Acknowledgment. The technical assistance of R. M. Swiatek, C. W. Dietrich, and L. Lardear is gratefully acknowledged.

Registry No. I, 86393-14-8; [Cu(CH_3CN)$_4$]BF_4, 15418-29-8; C_2H_2, 74-86-2; $NHpy_2$, 1202-34-2.

Supplementary Material Available: Tables of positional and thermal parameters (1 page). Ordering information is given on any current masthead page.

A Titanium Vinylidene Route to Substituted Allenes

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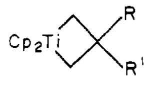
The unique structure and reactivity of allenes has prompted a long-term interest in these compounds by both synthetic and physical organic chemists.[2] In many cases, however, the synthesis of substituted allenes has proven difficult. Standard methods of allene synthesis include nucleophilic additions to propargyl halides[3] and acetates[4] and reductive cleavage of *gem*-dihalocyclopropanes.[5] These methods can lead to mixtures of the desired allene contaminated with the corresponding acetylenes, dienes, or other allenes.[6] Herein we report on a fundamentally different approach[7] for the preparation of a wide variety of di-, tri-, and tetrasubstituted allenes in good to excellent yield.

We have previously described the preparation and reactions of a variety of titanacyclobutanes of type **1**.[8] These metallacycles

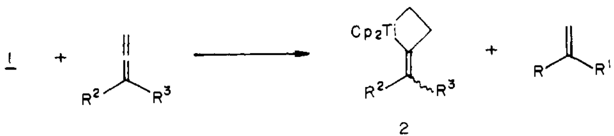


a) $R = R' = CH_3$
b) $R = CH_3$, $R' =$ n-propyl

1

have been shown to undergo a variety of synthetically and catalytically useful reactions.[9] More recently **1a** has been employed in the high yield synthesis of regiochemically pure titanium enolates using acid chlorides as substrates.[10]

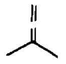
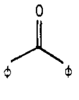
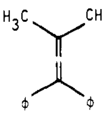
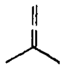
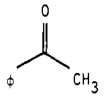
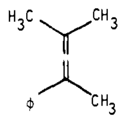
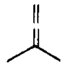
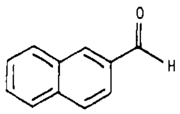
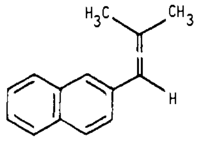
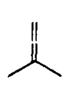
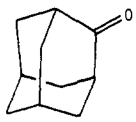
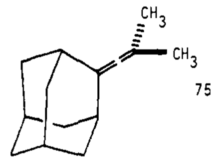
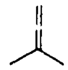
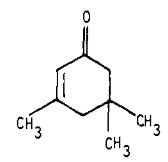
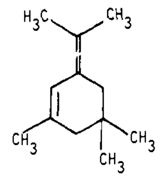
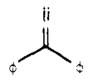
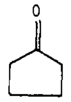
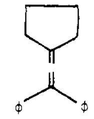
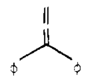
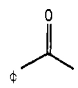
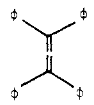
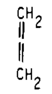
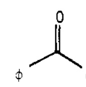
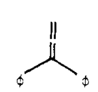
We have now found that the reaction of **1** with 1 equiv of a 1,1-disubstituted allene produces a quantitative yield (^1H NMR) of the new metallacycles **2** with the liberation of olefin (eq 1).[11]



2 (1)

In all cases these unsaturated metallacycles are obtained as the single regioisomer depicted as **2**. The structure of **2** has been assigned on the basis of ^1H and ^{13}C NMR data[12] and by their reaction chemistry.[13,14] When a benzene solution of **2** is treated with 1 equiv of a ketone for a period of 2–12 h at room tem-

Table I

starting allene	ketone	product allene^a	yield, %^{b}
			80^c
			56
			53
			75
			55
			72
			56
			58^c

^{a} All compounds were characterized by ^1H and ^{13}C NMR. ^{b} Isolated yields based on quantity of ketone used. ^{c} Ca. 3% 1,1-diphenylethylene was also isolated from this reaction.

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(1) Myron A. Bantrell Postdoctoral Fellow, 1982–1983.

(2) "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; Wiley-Interscience: New York, 1980.

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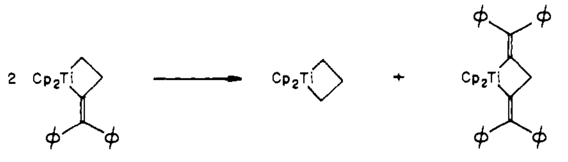
(7) For a different organometallic-based route to allenes see: Yoshida, T.; Negishi, E. *J Am. Chem. Soc.* **1981**, *103*, 1276.

(8) Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358.

(9) Straus, D. A.; Ho, S.; Buchwald, S. L.; Grubbs, R H., unpublished results.

(10) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 1664.

(11) Unsaturated metallacycles of type **2** appear to be thermally stable except in the case R = R' = Ph, where the following disproportionation occurs:



(12) For **2**, R = R' = CH_3: ^1H NMR (C_6D_6) δ 0.27 (m, 2 H), 1.80 (br s, 6 H), 2.6 (m, 2 H), 5.31 (s, 10 H); ^{13}C NMR $\{^1H\}$ (C_6D_6) δ -8.0, 22.1, 27.6, 66.7, 107.6, 124.6, 213.6.

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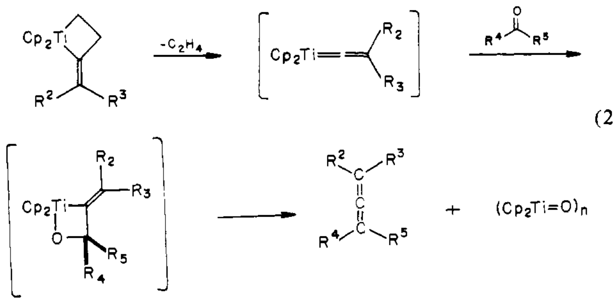
perature, a good to excellent yield of the substituted allene is formed (eq 2). We believe that this reaction, in analogy to the reaction of the Tebbe reagent[15] and metallacycles of type **1**, proceeds via the mechanism shown in eq 2.[16,17]



(2)

In Table I are shown the nature and yields of allenes formed using the above methodology. Experimentally the procedure is simple. In general 1 equiv of a 1,1-disubstituted allene is added to a benzene solution of metallacycle,[18] and the reaction is stirred at room temperature for 15 min. The ketone or aldehyde is added, and the reaction mixture is allowed to stir overnight at room temperature. At this point pentane is added and the solution rapidly filtered (Buchner funnel) through silica gel. Allenes of ca. 95% purity are obtained on evaporation of the filtrate. If necessary, the allene can be further purified by flash chromatography on silica gel.

In short we have developed a general synthesis of substituted allenes[19] that allows the preparation of a variety of structural types of these compounds. Moreover, the experimental ease of this method should enhance its attractiveness.

We are currently studying both the organometallic chemistry of the novel metallacycles **2** and further uses of these metallacycles in organic synthesis.[20]

Acknowledgment. We thank Dr. Steven Hentges for preliminary work. This research was supported by the National Science Foundation (Grant No. CHE-8214668).

Registry No. **2** ($R^2 = R^3 = \mathrm{CH_3}$), 86421-65-0; 1,1′-(3-methyl-1,2-butadienylidene)bisbenzene, 30979-53-4; (1,3-dimethyl-1,2-butadienyl)benzene, 17530-18-6; 2-(methyl-1,2-butadienyl)naphthalene, 86411-43-0; 2-(2-methyl-1-propenylidene)tricyclo[3.3.1.1^{3,7}]decane, 86411-44-1; 3-(2-methyl-1-propenylidene)-1,5,5-trimethylcyclohexene, 86411-45-2; 1,1′-((2-cyclopentylidene)ethenylidene)bisbenzene, 86411-46-3; 1,1′,1″,1‴-(1,2-propadiene-1,3-diylidene)tetrakisbenzene, 1674-18-6; 1,1′-(1,2-propadienylidene)bisbenzene, 14251-57-1; 3-methyl-1,2-butadiene, 598-25-4; 1,2-propadiene, 463-49-0; tricyclo[3.3.1.1^{3,7}]decanone, 700-58-3; 3,5,5-trimethyl-2-cyclohexen-1-one, 78-59-1; benzophenone, 119-61-9; acetophenone, 98-86-2; 2-formylnaphthalene, 66-99-9; cyclopentanone, 120-92-3; bis(cyclopentadienyl)-1,3-bis(diphenylmethylene)-1,3-propanediyltitanium, 86421-64-9.

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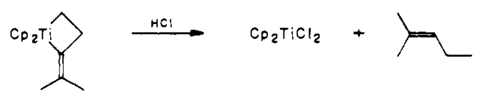
(13) Attempts to obtain crystals of **2**, $R = R' = \mathrm{CH_3}$, have not been successful.

(14) Hentges, S.; Grubbs, R. H., unpublished results, e.g.,



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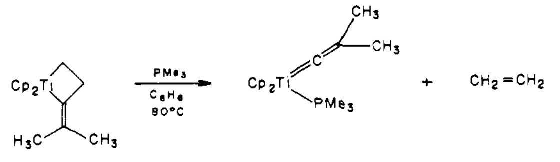
(16) Brown-Wensley, K. A. Ph.D. Thesis, California Institute of Technology, 1981.

(17) This mechanism is also supported by the following:[20]



(18) The use of the Tebbe reagent generally leads to lower yields and slightly less clean reactions.[20]

(19) Attempts to synthesize monosubstituted allenes have resulted only in low (~15–20%) yields of product. This is presumably due to the lability of **2**, $R = R' = H$, which readily adds a molecule of monosubstituted allene already formed, thus, diminishing the yield.

(20) Buchwald, S. L.; Grubbs, R. H., unpublished results.

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^{13}C CP-MAS NMR Spectra of Paramagnetic Solids

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Minneapolis, Minnesota 55455

Received April 4, 1983

High-resolution carbon-13 and other rare-spin nuclear resonances may now be obtained routinely by using cross-polarization magic angle spinning techniques (CP-MAS).[1] In small organic molecules there is no difficulty in resolving single carbon resonances with these methods; however, in large complex molecules the chemical shift dispersion may be insufficient to afford the resolution desired. In addition, other line-broadening mechanisms such as heteronuclear dipolar interactions that are not averaged by magic angle spinning because of quadrupole effects in the solid may decrease resolution.[2] We have therefore asked whether resolution enhancement methods using paramagnetic centers may be exploited in the solid as they are in the liquid.[3]

The use of paramagnetic molecules in the solid state to decrease T_1 of either the rare or the abundant spin is well-known and widely practiced;[4,5] however, the application of paramagnetically induced shifts in the solid is very largely unexplored. A very major difference between the liquid and solid application of the so-called shift reagent is that in the solid the paramagnetic molecule or ion may not diffuse rapidly among molecules of interest and give a fast exchange averaged resultant shift, the magnitude of which may be controlled by concentration of the paramagnetic species. In addition the lack of rapid molecular tumbling in the solid will permit the full development of the various origins of magnetic anisotropy in the solid and may have an important impact on the obtainable resolution. Finally, one expects that the obtainable resolution will depend on the battle between paramagnetically induced shift and relaxation. The latter may be severe in the solid because of short intermoment distances and longer electron relaxation times. Nevertheless, the potential benefits for the study of macromolecules such as proteins or metalloenzymes in the solid are great.

The ^{13}C NMR spectra of praseodymium acetate trihydrate with and without magic angle spinning obtained on a home built spectrometer to be described elsewhere are depicted in Figure 1 along with the magic angle spinning spectrum of the diamagnetic lanthanum acetate. The CP-MAS spectra demonstrate that though the interactions that cause line broadening may not all be inhomogeneous, magic angle spinning provides considerable narrowing of the solid-state spectrum. In fact, this narrowing is sufficient to be of quite general utility in analytical and structural applications.

The CP-MAS spectrum of praseodymium acetate is complicated by the presence of spinning sidebands, even at a spinning speed of 4.5 kHz. This result is consistent with the very large anisotropy apparent in the static spectrum (A). Comparison of the spectra obtained at 2.7 and 4.5 kHz demonstrates that the sharp line at 211 ppm and the three ill-resolved lines at 114, 66, and 28 ppm are invariant. The other lines in the CP-MAS spectra move with changes in spinning speed and are, therefore, assigned

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(3) See, for example: G. A. Webb, In "Nuclear Magnetic Resonance Spectroscopy of Paramagnetic Species"; Money, E. F., Ed.; Academic Press: New York, 1975, pp 1–145 and references therein.

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