

Al to V; (iii) alkyl transfer is also supported by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, which both exhibit two sets of characteristic resonances for  $\text{Me}_3\text{SiCH}_2$  groups on Al and V; and (iv) the  $^{17}\text{O}$  resonance at  $\delta$  825 indicates the presence of a V=O double bond, which is coordinated to aluminum in the molecular plane of symmetry because the methylene protons on  $\text{Al}(\text{CH}_2\text{SiMe}_3)$  groups are diastereotopic, while the methylene protons on the  $\text{V}(\text{CH}_2\text{SiMe}_3)$  group are equivalent.

Upon warming above  $-10$  °C, complex **4** undergoes a clean first-order reaction ( $t_{1/2} = 21$  min at  $5$  °C) to produce a new oxo-vanadium(V) alkyl complex, which affords poorly diffracting orange crystals from pentane ( $-40$  °C, 2 weeks, 45%). Solution molecular weight data, combustion analysis, and multinuclear NMR data strongly suggest that this complex is **5**.<sup>14</sup> The  $^{51}\text{V}$  resonance at  $\delta$  907 and the  $^{17}\text{O}$  resonance at  $\delta$  777 are both consistent with an oxo-vanadium(V) dialkyl moiety; the  $^{29}\text{Si}$  NMR spectrum indicates that the complex is still bisected by a molecular plane of symmetry and that there is only one V=O-Si linkage; the  $^1\text{H}$  NMR data reveal that the methylene protons on V- $(\text{CH}_2\text{SiMe}_3)$  groups are diastereotopic, while the methylene protons on the Al- $(\text{CH}_2\text{SiMe}_3)$  group are equivalent.

Complex **5** is indefinitely stable in toluene- $d_8$  at  $25$  °C, and there is no evidence for the formation of low-valent species. Exposure of toluene- $d_8$  solutions of **5** to ethylene (1 atm,  $25$  °C) quickly initiates olefin polymerization, which continues until gelation of the solution prevents further uptake of ethylene. The polymer obtained in this fashion is similar to the polyethylene produced from the reactions of **1** with  $\text{Me}_3\text{Al}$  or  $\text{Al}(\text{CH}_2\text{SiMe}_3)$ ,<sup>8,15</sup> but the polydispersity is somewhat larger ( $M_w/M_n = 5.72$ ). Numerous attempts were made to spectroscopically detect  $\text{Me}_3\text{SiCH}_2$  end groups on the polymer, but the number of these groups was too small to observe. Chain propagation and transfer are clearly much faster than initiation, and only a small amount of **5** (<5%) reacts before gelation occurs.<sup>16</sup>

The stoichiometric similarity of this system to several  $\text{SiO}_2$ -supported catalysts provides a compelling case for high-valent, oxo-vanadium(V) alkyl complexes as active sites in at least some of these systems.<sup>17</sup> It also suggests a new manifold of reactions for the alkylaluminum cocatalysts that are so often added to these catalysts. High-valent vanadium alkyl complexes are clearly reasonable candidates for active sites on  $\text{SiO}_2$ -supported polymerization catalysts. A full account of our efforts to elucidate the role of **5** in the polymerization of olefins, as well as its relationship to more conventional models for silica-supported vanadates (e.g.,  $\text{R}_{3-n}(\text{Ph}_3\text{SiO})_n\text{VO}$ ), will be reported in due course.

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(14) For **5**:  $^1\text{H}$  NMR (500.1 MHz,  $\text{C}_7\text{D}_8$ ,  $20$  °C)  $\delta$  3.43 (br d,  $J = 6$  Hz, 2 H,  $\text{VCH}_2\text{Si}(\text{CH}_3)_3$ ), 3.16 (br d,  $J = 6$  Hz, 2 H,  $\text{VCH}_2\text{Si}(\text{CH}_3)_3$ ), 2.10 (br m, 13 H), 1.70 (br m, 35 H), 1.30 (br m, 22 H), 1.00 (br m, 7 H), 0.56 (s, 9 H,  $\text{AlCH}_2\text{Si}(\text{CH}_3)_3$ ), 0.12 (s, 18 H,  $\text{VCH}_2\text{Si}(\text{CH}_3)_3$ ), -0.32 (s, 2 H,  $\text{AlCH}_2\text{Si}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.76 MHz,  $\text{C}_7\text{D}_8$ ,  $20$  °C)  $\delta$  120 (br s,  $w_{1/2} = 250$  Hz), 28.45, 28.18, 28.03, 27.87, 27.65, 27.54, 27.39, 27.25 ( $\text{CH}_2$ ), 25.45, 24.62, 24.03, 23.60 (CH, 2:3:1:1), 3.03 ( $\text{AlCH}_2\text{Si}(\text{CH}_3)_3$ ), 0.959 ( $\text{VCH}_2\text{Si}(\text{CH}_3)_3$ ), -6.75 ( $\text{AlCH}_2\text{Si}(\text{CH}_3)_3$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.35 MHz,  $\text{C}_7\text{D}_8$ ,  $20$  °C)  $\delta$  6.72 ( $\text{VCH}_2\text{Si}(\text{CH}_3)_3$ ), 1.52 ( $\text{AlCH}_2\text{Si}(\text{CH}_3)_3$ ), -67.08 (br sh), -67.22, -67.82, -68.18, -70.18 (1:1:2:1:2);  $^{51}\text{V}$  NMR (131.54 MHz,  $\text{C}_7\text{D}_8$ ,  $20$  °C)  $\delta$  +907 ( $w_{1/2} = 510$  Hz);  $^{17}\text{O}$  NMR (67.79 MHz,  $\text{C}_7\text{D}_8$ ,  $20$  °C)  $\delta$  +777 ( $w_{1/2} = 480$  Hz). Anal. Calcd (Found) for  $\text{C}_{54}\text{H}_{110}\text{Si}_{10}\text{O}_{13}\text{VAl}$ : C, 48.9 (48.4); H, 8.36 (8.02).

(15) IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra indicate that the polymer is comprised of linear chains with methyl and vinyl termini: GPC analysis,  $M_n = 22470$  and  $M_w = 128500$  Da; DSC analysis,  $T_m = 133.9$  °C.

(16) The amount of **5** consumed during the polymerization was monitored by comparing the integrated  $^1\text{H}$  NMR intensities of its methylene resonances (i.e.,  $\text{TMSCH}_2\text{V}$ ) versus a ferrocene internal standard. Numerous spectra were recorded using long recycle delays to ensure accurate integrated intensities.

(17) A referee has (correctly) noted that the formation of **5** only requires 1 equiv of  $\text{R}_3\text{Al}$  per V but that the system described in ref 8 is most active when **1** is reacted with  $\sim 2$  equiv of  $\text{R}_3\text{Al}$ . Although seemingly contradictory, it is important to realize that the "maximum activity" measured in ref 8 does not necessarily reflect the true stoichiometry of the catalyst-producing reaction. Possible roles for the "extra"  $\text{R}_3\text{Al}$  will be discussed in a forthcoming full paper.

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## 2-Butyne and Hydrogen Chloride Cocrystallized: Solid-State Geometry of $\text{Cl-H}\cdots\pi$ Hydrogen Bonding to the Carbon-Carbon Triple Bond

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Hydrogen bonding of the type  $\text{X-H}\cdots\pi$ , from a hydrogen-halide molecule  $\text{HX}$  to the  $\pi$ -electron density of the carbon-carbon double or triple bond, has been studied repeatedly and by various methods, mainly by microwave and IR spectroscopy as well as theoretical calculations.<sup>1-5</sup> Weakly bound complexes, considered to be the first stage of an electrophilic addition to the alkene or alkyne, are usually assigned a T-shaped configuration, i.e., with the X-H bond oriented perpendicular to the C-C multiple bond. Whereas most of the studies refer to the gaseous state or an argon matrix, the following<sup>6</sup> is a first report on relevant crystal structures, viz., of the two low-melting complexes 2-butyne-HCl and 2-butyne-2HCl.

The complexes were observed to form individual solid phases, melting at  $-100$  (decomposition) and  $-113$  °C, respectively, by applying difference thermal analysis to the whole underlying (quasi)binary system. Sample preparation and handling had to be done exclusively at low temperatures to avoid any irreversible attack on the triple bond, of which a large variety of possible products is known.<sup>7</sup> The melting diagram obtained differs from that of an earlier report.<sup>5</sup> In particular, a third intermediary solid phase, 2-butyne-4HCl, could not be confirmed.

Using simple cooling for 2-butyne-HCl and a miniature zone-melting technique<sup>8</sup> for 2-butyne-2HCl, single crystals of the complexes were grown in thin-walled quartz-glass capillaries on a Siemens AED2 four-circle diffractometer. The instrument was equipped with a low-temperature device and used also for the subsequent X-ray measurements with graphite-monochromatized  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073$  Å). The data were processed and all atoms directly localized and refined without constraints in the usual way; see Table I. The program system SHELXTL PLUS<sup>9</sup> was used on a VAXStation 3200 (Digital) computer. A somewhat lower accuracy for the 1:1 complex noticeably affects only the positions of the methyl H atoms, which appear less satisfactory than in the 1:2 complex, possibly connected with an inherent but not easily resolved disorder.

The molecular geometry of the complexes in the solid state, with interatomic distances and angles, is depicted in Figure 1. The T shape, as referred to above, is convincingly displayed by the

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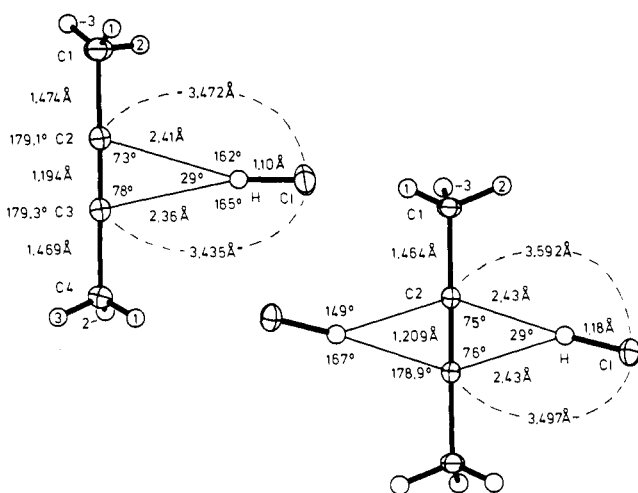
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**Table I.** Crystallographic Data and Experimental and Computational Values Related to the Structure Determinations

	2-butyne·HCl	2-butyne·2HCl
mp, °C	-100 dec	-113
measuring temp, °C	-150	-170
crystal system	monoclinic	monoclinic
space group; Z	$P2_1/c$ ; 4	$C2/c$ ; 4
lattice constants		
a, Å	4.123 (2)	13.373 (7)
b, Å	13.675 (8)	7.679 (4)
c, Å	9.917 (6)	6.921 (4)
$\beta$ , deg	95.56 (4)	90.47 (4)
V, Å <sup>3</sup>	556.5 (5)	710.7 (7)
calcd density, g/cm <sup>3</sup>	1.08	1.19
range of 2 $\theta$ , deg	3-70	3-70
unique data: obsd, <sup>a</sup> all	1871; 2431	1318; 1573
variables in last cycle	74	44
weighting g <sup>b</sup>	0.0004	0.0004
R; <sup>c</sup> R <sub>w</sub> <sup>c</sup>	0.063; 0.087	0.042; 0.055
$\Delta\rho$ , e/Å <sup>3</sup> : min; max	-0.45; 0.48	-0.46; 0.47

<sup>a</sup> With  $|F_o| \geq 3.92\sigma_F$ . <sup>b</sup> g in  $w = 1/(\sigma_F^2 + g|F_o|^2)$ . <sup>c</sup> For observed reflections only.



**Figure 1.** Solid-state molecular geometry of the complexes 2-butyne·HCl (upper left) and 2-butyne·2HCl (lower right), with interatomic distances and angles. The standard deviations, with (without) participation of the H atoms, are 0.003 (0.03–0.04) Å and 0.2° (0.4–3°) for the 1:1 complex and 0.001–0.002 (0.03) Å and 0.1° (0.3–2°) for the 1:2 complex. Projections from infinity onto the plane Cl, C2, C3 and along the crystallographic 2-fold axis, respectively; 25%-probability ellipsoids for the Cl and C atoms.

1:1 complex, but only approximately so, probably due to packing interactions, by the 1:2 complex, where *both* HCl molecules, related by a crystallographic  $C_2$  axis across its center, approach the triple bond. The distance between the Cl atoms and the triple bond is 3.40 Å for the 1:1 complex and 3.48 Å for the 1:2 complex and thus in both cases distinctly smaller than the 3.699 Å derived for the gas-phase acetylene–HCl dimer.<sup>1</sup> Nevertheless, the geometry of the 2-butyne molecule appears largely undisturbed and comparable to that in the crystal structure of the alkyne alone.<sup>10</sup> In the 1:2 complex, the dihedral angle at the triple bond between the two Cl atoms is 112°.

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**Supplementary Material Available:** Tables of atomic parameters and methyl-group geometries for 2-butyne·HCl and 2-butyne·2HCl (2 pages); listing of observed and calculated structure factors for 2-butyne·HCl and 2-butyne·2HCl (13 pages). Ordering information is given on any current masthead page.

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## Catalytic and Regioselective Acylation of Aromatic Heterocycles Using Carbon Monoxide and Olefins<sup>1</sup>

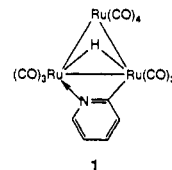
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Many transition metal compounds are known to be excellent reagents for the selective activation of alkyl or aryl carbon–hydrogen bonds.<sup>2</sup> Although there are numerous examples of stoichiometric C–H bond oxidative addition to metal centers, catalytic functionalization of the C–H bond is still a relatively rare phenomenon.<sup>3</sup> The low catalyst turnover frequencies (ca. 0.05–4/h) observed for these catalytic reactions limit their practical utility; thus, a current challenge is to increase the rate of reaction while still maintaining high selectivity to desired products. We report our initial studies in this area using the cluster compound  $Ru_3(CO)_{12}$ , carbon monoxide, and olefins to catalytically acylate the ortho positions of aromatic heterocycles with extremely high regioselectivity and moderate catalyst turnover frequencies up to 300/h.

The goal of our work was to develop a method to catalytically functionalize the ortho positions of aromatic heterocycles with alkyl or acyl groups.<sup>4</sup> Triruthenium dodecarbonyl is reported to selectively activate the ortho positions in pyridine and other nitrogen-containing aromatic heterocycles to form ortho-metalated species **1**.<sup>5</sup>



It was our hope that these species might be prepared in situ and be made to react with olefins to form alkyl-substituted

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