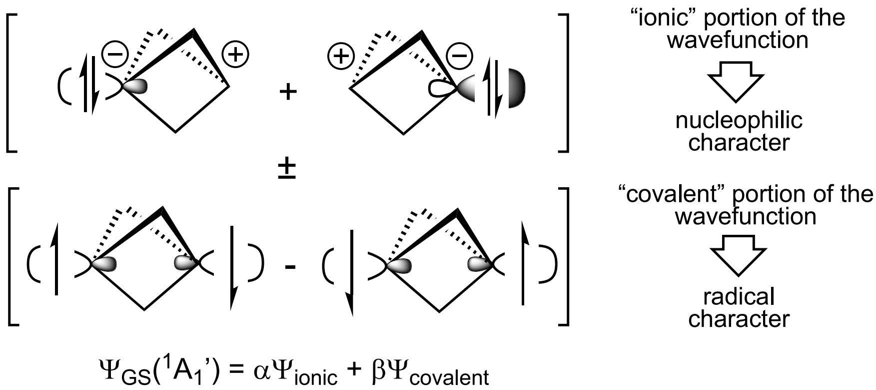
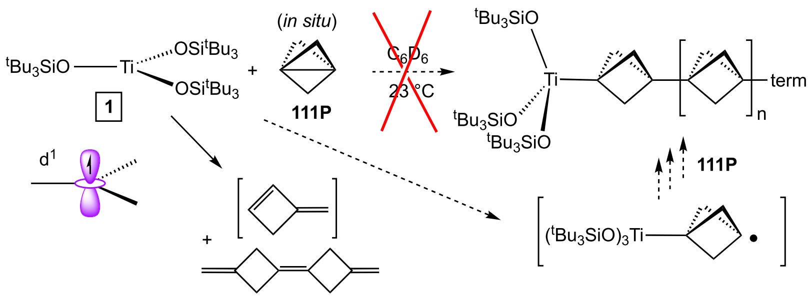


Figure 1. Using the conventional two-orbital, two-electron, four-state paradigm, the ground state of **111P** possesses electrophilic, nucleophilic, and singlet diradical character.

Scheme 2. Attempts to Observe Radical 111P Oligomerization via (silox)$_3$Ti (1) Afforded Only 3-*exo*-Methylenecyclobutylidene-Derived Products



covalent−ionic resonance energy plays the critical role in stabilization, akin to that found in bonds between very electronegative elements, such as in F_2.[17,18] Regardless of theory, the upshot is that the ground state of **111P**, with its orbital protruding to the periphery of the propellane cage, can interact as a nucleophile or exhibit radical reactivity.

The utility of **111P** in Ru and Os systems,[6] and its lack of byproducts, suggested that this methodology could be applied to metals previously incapable of generating metathesis-active alkylidenes. An exhaustive search for formally Fe(IV) complexes ensued,[19,20] based on Hoffmann's criteria that olefin metathesis (OM) was most likely to be found in complexes possessing d^n ($n \leq 4$) configurations.[21] Unfortunately, all formally Fe(IV) alkylidenes known to date fail at OM,[22−36] and all propellane approaches using different ligand platforms on iron failed to elicit alkylidene formation.[20] A rationalization has been proffered for the absence of OM reactivity in iron(IV),[19] based on a lack of the covalency needed for the reversible 2 + 2 reactivity mandated by the conventional Chauvin mechanism.[37] While new mechanisms may be operational,[38−40] attention to metals earlier in the periodic table appeared warranted.

Herein the chemistry of **111P** as applied to some electrophilic early transition metals is reported. Historically, previous exploration of mostly late transition metal complexes with **111P** resulted in 3-*exo*-methylenecyclobutanylidene rearrangement, dimerization, and related cyclopropanations,[41] most recently exploited by Aggarwal using nickel catalysis.[42] As most early-metal systems comply with the d^4 or less requirement, a greater chance at identifying OM-active catalysts is readily apparent. As described, a variety of titanium, vanadium, and chromium silox (silox = ^{t}Bu$_3$SiO) derivatives[43] were exposed to **111P**, prepared *in situ*, in order to probe the chemistry of this unusual molecule.

■ RESULTS AND DISCUSSION

(silox)$_3$Ti (1) and 111P. Oligomerization of **111P** can be initiated via radicals,[44,45] and its exposure to (silox)$_3$Ti (**1**) was anticipated to facilitate this process. Trigonal **1** has a $^2A_1'$ ground state due to single occupancy of its d_{z^2} orbital,[46,47] and this "metallaradical" was expected to react with the spatially external $sp^{1.6}$ orbitals[17] of **111P**. As illustrated in Scheme 2, no reaction occurred until the known degradation of **111P** to 3-*exo*-methylenecyclobutylidene dimer[41,48] and presumably volatile 3-*exo*-methylenecyclobutylene.

The decomposition of **111P** has historically been somewhat confusing, as polymerization, apparently initiated by trace impurities or somehow self-initiated, competes with products derived from 3-*exo*-methylenecyclobutylidene and 1,2-bis-methylenecyclopropane, a product unlikely to occur via the transient carbene but perhaps via scission of C_b-CH_2 bonds. As a consequence, there is no discrete, reproducible degradation rate and associated products, including reinvestigations from these laboratories.

(silox)$_3$V(THF) (2-THF) and 111P. As a practical matter, (silox)$_3$V(THF) (**2**-THF)[47] is more easily synthesized than trigonal (silox)$_3$V (**2**)[49] and was utilized instead. As Scheme 3 reveals, the exposure of **2**-THF to **111P**, prepared *in situ*, resulted in a color change from light to dark blue, and 3-*exo*-methylenecyclobutylidene (silox)V═(^{c}C$_4$H$_4$)═CH$_2$ (**2**═C$_5$H$_6$) was isolated in nearly quantitative yield (97%) as a dark blue powder. The THF in **2**-THF is known to be labile, and (silox)$_3$V (**2**) possesses a $^3A_2'$ ground state by virtue of double occupation of the $(e'')^2$ (i.e., d_{xz}, d_{yz}) orbitals.[49] As a

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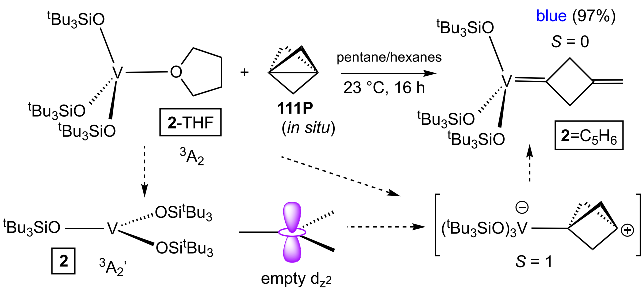
Scheme 3. Reaction of $(silox)_3V$ (2) with 111P Showing the 3-*exo*-Methylenecyclobutanylidene Product $(silox)V{=}({}^cC_4H_4){=}CH_2$ ($2{=}C_5H_6$) and Probable Electrophile/Nucleophile Compatibility of the Reactants



consequence, d_{z^2} is empty, presenting a clear electrophilic target for the propellane, whose electron density in the HOMO C−C bonding orbital is disposed to the outside of the cage, rendering it nucleophilic. Alternatively, associative attack on pseudotetrahedral **2**-THF by **111P** would also likely utilize an empty d_{z^2}/p_z orbital. It is interesting to note that while the conversion to $\mathbf{2}{=}C_5H_6$ is formally spin-forbidden from **2** or **2**-THF, the initial electrophilic attack is not. The reaction occurs rapidly after a pentane/hexanes solution of **111P** was distilled onto solid **2**-THF at −78 °C. The spin conversion to a diamagnetic product is not surprising, given that orbital symmetry considerations are of greater importance in transition metals where spin−orbit coupling likely provides enough mixing to allow an adiabatic transition between surfaces of different spin.[49]

The ^1H NMR spectrum reveals two broad singlets at δ 4.59 and δ 5.92 integrating to 2:4 relative to an 81H singlet at δ 1.29. The spectrum is somewhat broad at 23 °C, and cooling a THF-d_8 solution of **2** to −80 °C sharpened the signals without incurring any chemical shift changes (see the Supporting Information), likely due to slower vanadium quadrupolar relaxation rates.[50,51] The accompanying $^{13}C\{^1H\}$ NMR spectrum manifests the silox-methyl and SiC carbon resonances at δ 31.04 and 23.80, respectively, a methylene signal at δ 61.53, and alkene resonances at δ 105.42 (CH_2) and 143.43 (C). The alkylidene carbon was not observed and was probably significantly severely broadened through interaction with the ^{51}V quadrupole. The ^{51}V shift at δ −705.8 ($\nu_{1/2} \approx 200$ Hz) is quite negative (shielded) relative to most V(V) complexes but is in line with tris-alkoxide-imido[50] and -oxo[51] species.[52]

Structure of $(silox)V{=}({}^cC_4H_4){=}CH_2$ ($2{=}C_5H_6$). Shown in Figure 2 is a molecular view of $(silox)V{=}({}^cC_4H_4){=}CH_2$ ($\mathbf{2}{=}C_5H_6$), as determined from a single-crystal X-ray structure determination. The 3-*exo*-cyclobutylidene is pseudoplanar with the O1−V−O3 angle and aligned 90° to the V−O2 bond. This orientation has subtle effects on the siloxide bonds, as *d*(V−O2) is 1.8265(9) Å, which is slightly longer than *d*(V−O1) = 1.7695(8) Å and *d*(V−O3) = 1.7857(8) Å, perhaps a consequence of filled−filled π-interactions of the siloxide and the alkylidene. The O1−V−O3 angle is slightly splayed at 122.84(4)°, relative to the related O1−V−O2 and O2−V−O3 angles of 112.75(4) and 109.01(4)°, respectively, perhaps helping to maximize V=C π-overlap. The alkylidene C−V−O angles relative to siloxides O1, O2, and O3 are 103.67(5), 105.25(5), and 100.99(5)°, respectively, and appear relatively unresponsive to the alkylidene orientation. The *d*(V=C) distance of 1.8581(12) Å is amid previously reported *d*(V=C) values, which average 1.852(37) Å yet range from 1.787 to 1.92 Å.[53−59] The 3-*exo*-methylenecyclobutylidene C(sp^3)−C(sp^2) bonds average 1.524(5) Å, and its *d*(C=C) distance of 1.309(2) Å is relatively short, conceivably a consequence of greater s-character in the bond due to ring constraints.[60]

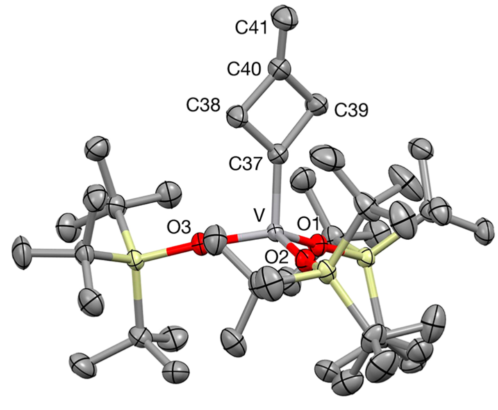
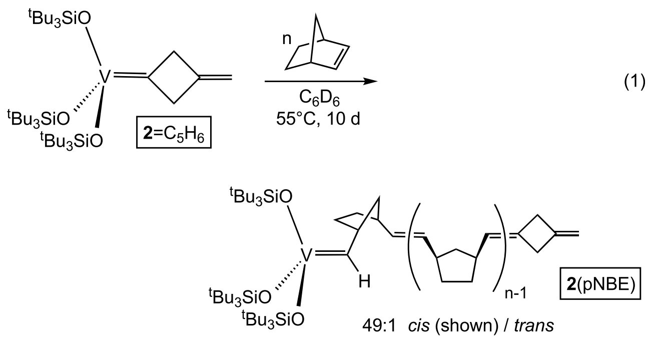


Figure 2. Molecular structure of $(silox)V{=}({}^cC_4H_4){=}CH_2$ ($\mathbf{2}{=}C_5H_6$). Selected bond distances (Å) and angles (deg): V−O1, 1.7695(8); V−O2, 1.8265(9); V−O3, 1.7857(8); V−C37, 1.8581(12); C37−C38, 1.5241(17); C37−C39, 1.5225(18); C38−C40, 1.5190(19); C39−C40, 1.5299(19); C40−C41, 1.309(2); O1−V−O2, 112.75(4); O1−V−O3, 122.84(4); O2−V−O3, 109.01(4); O1−V−C37, 103.67(5); O2−V−C37, 105.25(5); O3−V−C37, 100.99(5); V−C37−C38, 127.78(9); V−C37−C39, 140.05(9); C37−C38−C40, 87.87(10); C37−C39−C40, 87.53(10); C38−C40−C41, 134.65(14); C39−C40−C41, 133.39(14).

Norbornene ROMP with $(silox)V{=}({}^cC_4H_4){=}CH_2$ ($2{=}C_5H_6$). The exposure of $(silox)V{=}({}^cC_4H_4){=}CH_2$ ($\mathbf{2}{=}C_5H_6$) to norbornene (NBE, ∼7.5 equiv) in benzene-d_6 was monitored by ^1H NMR spectroscopy over the course of 10 days at 55 °C. During this period, a modest loss of $\mathbf{2}{=}C_5H_6$ (10%) was observed concomitant with signals consistent with *cis*-polynorbornene vs *trans* with a ratio of 49:1. Careful scrutiny of the spectrum identified resonances at δ 4.94 and δ 3.30 consistent with a 3-*exo*-methylenecyclobutylidene end group.



(1)

Since vanadium species are well-known polymerization catalysts for NBE,[54,56,57,61−64] no further studies were conducted for this slow system, whose efficiency is likely hampered by significant steric inhibition. In an effort to observe ring-closing olefin metathesis, $\mathbf{2}{=}C_5H_6$ was subjected to a prototypical substrate, diallyl(tosyl)amine, but no appearance of the expected (tosyl)azocyclopent-3-ene or ethylene was discerned.

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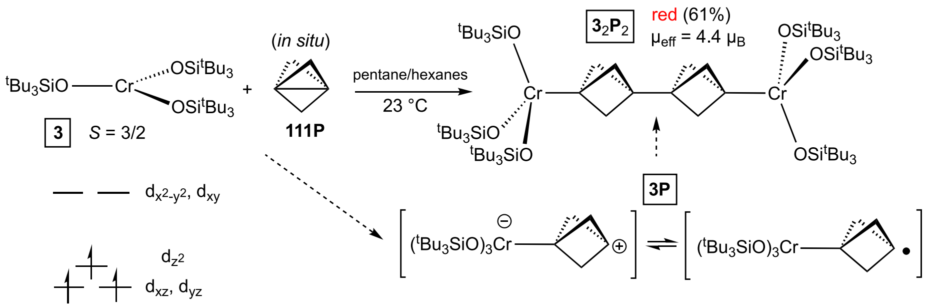
Scheme 4. Reaction of $(silox)_3Cr$ (3) with 111P to Afford $(silox)_3Cr(C_5H_6)_2Cr(silox)_3$ (3_2P_2)



$(silox)_3$Cr and 111P. The possibility of a Cr(V) alkylidene complex was intriguing,[65,66] provided $(silox)_3Cr$ (**3**),[67] which possesses a $^4A_2'$ ground state, could rearrange electronically to a $^2E''$ state, thereby permitting a consequentially empty d_{z^2} orbital to electrophilically attack **111P**. Once again, *in situ* preparation of **111P** and addition to **3** resulted in a color change from emerald green to dark red, but the resulting paramagnetic complex, identified by X-ray crystallography, was not the alkylidene. The dimer $(silox)_3Cr(C_5H_6)_2Cr(silox)_3$ (**3_2P_2**) was isolated in 61% yield as a red powder from hexanes/pentane (Scheme 4). An Evans method[68] measurement on **3_2P_2** gave 4.4 μ_B, a value between spin-only values of noninteracting centers (μ_{SO} = $2[1(2) + 1(2)]^{1/2}$ = 4.0) and completely coupled centers (μ_{SO} = $2[2(3)]^{1/2}$ = 4.9). No interaction between the chromium atoms, which are 9.054 Å apart (*vide infra*), is expected, and two Cr(IV) centers, each with a $d_{xz}{}^1d_{yz}{}^1$ configuration, are not expected to have any orbital contribution. It is conceivable that some long-range coupling occurs through the $C_{10}H_{12}$ bridge. Broad resonances at δ 1.06 ($\nu_{1/2} \approx$ 56 Hz) and 4.89 ($\nu_{1/2} \approx$ 70 Hz) assigned to the silox and methylene hydrogens are hardly shifted from the corresponding signals in the diamagnetic species.

Once again, no oligomerization of **111P** was noted,[45,48] even though the dimer is easily envisaged as occurring via dimerization of $(silox)_3Cr(C_5H_6)$ (**3P**), the "metallaradical" formed from radical opening of **111P** by $(silox)_3Cr$ (**3**). Since $(silox)_3Ti$ (**1**), which is less sterically congested, failed to ring-open **111P**, perhaps the electronic changes incurred by **3P** are not so simply considered. While no evidence of reversibility was observed at room temperature, degradation was noted to slowly occur at 85 °C, with a rough $t_{1/2}$ value of 5 × 10^5 s, assuming a first-order process, and **3** was the only identified product.[48]

Structure of $(silox)_3Cr(C_5H_6)_2Cr(silox)_3$ (3_2P_2). Chromium dimer $(silox)_3Cr(C_5H_6)_2Cr(silox)_3$ (**3_2P_2**) is centered on a 2-fold axis; hence, half the molecule is the asymmetric unit, as indicated in Figure 3. The core is slightly splayed due to bulky silox groups, with the O−Cr−O angles averaging 117.6(3)° and O−Cr−C angles of 99.1(19)° (average). The *d*(Cr−C) distance of 2.0071(15) Å is slightly longer than the sum of covalent radii (Cr (1.18 Å), C(sp^3) (0.77 Å)) but shorter than typical σ-alkyls of Cr (2.075 Å) and more in line with alkenyl species (2.035 Å),[69] suggesting that the constraints imposed by the C_5 cage engender more s-character to the bond. In corroboration, the unique C−C bond linking the cages is also short at 1.499(3) Å, a value less than those of virtually all C(sp^3)−C(sp^3) bonds[60] and one estimated to have a BDE of ∼105 kcal/mol.[70]

Chromium(II) Species and 111P. A spate of Cr(II) sources originating from these laboratories were also subjected to **111P** generated *in situ*, as illustrated in Scheme 5: $[(silox)_3Cr](Na(C_6H_6))$ (**4a**), $[(silox)_3Cr]$(Na(dibenzo-18-c-6)) (**4b**), $[(\mu\text{-Cl})Cr(\mu\text{-OSi}^tBu_3)]_4$ (**5**), and $[(silox)Cr(\mu\text{-OSi}^tBu_3)]_2$ (**6**).[67,71] The pseudo-trigonal derivatives **4a**,**b** containing a $[(silox)_3Cr]^-$ anion are high spin and possess an unoccupied orbital in the *xy* plane, but none of these species afforded a tractable alkylidene or organometallic product. The chromium "box" $[(\mu\text{-Cl})Cr(\mu\text{-OSi}^tBu_3)]_4$ (**5**) is essentially a complex containing four pseudo-square-planar Cr(II) centers, exhibits complicated antiferromagnetic coupling, and was considered a source of "(silox)CrCl" or lower aggregates. The weakly coupled dimer $[(silox)Cr(\mu\text{-OSi}^tBu_3)]_2$ (**6**) was also an obvious source of low-coordinate Cr(II), but none of these di- or multimetalllic starting materials permitted isolation of any organometallics. Due to the nature of the assays involving these species, the volatile 3-*exo*-methylenecyclobutene was not observed, but the dimer of 3-*exo*-methylenecyclobutylidene was identified in varied amounts, indicative of the catalyzed decomposition of **111P**.

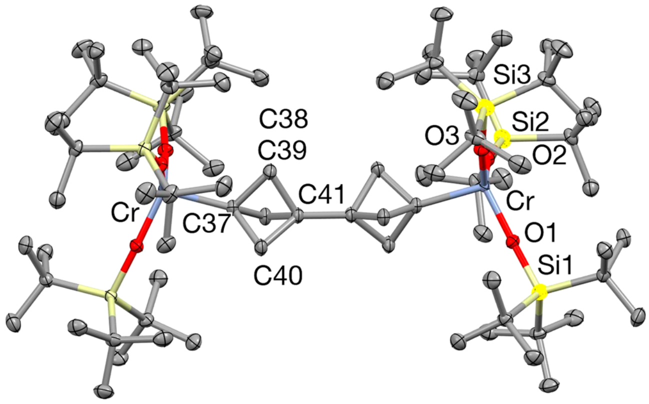


Figure 3. Molecular structure of $(silox)_3Cr(C_5H_6)_2Cr(silox)_3$ (**3_2P_2**). Selected bond distances (Å) and angles (deg): Cr−O1, 1.7682(11); Cr−O2, 1.7790(10); Cr−O3, 1.7781(10); Cr−C37, 2.0071(15); O1−Si1, 1.6634(11); O2−Si2, 1.6625(10); O3−Si3, 1.6643(11); C37−C38, 1.553(2); C37−C39, 1.564(2); C37−C40, 1.565(2); C38−C41, 1.548(2); C39−C41, 1.550(2); C40−C41, 1.558(2); C41−C41′, 1.499(3); O1−Cr−O2, 117.48(5); O1−Cr−O3, 117.25(5); O2−Cr−O3, 117.91(5); O1−Cr−C37, 101.27(6); O2−Cr−C37, 98.03(6); O3−Cr−C37, 98.01(6); Cr−C37−C38, 119.92(11); Cr−C37−C39, 126.88(10); Cr−C37−C40, 133.11(10); C37−C38−C41, 73.54(11); C37−C39−C41, 73.18(10); C37−C40−C41, 72.93(10); C38−C37−C39, 87.94(11); C38−C37−C40, 87.73(11); C39−C37−C40, 87.66(11); C38−C41−C41′, 120.05(9); C39−C41−C41′, 126.12(16); C40−C41−C41′, 132.54(13).

Calculations Concerning 111P Ring Opening. The trichotomy of **111P** ring opening depending upon the

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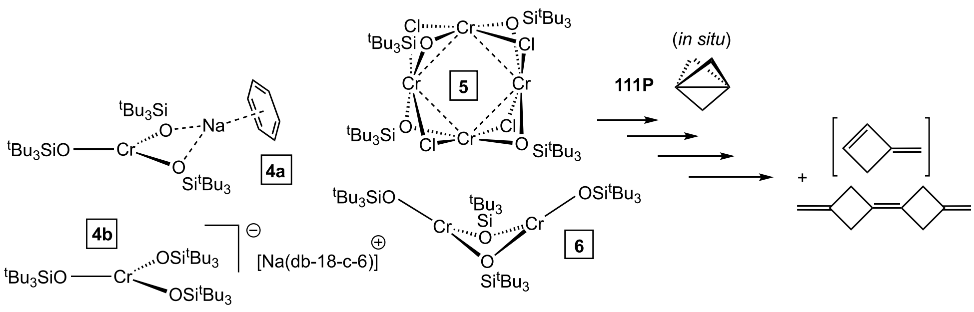
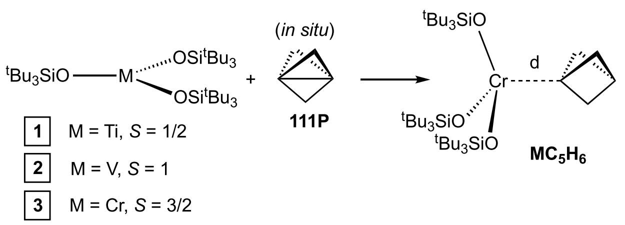
Scheme 5. Exposure of 111P to Various Cr(II) Siloxide Complexes, [(silox)$_3$Cr](Na(C$_6$H$_6$)) (4a), [(silox)$_3$Cr](Na(dibenzo-18-c-6)) (4b), [(μ-Cl)Cr(μ-OSi^{t}Bu$_3$)]$_4$ (5), and [(silox)Cr(μ-OSi^{t}Bu$_3$)]$_2$ (6), Leads Only to Products of 3-*exo*-Methylenecyclobutylidene





	Ti	V	Cr
ΔH° (kcal/mol)	-12.3	-12.1	-11.2
ΔS° (cal/mol·K)	-45.5	-54.6	-47.4
ΔG° (kcal/mol)	1.3	4.2	2.9
d (Å)	2.82	2.25	2.79

Figure 4. Calculated (ONIOM(M06/6-311+G(d):UFF)) energies of **111P** binding to (silox)$_3$M (M = Ti (**1**), V (**2**), Cr (**3**)).

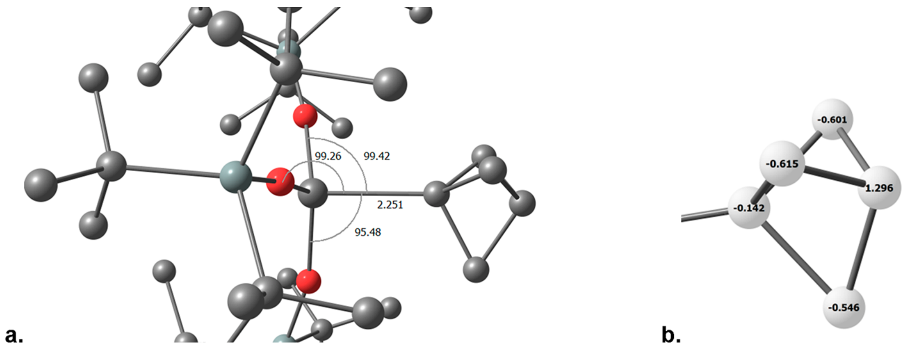


Figure 5. (a) Core geometry of ONIOM(M06/6-311+G(d):UFF) optimized (silox)$_3$V(C$_5$H$_6$) (**VC$_5$H$_6$**) with hydrogen atoms removed for clarity. (b) Mulliken charges (e$^-$) on the propellane carbons of **VC$_5$H$_6$**. In isolated **111P**, the Mulliken charges are +0.78 e$^-$ on the bridgehead carbons and −0.82 e$^-$ on the methylene carbons.

(silox)$_3$M reagent is in part readily explained, as only vanadium[47,49] can generate a relatively common diamagnetic alkylidene complex. The remaining metals diverge in reactivity, as (silox)$_3$Ti (**1**)[46] catalyzes the typical degradation to products of 3-*exo*-methylenecyclobutylidene, whereas (silox)$_3$Cr (**3**)[67] does not trigger ring opening but couples two **111P** entities via C−C bond formation. QM/MM calculations (see the Supporting Information) were performed to help understand the differences in reactivity; details are provided in the Supporting Information. The QM region (M06/6-311+G(d) level of theory) was defined by the substrate, the metal, and the O and Si atoms of the silox supporting ligands, and the *tert*-butyl groups of the silox ligands were modeled with the UFF force field.

111P Binding. Propellane **111P** forms weakly bound adducts (**MC$_5$H$_6$**) with (silox)$_3$M (M = Ti[46] (**1**), V[49] (**2**), Cr[67] (**3**)), as shown in Figure 4. In each case the lowest energy spin state for the adduct is the same as that for the trigonal precursor (**1**, $S = 1/2$; **2**, $S = 1$; **3**, $S = 3/2$). For **VC$_5$H$_6$**, the open-shell singlet adduct was ~39 kcal/mol higher in free energy than the triplet, while the doublet of **CrC$_5$H$_6$** was about 35 kcal/mol above the quartet. Mild exothermic binding energies of −11 to −12 kcal/mol are offset by significantly negative entropies such that the free energies of binding are slightly endergonic.

Perhaps the most interesting difference among the **111P** adducts concerns the distance between the metal and proximal bridgehead propellane carbon (e.g., d(M···C$_b$)). The Ti and Cr adducts manifest significantly longer interatomic lengths (~2.8 Å) than the V adduct, whose more negative entropy of binding correlates with presumably greater constraints of its tighter **111P** binding (2.25 Å), as Figure 5a illustrates. For comparison, at the same level of theory, M−CH$_3$ bond lengths for (silox)$_3$MCH$_3$ complexes are 2.07 (^{1}Ti−Me), 2.02 (^{2}V−Me), and 2.01 Å (^{3}Cr−Me). As a further point of comparison, d(V−C) in the more hindered (silox)$_3$V−CMe$_3$ (^{2}V^{t}Bu) is 2.12 Å upon optimization; thus, unlike the Ti and Cr congeners, the d(V···C$_b$) distance of **VC$_5$H$_6$** is within 0.13 Å of a comparable vanadium−carbon single bond. It is reasonable to assume that the proximity of **111P** to the metal center may play a role in the subsequent reactivity, and

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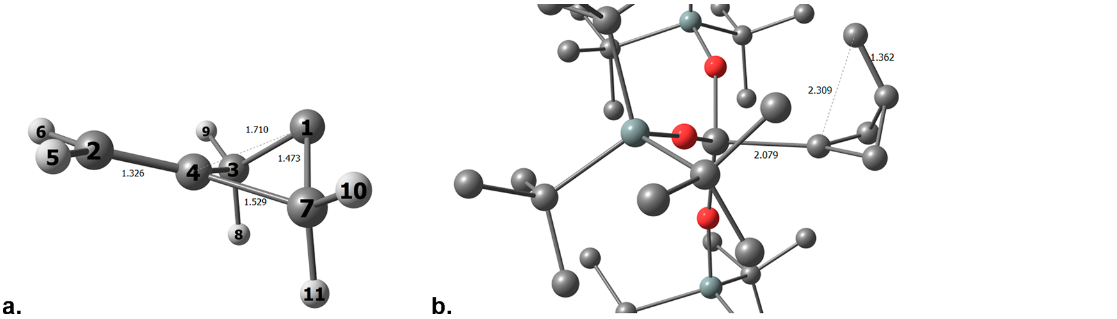

Figure 6. (a) M06/6-311+G(d) optimized transition state for ring opening of **111P**. The C_1-C_2 distance is 2.91 Å, suggesting a very "late" transition state. (b) Core geometry of the ONIOM(M06/6-311+G(d):UFF)-optimized $^3V(silox)(C_4H_4{=}CH_2)$ (**$MC_4H_4{=}CH_2$**) transition state. Hydrogen atoms are omitted for clarity.

the tightness of the vanadium interaction is a portent of the **111P** ring opening.

As an additional test of the obtained geometries, the **MC_5H_5** (M = Ti, Cr) complexes were first optimized with the $M\cdots C_b$ bond lengths frozen at the **VC_5H_5** value of 2.25 Å. This constrained "stationary point" was subjected to a full geometry optimization. In both cases, the **111P** ligand relaxed to the outer coordination sphere observed in the initial geometry optimizations.

Even for the more tightly bonded **VC_5H_5** adduct there is minimal spin density on the 1.1.1-propellane ligand. For free **111P**, calculated Mulliken charges are +0.78 e^- on the bridgehead carbons, −0.82 e^- on the methylene carbons, and +0.15 e^- for each H. Upon formation of **VC_5H_5**, Figure 5b indicates a modest amount of charge transfer such that the **111P** ligand has an overall charge of +0.11 e^-. For the related Ti and Cr adducts, there is minimal spin density on the **111P** ligand and minimal charge transfer, as judged by the Mulliken populations.

111P Ring-Opening Transition States. The ring-opening transition states for conversion of **111P** in **MC_5H_5** to the corresponding *exo*-methylenecyclobutylidene complex **$MC_4H_4{=}CH_2$** was identified for all three metals under consideration. Intriguingly, the enthalpic and entropic barriers were computed to be quite similar for the two earlier metals titanium ($\Delta H^\ddagger$ = 21.8 kcal/mol, $\Delta S^\ddagger$ = −6.81 cal/(mol K))[72−75] and vanadium ($\Delta H^\ddagger$ = 20.6 kcal/mol, $\Delta S^\ddagger$ = −1.73 cal/(mol K)) and much higher for chromium ($\Delta H^\ddagger$ = 36.0 kcal/mol, $\Delta S^\ddagger$ = −2.98 cal/(mol K)).[76,77]

As a reference, the ring-opening barrier for the **111P** is 37.3 kcal/mol ($C_b\cdots C_{exo}$ = C_1-C_2 = 2.96 Å) using the high-accuracy G3B3 *ab initio* composite method and 38.8 kcal/mol with the M06/6-311+G(d) level of theory ($C_b\cdots C_{exo}$ = 2.91 Å). Its geometry is shown in Figure 6a. The chromium complex **3** ring-opens **111P** with a free energy barrier close to the uncatalyzed limit, thus rationalizing the retention of the tricyclic core in the ultimate dimerization of **CrC_5H_6** to form $(silox)_3Cr(C_5H_6)_2Cr(silox)_3$ (**3_2P_2**).

For a given metal, the $M(silox)_3$ reactants, the **MC_5H_6** adducts, and the ring-opening transition states (TSs) **$MC_4H_4{=}CH_2$** were all computed to be the lowest in free energy for the same multiplicities. For **$VC_4H_4{=}CH_2$**, the unrestricted singlet TS was ∼20 kcal/mol higher than the lowest-energy triplet. For **$CrC_4H_4{=}CH_2$** the doublet was calculated to be 26.0 kcal/mol higher than the quartet TS. As a consequence, since the metal-catalyzed ring opening of **111P** is not computed to involve any spin flips, any spin crossing that accompanies ring opening of **111P** presumably occurs after the TS.

The core transition state geometries are similar among the three metals studied. The metal−C_b bond lengths are 2.14 (Ti), 2.08 (V), and 2.03 (Cr) Å, and the calculated TS for **$VC_4H_4{=}CH_2$** is illustrated in Figure 6b. It is interesting to note that the C_b distances to the C_{exo} that becomes the *exo*-methylene of the ultimate products are computed to be 2.08 (Ti), 2.31 (V), and 2.48 Å (Cr), which are considerably less than the corresponding ∼2.9 Å distance in the uncatalyzed ring opening. Hence, the C_b-C_{exo} distance is suggestive of a late transition state with the TS becoming later in the order Ti < V < Cr ≪ **111P** (free organic).

Thermodynamics of Ring Opening. The conversion of **MC_5H_6** to the *exo*-methylenecyclobutylidene complex was computed to be exothermic (−6.7 kcal/mol) and exergonic (−6.3 kcal/mol) for vanadium (ΔS° = −1.36 cal/(mol K)). Note that the calculated vanadium−alkylidene product corresponding to $(silox)V{=}(^cC_4H_4){=}CH_2$ (**$2{=}C_5H_6$**) is a singlet, as expected of a formally d^0 complex, but a triplet was only 2.9 kcal/mol higher in free energy. The corresponding thermodynamics for the formation of the doublet titanium alkylidene are ΔH° = −17.1 kcal/mol, ΔG° = −16.3 kcal/mol, and ΔG° = −2.4 kcal/mol. Obviously, this product must be unstable with respect to $(silox)_3Ti$ (**1**) and products of free 3-*exo*-methylenecyclobutylidene. Chromium was similar to vanadium, and the computed thermodynamics for the hypothetical ring-opening are ΔH° = −12.7 kcal/mol, ΔG° = −13.5 kcal/mol, and ΔS° = +2.49 cal/(mol K).

Different Pathways. There is an interesting trichotomy among the 3d metal silox complexes in terms of their observed reactivity with **111P**. The doublet $(silox)_3Ti$ (**1**) affords only products derived from 3-*exo*-methylenecyclobutylidene. $(silox)_3V$ (**2**) or $(silox)_3V(THF)$ (**2**-THF) reacts to provide the stable alkylidene $(silox)V{=}(^cC_4H_4){=}CH_2$ (**$2{=}C_5H_6$**), and $(silox)_3Cr$ (**3**) dimerizes to $(silox)_3Cr(C_5H_6)_2Cr(silox)_3$ (**3_2P_2**) without degradation of the tricyclic frame of **111P.**

The computed free energy barriers to the ring opening of **111P** relative to the pertinent ground-state reagents used experimentally are as follows: 25.1 kcal/mol ($^2Ti(silox)_3$ (**1**) + **111P** → **$^2TiC_4H_4{=}CH_2$**), 22.3 kcal/mol ($^3V(silox)_3(THF)$ + **111P** → **$^3VC_4H_4{=}CH_2$** + THF), and 38.9 kcal/mol ($^4Cr(silox)_3$ (**3**) + **111P** → **$^4CrC_4H_4{=}CH_2$**). No spin changes occur prior to the TSs, and the barrier for ring opening for **3** precludes this path relative to a lower energy path for dimerization.

Vanadium. $^3V(silox)_3(THF)$ (**2**-THF) has the smallest computed barrier ($\Delta G^\ddagger$ = 22.3 kcal/mol) to ring opening of

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111P, which binds to the inner coordination sphere of the vanadium. In addition, the free energy for dissociation of THF from **2**-THF is calculated to be −3.0 kcal/mol; thus, solvent loss is not an impediment. The unrestricted singlet ring-opening transition state was found and is computed to be ∼20 kcal/mol higher than the corresponding triplet TS, suggesting that the "spin-flip" from the triplet to the singlet surface occurs after the transition state, and ring opening occurs with great alacrity to afford the stable, d^0-alkylidene ^{1}(silox)-V=($^cC_4H_4$)=CH_2 (**2**=C_5H_6).

Chromium. ^{4}Cr(silox)$_3$ (**3**) has a very large computed barrier to ring opening of 1.1.1-propellane, essentially being equivalent to the metal-free $\Delta G^‡$ of 36.9 kcal/mol, and the corresponding doublet TS is much higher in energy. Given the large barrier to ring opening and alkylidene formation,[76,77] the weakly bound adduct dimerizes to the calculational equivalent of (silox)$_3$Cr(C_5H_6)$_2$Cr(silox)$_3$ (**3**$_2$**P**$_2$) in a reaction that is exothermic (−13.1 kcal/mol) and only mildly endergonic (+4.3 kcal/mol), ΔS = −58.5 cal/(mol K). The most stable form of the dimer is a quintet with a $C_b'-C_b'$ bond of 1.48 Å and Cr−C_b distances of 2.04 Å, close to the experimental values. A septet, ^{7}**3**$_2$**P**$_2$, is 16.0 kcal/mol higher in free energy and has an asymmetric structure (CrC_b = 2.06 and 3.16 Å, Cb′−Cb′ = 1.51 Å) reminiscent of (silox)$_3$Cr−P−P···^{4}Cr-(silox)$_3$. An additional triplet is similar in free energy to the septet. While the mechanism to form the chromium dimer is not entirely clear, it must proceed at an appreciable rate, as it is swift at room temperature and much more competitive than the ring-opening path.

Titanium. For ^{2}Ti(silox)$_3$ (**1**) the computed free energy barrier to ring opening is 25.1 kcal/mol relative to **1** and **111P**, or ∼2.8 kcal/mol higher than the vanadium system. If the $\Delta\Delta G^‡$ value is accurate, it corresponds to a ca. 2 orders of magnitude slower rate of ring opening at the experimental temperature of 23 °C. **111P** forms only a weak outer-sphere complex with Ti(silox)$_3$ (**1**), and conversion of the adduct **M**$\mathbf{C_5H_6}$ to the ring-opening TS (^{2}**Ti**$\mathbf{C_4H_4}$=$\mathbf{CH_2}$) leads to a product that does not have the capability to form an alkylidene.[72−75] Its structure is best construed as a titanium-substituted organic radical, with less spin density on the titanium (0.26 e^-) versus 0.73 e^- spin density on the attached carbon (C_b). Presumably, dissociation of 3-*exo*-methylenecyclobutylidene is facile as a consequence of this "half π-bond". This catalyzed degradation of **111P** must be quite fast, as the computed formation of a diamagnetic dimer akin to **3**$_2$**P**$_2$, i.e. (silox)$_3$Ti(C_5H_6)$_2$Ti(silox)$_3$ (^{1}**1**$_2$**P**$_2$), is highly exothermic (−74.6 kcal/mol) and exergonic (−55.6 kcal/mol).

■ CONCLUSIONS

The experiments and calculations provide a reasonable rationale for the trichotomy in reactivity of **111P** with (silox)$_3$M (M = Ti (**1**), V (**2**) (or M = V(THF) (**2**-THF) Cr (**3**))). Facile ring opening of **111P** adducts occurs for M = Ti, V, but only the latter can form the metal−carbon double bond crucial for stability. The titanium is short 1 e^-, and consequently, the titanium−carbon bond of order 1.5 is prone to release of the 3-*exo*-methylenecyclobutylidene fragment, which forms the standard stable rearrangement products. As a first-order degradation process, it outcompetes a potential dimerization of adduct **Ti**$\mathbf{C_5H_6}$ to afford a coupled product akin to the chromium case, even though the latter is considerably favorable thermodynamically. For **3**, and adduct **Cr**$\mathbf{C_5H_6}$, the barrier to **111P** ring opening is simply too high, and dimerization to (silox)$_3$Cr(C_5H_6)$_2$Cr(silox)$_3$ (**3**$_2$**P**$_2$), despite its high unfavorable entropy, proves to be the dominant path.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.2c00313.

Experimental details on all procedures, spectroscopic data, and X-ray crystallographic information pertaining to (silox)V=($^cC_4H_4$)=CH_2 (**2**=C_5H_6) (CCDC-2181579) and (silox)$_3$Cr(C_5H_6)$_2$Cr(silox)$_3$ (**3**$_2$**P**$_2$) (CCDC-2181580) (PDF)

Accession Codes

CCDC 2181579−2181580 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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