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.

(11) Lacrampe, G.; Lavayssière, H.; Rivière-Baudet, M.; Satgé, J. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 21.

Metallacyclobutanes from (η^3-Crotyl)rhodium Complexes: Regioselectivity Dependence on Allyl Ligand Configuration. Reinvestigation of Nucleophilic Additions to Two Isomers of [CpRh(^{i}Pr$_3$P)(η^3-crotyl)]$^+$BF$_4^-$

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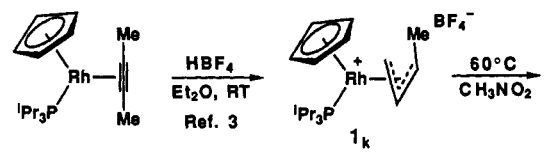
Summary: Nucleophilic addition to the exo, syn isomer of [(C_5H_5)Rh(^{i}Pr$_3$P)(η^3-crotyl)]$^+$BF$_4^-$ is shown to yield metallacyclobutane complexes in high yield, in contrast to a previous report. The β-unsubstituted metallacycle from hydride addition is unstable with respect to rearrangement to 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(^{i}Pr$_3$P)(η^3-crotyl)]$^+$BF$_4^-$ suffers kinetic nucleophilic addition exclusively at the allyl terminal carbon, giving (*Z*)-olefin complexes.

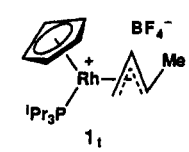
Metallacyclobutane formation by kinetic nucleophilic addition to the η^3-allyl central carbon is general for complexes of the form [(C_5Me_5)M(L)(η^3-allyl)]$^+$X$^-$ (M = Rh, Ir; L = Me_3P, C_2H_4; X = BF_4, PF_6, OTf).[1,2] It is therefore surprising that two isomers of the closely related cyclopentadienyl complex [(C_5H_5)Rh(^{i}Pr$_3$P)(η^3-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(^{i}Pr$_3$P)(2-butyne) and HBF_4·OEt_2, as reported (eq 1).[3] The dramatic differences observed in the



1_k

(1)



1_t

^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) (a) Tjaden, E. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6420. (b) Wakefield, J. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7057. (c) Tjaden, E. B.; Schwiebert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.*, in press.

(2) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3388. Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346.

(3) Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164.

(4) We report[5] spectroscopic data in $CDCl_3$ for the BF_4 salts of complex 1, complementing Werner's data in CD_3NO_2 for the PF_6 complexes.

(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.

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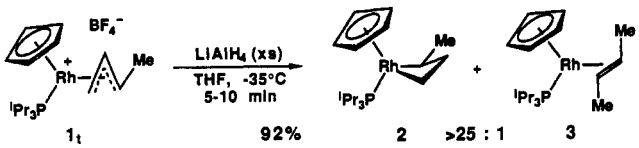
data clearly demonstrate that the kinetic isomer 1_k has the endo, anti rather than exo, anti configuration previously assigned to this complex. Analogous NOE experiments confirm that the thermodynamic isomer 1_t is the exo, syn isomer, as assigned.

The reaction of exo, syn complex 1_t with $LiAlH_4$ in THF at −78 °C to room temperature reportedly leads to a mixture of products that could not be separated or characterized definitively by NMR spectroscopy.[3] On detailed investigation, however, we find that this reaction gives a mixture of metallacyclobutane complex **2** and (*E*)-2-butene complex **3** (eq 2), in a ratio highly dependent on reaction

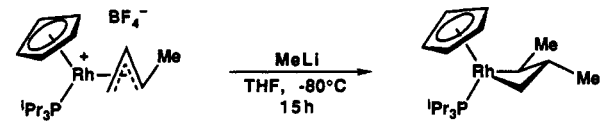


(2)

conditions. Under optimized conditions, metallacyclobutane formation is strongly favored, leading to a >25:1 ratio of complexes **2** and **3** in 92% isolated yield.[8] Both of these materials have been characterized by spectroscopy and by high-resolution mass spectrometry,[5,8] with the metallacyclobutane complex exhibiting characteristic high-field ^1H and ^{13}C NMR signals for the α-metallacycle protons and carbons.[1,2] Complex **2** rearranges and decomposes slowly on attempted recrystallization, yielding complex **3** and, surprisingly, minor amounts of a pentane-insoluble complex tentatively identified as cationic crotyl 1_t, but with an unidentified counterion. The rearrangement of complex **2** to **3** occurs even at low temperature and in the semisolid phase. Because of this instability, persistent, analytically pure samples of complexes **2** and **3** could not be obtained.

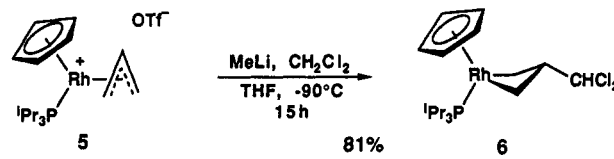
Lower isolated yields and decreased selectivity for the metallacyclobutane are observed using $LiAlH_4$ at higher concentration or prolonged reaction time, presumably accounting for the results described previously.[3] The use of $NaBH_4$, $LiBEt_3H$, or $LiAl(O^tBu)_3H$ also leads to markedly lower selectivity, tentatively attributed to either a less selective kinetic partitioning or faster metallacyclobutane rearrangement induced by these reagents. Mechanistic aspects of this reaction and determination of the factors that promote both rearrangement and conversion to cationic materials are under investigation.

The reactions of complex 1_t with carbon-based nucleophiles are more straightforward, leading to β-substituted metallacyclobutanes from alkylation at the allyl central carbon. The nucleophilic addition is stereospecific, leading to metallacyclobutane complexes with the β-substituents syn to the phosphine ligand.[9] Thus, addition of MeLi to complex 1_t in THF at −80 °C gives metallacyclobutane **4** (eq 3) as a spectroscopically pure oil in 71% yield after



(3)

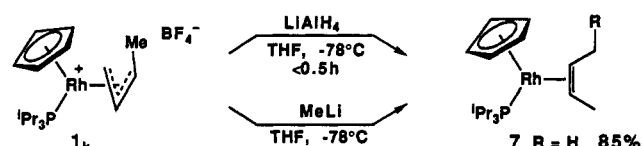
trituration with pentane and chromatography on deactivated neutral alumina under an inert atmosphere.[5] To obtain crystalline metallacyclobutane complexes, the use of chlorinated carbon nucleophiles was investigated. Conveniently, the low THF solubility and mild electrophilicity of the η^3-allyl complexes in this series allow such metastable nucleophiles to be generated in situ at low temperature. To illustrate, the addition of methyllithium (1.1 equiv) to a suspension of unsubstituted η^3-allyl complex **5**[5,10] in THF containing excess CH_2Cl_2 (ca. 10 equiv) at −90 °C leads exclusively to the crystalline, air-stable metallacyclobutane complex **6**, isolated in >80% yield (eq 4).[5]



(4)

In contrast to complex **2**, metallacyclobutane complexes **4** and **6** do not rearrange in solution. Stabilization toward decomposition thus requires replacing only the β-hydrogen syn to the phosphine ligand, suggesting that the rearrangement occurs by β-elimination[11] *stereospecifically* on the "underside" of the metallacyclobutane ring. This hypothesis will be evaluated both by labeling studies and by assessing the stability of substituted metallacyclobutane complexes epimeric at the β-position.

The reaction of endo, anti complex 1_k with $LiAlH_4$ is reported to give (*Z*)-olefin complex **7** in high yield (eq 5).[3]



(5)

Our investigation confirms this result, even using conditions optimized for metallacyclobutane formation. The metallacyclobutane complex anticipated from hydride delivery to complex 1_k is identical to that obtained from the exo, syn isomer 1_t, which we have shown to be sufficiently stable under these conditions to be both detected and isolated. Treatment of 1_k with MeLi under optimal conditions also leads exclusively to terminal adduct **8** (eq

(7) Irradiation of the allyl central proton resonance in kinetic isomer 1_k leads to significant enhancements in the signals for the phosphine isopropyl protons (6.0%) and the proton adjacent to the allyl methyl substituent (4.1%). Irradiation of this methyl group leads, inter alia, to enhancement of the C_5H_5 signal (5.2%). Finally, irradiation of the phosphine methyl groups leads to enhancements in the allyl central proton (3.1%) and both syn proton resonances (10.9, 6.5%).[5]

(8) Complex 1_t in dry, deoxygenated THF (0.01 M) under N_2 was treated with $LiAlH_4$ (4 equiv) at −35 °C. After 5 min, the solvent was removed in vacuo at low temperature, the residue was triturated with pentane, and the pentane extracts were concentrated. Partial data[5] for complex **2**: ^1H NMR (300 MHz, C_6D_6) δ 5.17 (d, J = 1.8 Hz, 5 H, C_5H_5), 3.71 (m, 1 H, H_β), 2.55 (m, 1 H, H_β), 2.06 (m, 1 H, H_α), 1.93 ("octet", $J_{PH} \approx J_{HH}$ = 7.3 Hz, 3 H, C*H*Me$_2$), 1.60 (d, J = 6.6 Hz, 3 H, α-CH$_3$), 0.99 (dd, J_{PH} = 12.6 Hz, J_{HH} = 7.4 Hz, 9 H, CH*Me*$_2$), 0.98 (dd, J_{PH} = 12.8 Hz, J_{HH} = 8.1 Hz, 9 H, CH*Me*$_2$), ~0.98 (m, 1 H, obscured by phosphine methyl resonance, H_α), 0.27 (m, 1 H, H_α); ^{13}C NMR (75 MHz, C_6D_6) δ 90.8 (br s, C_5H_5), 43.9 (d, J_{RhC} = 6.6 Hz, C_β), 31.4 (s, α-CH$_3$), 27.1 (d, J_{PC} = 20.0 Hz, CHMe$_2$), 20.4 (s, CH*Me*$_2$), 20.3 (s, CH*Me*$_2$), −10.6 (dd, J_{RhC} = 19.5 Hz, J_{PC} = 8.3 Hz, C_α), −30.9 (dd, J_{RhC} = 19.3 Hz, J_{PC} = 8.9 Hz, C_α); HRMS, M^+ calcd for $C_{18}H_{34}PRh$ 384.1439, found 384.1457. $[M - C_4H_8]^+$ calcd for $C_{14}H_{26}PRh$ 328.0815, found 328.0831.

(9) The stereochemistry at the β-position is inferred from determinations in the C_5Me_5 series[1] and has been recently confirmed by crystallographic data for a metallacycle in the Me_3P series.

(10) Complex **5** was prepared by a general new C–Si bond activation procedure to be reported separately: Tjaden, E. B.; Wakefield, J. B.; Schwiebert, K. E.; Stryker, J. M., manuscript in preparation.

(11) The terminology is phenomenological and is not meant to convey a detailed mechanistic pathway. In somewhat related platinacyclobutane systems, "β-elimination" proceeds via initial α-hydrogen elimination followed by a 1,2-hydrogen migration: Al-Essa, R. J.; Ling, S. S. M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 951 and references therein.

5), a product clearly inconsistent with kinetic central carbon alkylation and subsequent rearrangement.

The site of kinetic nucleophilic addition in this system is thus dependent on the coordination geometry of the crotyl ligand. It is not yet possible, however, to completely isolate the electronic effects of allyl configuration from the steric effects of substituent stereochemistry; unfortunately, neither the exo, anti crotyl nor the unsubstituted endo allyl complex can be prepared by standard methods. Both exo and endo configurational isomers of the structurally analogous $[(C_5Me_5)Ir(C_2H_4)(\eta^3\text{-allyl})]^+OTf^-$ react with strong nucleophiles to give metallacyclobutane complexes exclusively,[1b,12] but the comparison is acutely limited by the electronic differences in the ancillary ligand. The strong donor phosphine is expected to accentuate differences in coordination geometry and electron distribution in the isomeric allyl complexes, requiring a combination of crystallography, molecular orbital calculations,[13] and molecular mechanics to provide the insight necessary to rationalize the observed reactivity.

Acknowledgment. Financial support from the National Science Foundation, the NIH-BRSG program, a Union Carbide Innovation Recognition Award, and an American Cyanamid Faculty Award is gratefully acknowledged. We thank Johnson Matthey, Inc., for a generous loan of precious metals.

Supplementary Material Available: Spectroscopic and analytical data (including difference NOE spectra) for complexes 1-8 (5 pages). Ordering information is given on any current masthead page or may be obtained by writing directly to J.M.S.

(12) The overriding kinetic preference for metallacyclobutane formation in the iridium system is observed despite significant differences noted in the electrophilicity of potential reaction sites in the two isomers. A pronounced configuration dependence in this system for the addition of softer "nonkinetic" nucleophiles has, in fact, been noted.[1b]

(13) This degree of subtlety in reactivity is not readily accommodated by current theoretical treatments of the regioselectivity issue: (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047. Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Vol. 1, pp 897-937. (b) Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.

Photoinduced [6 + 2] Cycloadditions of Alkynes to Tricarbonyl(cycloheptatriene)chromium(0)

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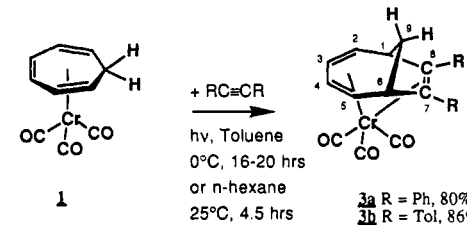
Summary: Photolysis of $[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$ (**1**) and RC≡CR (**2a**, R = Ph; **2b**, R = Tol) in toluene or *n*-hexane results in the formation of $[(\eta^2\text{:}\eta^4\text{-}C_9H_8R_2)Cr(CO)_3]$ (**3a,b**) in 70-85% isolated yield via a [6 + 2] cycloaddition reaction. Heating **3a,b** in toluene gives the bicyclo[4.2.1]nona-2,4,7-trienes **4a,b** and $[(\eta\text{-}C_6H_6Me)Cr(CO)_3]$. Photolysis of **1** and excess DMAD (dimethyl acetylenedicarboxylate, **5**) in toluene at 0 °C yields the bicyclotriene **4c** as the major product and small amounts of the arene $C_6(CO_2Me)_6$ and the [4 + 2] cycloadduct between **4c** and **5**.

Transition-metal-mediated higher order ([6 + 2], [4 + 4], and [6 + 4]) cycloaddition reactions have been demonstrated by a number of groups[1] and show a high selectivity for the higher order process over the competing [4 + 2] process. For example, Rigby and co-workers have recently reported that photolysis of solutions of $[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$ (**1**) and electron-deficient olefins leads to good yields of functionalized bicyclo[4.2.1]nona-2,4-dienes.[1a] Titanium-catalyzed [6 + 2] cycloadditions of bulky internal alkynes to cyclohepta-1,3,5-triene have also been reported,[1f,g] although the scope of this reaction is limited by a competing cyclotrimerization of the trienophile when smaller alkyne substituents are present. We now report photoinduced [6 + 2] cycloadditions between $[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$ (**1**) and alkynes that lead to complexes of bicyclo[4.2.1]nona-2,4,7-trienes as well as the free organic species.

Photolysis (450-W Conrad-Hanovia medium-pressure Hg vapor lamp, Pyrex glassware) of toluene solutions of **1** and 1 equiv of the alkynes RC≡CR (**2a**, R = Ph; **2b**, R = Tol) at 0 °C for 16-20 h resulted in a gradual disappearance of **1**, as monitored by IR spectroscopy, and formation of $[(\eta^2\text{:}\eta^4\text{-}C_9H_7R_2)Cr(CO)_3]$ (**3a**, R = Ph; **3b**, R = Tol) (eq 1).



(1)

Complexes **3a,b** were isolated as analytically pure deep red crystalline solids in 80% and 86% yields, respectively, and characterized using IR, ^1H NMR, and ^{13}C NMR

(1) (a) Rigby, J. H.; Henshilwood, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 5122. (b) Rigby, J. H.; Ateeq, H. S. *J. Am. Chem. Soc.* **1990**, *112*, 6442. (c) Kreitner, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297-375 and references therein. (d) Davis, R. E.; Dodds, T. A.; Hseu, T.-H.; Wagnon, J. C.; Devon, T.; Tancrede, J.; Mckennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 7562. (e) Nagashima, H.; Matsuda, H.; Itoh, K. *J. Organomet. Chem.* **1983**, *258*, C15. (f) Mach, K.; Antropiusova, H.; Petrusova, L.; Hanus, V.; Turecek, F.; Sedmera, P. *Tetrahedron* **1984**, *40*, 3295. (g) Mach, K.; Antropiusova, H.; Sedmera, P.; Hanus, V.; Turecek, F. *J. Chem. Soc., Chem. Commun.* **1983**, 805. (h) Bourner, D. G.; Brammer, L.; Green, M.; Moran, G.; Orpen, A. G.; Reeve, C.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1409.

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