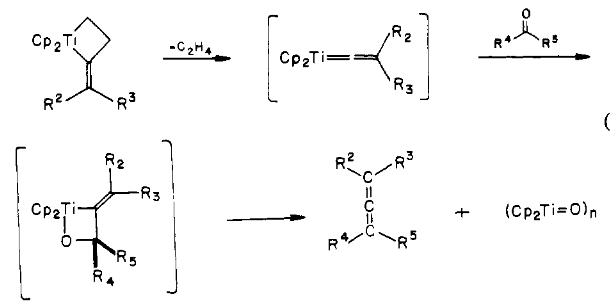
perature, a good to excellent yield of the substituted allene is formed (eq 2). We believe that this reaction, in analogy to the reaction of the Tebbe reagent[15] and metallacycles of type **1**, proceeds via the mechanism shown in eq 2.[16,17]



(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** ($R^2 = R^3 = CH_3$), 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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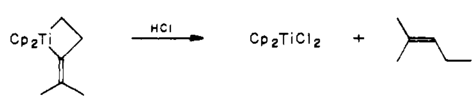
[13] Attempts to obtain crystals of **2**, $R = R' = CH_3$, have not been successful.

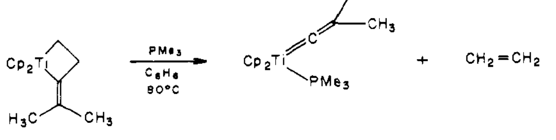
[14] Hentges, S.; Grubbs, R. H., unpublished results, e.g.,



[15] Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

[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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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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[1] Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031-1032.

[2] Naito, A.; Ganapathy, S.; McDowell, C. A. *J. Chem. Phys.* **1981**, *74*, 5393-5398.

[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.

[4] Bloembergen, N. *Physica (Amsterdam)* **1949**, *15*, 386-426.

[5] Ganapathy, S.; Naito, A.; McDowell, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 6011-6015.

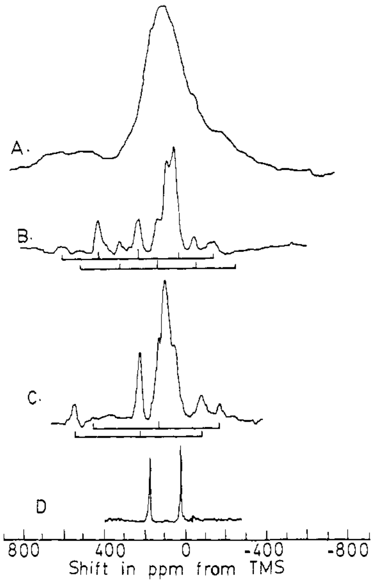

Figure 1. Proton decoupled solid-state ^{13}C cross-polarization spectra at 14.19 MHz of (A) praseodymium acetate, nonspinning; (B) praseodymium acetate, magic angle spinning at 2.7 kHz; (C) praseodymium acetate, magic angle spinning at 4.5 kHz; and (D) lanthanum acetate, magic angle spinning at 2.7 kHz. The expected positions of the spinning sidebands are indicated.

to spinning sidebands. The expected positions of the first- and second-order spinning sidebands are marked by stick diagrams below the spectra. The lines at 66 and 28 ppm have no observable sidebands.

From the chemical composition of praseodymium acetate one expects two ^{13}C resonances, one for the methyl group and the other for the carboxylate group. In aqueous solution two ^{13}C resonance lines are observed, one at 174.4 ppm and the other at 45.5 ppm. The CP–MAS spectra suggest the possibility that two chemically nonequivalent acetate ions may be present in the crystal. To the best of our knowledge the crystal structure of praseodymium acetate is unavailable. However, a detailed structural study has been reported[6] for the trifluoroacetate analogue, where two different types of trifluoroacetate groups are reported. Of the four resonances observed in the solid state it is reasonable to assign the 211 and 114 ppm lines to carboxylate groups, on the basis of the very large chemical shift anisotropy observed. This large shift difference (97 ppm) must arise from the paramagnetic shielding anisotropy. The difference between the isotropic shifts of the remaining two resonances, presumably arising from the methyl groups of nonequivalent acetate ions, is much smaller (~38 ppm). From the relative intensities of the spinning side bands and the low-field portion of the nonspinning spectrum it appears that the carboxylate carbon with the isotropic shift of 211 ppm has considerably larger chemical shift anisotropy than the one at 114 ppm. A more detailed analysis is in progress.

The high-speed spinning spectra of praseodymium acetate, lanthanum acetate, and the solution-state spectra of both indicate that (1) high resolution in the solid is not only possible for the paramagnetic compound but very good, (2) the chemical shifts for the resonances in the paramagnetic solid are not identical with those in the solution case, and (3) this difference is due to the paramagnetism of the praseodymium ion. We have also investigated the NMR spectra of several other ligands and paramagnetic ions. In some cases the resonances of carbon atoms closest to the metal center are unobservable, in other cases the electron relaxation rate of the lanthanide ion in the solid is sufficiently slow that all resonances are very broad or even unobservable. However, praseodymium is not unique in providing usable spectra. Spectral parameters are compared for several acetates in Table I.

Table I. Carbon-13 Chemical Shifts in Lanthanide Acetates[a]

	carboxyl		methyl	
	liquid	solid	liquid	solid
La^{3+}	185.1	185	23.9	23
Pr^{3+}	174.4	211	45.5	66
		114		28
Eu^{3+}	253.3		25.7	−47

[a] ppm with respect to external Me_4Si. Here liquid-state shifts were measured in saturated solutions in ^2H_2O at ambient temperature.

The chemical shift dispersion gained in the paramagnetic complex may not appear very great when compared with the increase in line width observed at this magnetic field strength. However, the absence of molecular tumbling to modulate the chemical shift anisotropy in the solid should eliminate the usual broadening associated with a paramagnetic shift reagent at higher magnetic field strengths, which limits to some extent their utility in solution-phase studies. Thus, the 35-ppm line width for the methyl resonance of the europium compound will probably drop to 7 ppm or less in a 300-MHz proton field, making the shift 10 times the broadening. It should be noted that for an electron–nuclear dipolar interaction modified by the anisotropy of the g factor and zero-field splittings,[7] the axis of quantization of the electron magnetization will be tipped away from the nuclear Zeeman direction. Fortunately however, a very short electron T_1 should average the electron nuclear dipole–dipole interaction considerably. Mechanical spinning may not eliminate all the residual inhomogeneous broadening because, as in the case of coupling to quadrupole nuclei,[5] the magic angle directions for the electron and nucleus may differ. The resolution cannot improve without bound, however, since increasing the magnetic field strength may be accompanied by an increase in the electron T_1.

Acknowledgment. This work was supported by the National Institutes of Health (GM-29428).

Registry No. Praseodymium acetate, 6192-12-7; europium acetate, 1184-63-0.

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Metal–Metal Interactions in Binuclear Platinum(II) Diphosphite Complexes. Resonance Raman Spectra of the $^1A_{1g}(d\sigma^*)^2$ and $^3A_{2u}(d\sigma^*p\sigma)$ Electronic States of $Pt_2(P_2O_5H_2)_4{}^{4-}$

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Recent spectroscopic studies have established that certain binuclear d^8-d^8 complexes exhibit substantial metal–metal bonding interactions in their ground and lowest electronic excited states.[2-8]

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(1) (a) California Institute of Technology. (b) University of Texas at Austin.

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