from >95% $CpRe(CO)_2D_2$ and KH) with **5** in THF was followed by ^2H NMR spectroscopy. Only one signal at δ 4.05 due to $Cp(CO)_2Re(CH_2{=}CDCH_3)$ (**6-*d***) was detected.

We have attempted to independently synthesize the intermediate II proposed for alkyne hydrogenation by Re–Pt dihydride **1**. Although II was not observed, the risky prediction of Re alkene complex formation with retention of vinyl stereochemistry was borne out, consistent with our hypothesis that II is a precursor of rhenium alkene complexes. The reactions of vinylplatinum compounds with $Cp(CO)_2ReH^-$ (**3**) are rare examples of the cleavage of a vinyl–transition-metal bond by a transition-metal hydride.[9]

Acknowledgment. Financial support from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged. We thank Johnson-Matthey for a generous loan of precious metals.

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[3 + 1] Cycloaddition: Reaction of Dichlorogermylene with Hexafluoro-2-propanethione 1-Adamantylimide

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Summary: Reaction of hexafluoro-2-propanethione 1-adamantylimide (**1**) and dichlorogermylene at room temperature gives the [3 + 1] cycloadduct $(CF_3)_2CSN(R)GeCl_2$ (**2**; R = adamantyl). The bond angles of the four-membered CSNGe heterocycle **2** are all close to 90°. This compound exhibits an unexpected stability at room temperature.

Cycloaddition reactions play an important role in organic chemistry, but only a few publications have appeared that deal with [3 + 1] cycloaddition reactions.[1-6] To our knowledge, there have so far been no reports on [3 + 1] cycloaddition reactions with carbenes or their homologues.[7] Heterocumulenes are important precursors for cycloaddition reactions.[8]

Recently we described the synthesis of $(CF_3)_2C{=}S{=}NR$ (**1**; R = 1-adamantyl) using $Cl(CF_3)_2CSN(H)R$ as starting material.[9] The latter compound reacts with $NaN(SiMe_3)_2$ or $LiN(SiMe_3)_2$ in a 1,3-dehydrochlorination reaction to yield **1**. We have shown that **1** reacts with norbornene in a [2 + 3] cycloaddition reaction to yield the isothiazolidine.[9]

Herein we describe the reaction of **1** with dichlorogermylene–dioxane to yield $(CF_3)_2CSN(R)GeCl_2$ (**2**).

The reaction of **1** with 1 molar equiv of dichlorogermylene–dioxane in Et_2O at 20 °C afforded **2** (mp 103 °C) in 42% yield. After recrystallization from THF at −20 °C, yellow crystals of **2** are obtained that hydrolyze readily when exposed to air. In the ^{19}F NMR spectrum of **2** a single line at −62.3 ppm is consistent with formation of the four-membered heterocyclic cycloaddition product. This has been confirmed by the single-crystal X-ray structure[10] (Figure 1).

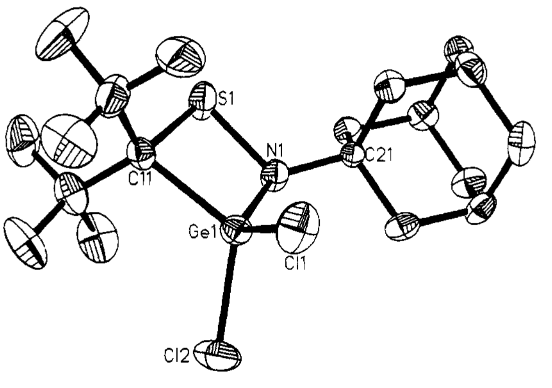
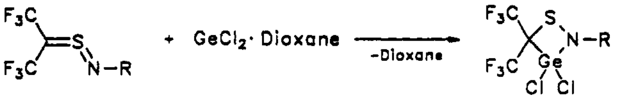


Figure 1. Structure of **2**, shown with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Ge1–N1 = 1.813 (3), Ge1–Cl1 = 2.008 (4), N1–S1 = 1.787 (4), S1–C11 = 1.819 (4); N1–Ge1–Cl1 = 82.9 (2), Ge1–N1–S1 = 96.9 (2), N1–S1–C11 = 89.3 (2), S1–C11–Ge1 = 89.4 (2).

Scheme I



1 2

R= 1-Adamantyl-

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[10] Crystal data for $C_{13}H_{15}Cl_2F_6GeNS$ (**2**) at −120 °C: $a = 11.811$ (2) Å, $b = 11.431$ (2) Å, $c = 12.800$ (2) Å, $\beta = 91.42$ (2)°, $V = 1727.6$ (5) $Å^3$, $Z = 4$, $d_{calcd} = 1.83$ g/cm^3, space group $P2_1/c$. A total of 2661 reflections were measured on a STOE-Siemens-AED diffractometer. After equivalent reflections were merged, 1937 reflections with $F > 3\sigma(F)$ were used for all calculations (all programs written by G.M.S.): final residual R = 0.039, R_w = 0.033. A riding model with idealized hydrogen geometry was employed for H atom refinement. Further details of the structure determination (atomic coordinates, complete bond lengths and angles, structure factors, and displacement parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote the full literature citation and the reference number (CSD 55654).

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The S–N (1.787 (4) Å) and the S–C bond (1.819 (4) Å) are about 0.2 Å longer than in 1 (1.544 and 1.646 Å, respectively), which indicates that the double bonds have become single. The NSC angle is reduced from 108.9° (1) to 89.3° (2). Although the bond angles of the four-membered heterocycle 2 are all close to 90°, this compound exhibits an unexpected stability at room temperature. No evidence for dimerization or ring expansion of 2 was found even after prolonged storage at room temperature. This illustrates the ability of the trifluoromethyl groups to stabilize strained ring systems.[11]

Experimental Section. All operations were conducted under an inert atmosphere. A 13.25-g (40-mmol) amount of 1 was added at room temperature to a suspension of 9.26 g (40 mmol) of dichlorogermylene–dioxane in 60 mL of anhydrous Et_2O. After 72 h the reaction mixture was filtered and the solvent removed in vacuo. The residue was crystallized from anhydrous THF at −20 °C, giving 8.0 g (42%) of a yellow solid, mp 103 °C. IR (Nujol 1270–1190 (vs, br), 980 (vs), 690 (vs), 450 (vs). ^1H NMR (C_6D_6; δ, ppm): 1.73 (m, 3 H), 1.52 (m, 6 H), 1.27 (m, 6 H). ^{19}F NMR (C_6D_6; δ, ppm): −62.3 (s). ^{13}C NMR (C_6D_6; δ, ppm): 123.7 (mq, $^1J_{CF}$ = 281 Hz, CF_3), 72.5 (sep, $^2J_{CF}$ = 32 Hz, $C(CF_3)_2$), 58.7 (s, Ad), 35.7 (s, Ad), 29.7 (s, Ad). Mass spectrum (70 eV; m/e (relative intensity)): 475 (10), 135 (100). Anal. Calcd for $C_{13}H_{15}Cl_2F_6GeNS$: C, 32.9; H, 3.2; N, 2.9. Found: C, 31.4; H, 3.6; N, 2.3.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Supplementary Material Available: Tables of crystal data and details of the structure solution and refinement, positional and thermal parameters, and bond distances and angles (7 pages); a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Metallacyclobutanes from (η^3-Crotyl)rhodium Complexes: Regioselectivity Dependence on Allyl Ligand Configuration. Reinvestigation of Nucleophilic Additions to Two Isomers of $[CpRh(^iPr_3P)(\eta^3\text{-crotyl})]^+BF_4^-$

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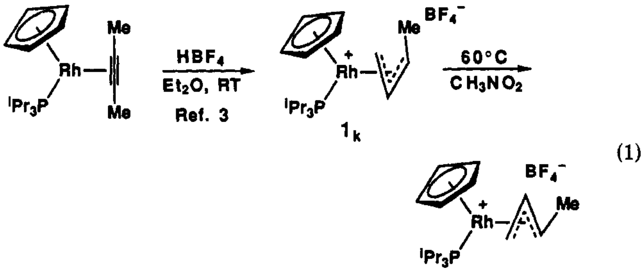
Summary: Nucleophilic addition to the exo, syn isomer of $[(C_5H_5)Rh(^iPr_3P)(\eta^3\text{-crotyl})]^+BF_4^-$ is shown to yield metallacyclobutane complexes in high yield, in contrast to a previous report. The β-unsubstituted metallacycle from hydride addition is unstable with respect to rearrangement to the (*E*)-2-butene complex, but β-monosubstituted metallacycles from carbon nucleophile addition are indefinitely stable. In contrast, the corresponding endo, anti isomer of $[(C_5H_5)Rh(^iPr_3P)(\eta^3\text{-crotyl})]^+BF_4^-$ suffers kinetic nucleophilic addition exclusively at the allyl terminal carbon, giving (*Z*)-olefin complexes.

Metallacyclobutane formation by kinetic nucleophilic addition to the η^3-allyl central carbon is general for complexes of the form $[(C_5Me_5)M(L)(\eta^3\text{-allyl})]^+X^-$ (M = Rh, Ir; L = Me_3P, C_2H_4; X = BF_4, PF_6, OTf).[1,2] It is therefore surprising that two isomers of the closely related cyclopentadienyl complex $[(C_5H_5)Rh(^iPr_3P)(\eta^3\text{-crotyl})]^+X^-$ (1; η^3-crotyl = 1-methyl-η^3-allyl; X = PF_6, BF_4) are reported not to give metallacyclobutane complexes on treatment with $LiAlH_4$ at low temperature.[3] To probe the origin of this discrepancy in reactivity, we have reinvestigated nucleophilic additions to this and related systems. In this communication, we report the reassignment of the η^3-crotyl configuration in one isomer of complex 1 and a complete divergence in reactivity between the two configurational isomers, only one of which kinetically yields the anticipated metallacyclobutane complexes. In addition, we find that an alkyl substituent on the metallacycle β-carbon syn to the phosphine ligand stabilizes the rhodacyclobutane complexes toward both rearrangement and decomposition.

The isomeric η^3-crotyl complexes 1_k and 1_t were prepared from $(C_5H_5)Rh(^iPr_3P)$(2-butyne) and $HBF_4 \cdot OEt_2$, as reported (eq 1).[3] The dramatic differences observed in the ^1H NMR resonances of the crotyl ligand,[4,5] coupled with our previous experience with isomeric η^3-allyl complexes of iridium,[1b] led us to suspect that these complexes were configurational isomers[6] as well as stereoisomers at the methyl substituent, as previously assigned. Difference NOE spectroscopy was used to resolve this ambiguity;[7] the



(1)

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[5] Spectroscopic and analytical data are provided as supplementary material.

[6] In the conventional nomenclature for η^3-allyl complexes of this type, exo refers to the allyl orientation "point up" toward the C_5R_5 ligand and endo to the corresponding "point down" configuration. Syn and anti refer to the orientation of the allyl substituent in relation to the allyl central proton.