

the spectral parameters of the pure gauche conformer. Using these parameters as an approximation for those of the gauche conformers, we obtained the room temperature trans-gauche populations summarized in Table I. The agreement between the trans-gauche populations calculated using both the N and L parameters supports the supposition that the low temperature spectral parameters are good approximations to those of the pure gauche rotamer.

On the basis of the available data it is difficult to ascertain whether or not the spectral parameters of the pure gauche forms of Ch and ACh are the same. However, we can conclude that for both Ch and ACh the free energy difference between the rotamers ($\Delta G^\circ = -RT \ln n_g/2n_t$) is no more than 1 kcal/mol, and for Ch it may in fact be lower. This conclusion is in accord with the theoretical predictions presented by some investigators^{12,13} and with the recent ¹³C studies of Behr and Lehn,⁸ but it is in disagreement with a number of more recent MO calculations.^{14,15} However, one should not necessarily expect the results of this study to be in full agreement with the theoretical studies, where account of environmental and other possibly important effects are not included. Also, the experimental results refer to ΔG° and the theoretical results refer to ΔE° , further complicating any comparisons.

The significant difference, at least in the case of ACh, between the experimental limiting spectral parameters and those predicted for the pure rotamers by the empirical relationships would seem to undermine their usefulness. For the present case, however, it seems reasonable to attribute the departure in terms of conformational deviations of the "gauche" conformer from pure gauche as a result of some steric interactions. If one assumes that the Karplus²¹ equation is applicable here, and moreover that the empirical spectral parameters are in fact correct for the pure gauche form, the limiting N and L values at -60° may be taken to infer gauche rotamers with dihedral angles of $\sim 65^\circ$ and $\sim 69^\circ$, respectively. These deductions are in satisfactory agreement with the solid state structure.¹⁰ Whether similar structural deviations occur for the "gauche" rotamer of Ch cannot be inferred at this time.

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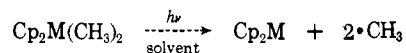
Photochemical Reactions of Dimethyl Derivatives of Titanocene, Zirconocene, and Hafnocene

Sir:

Photochemical reactions involving metal carbonyls have been extensively investigated in recent years since the pioneering work of Strohmeier and others in this

area,¹ and photochemically induced substitution reactions have proved to be an elegant way to prepare new metal carbonyls containing other π -bonded ligands. At the present time, however, no systematic studies concerning photochemical reactions of σ -bonded organic derivatives of the transition metals have been described, except for certain σ -alkylcobalt complexes of the cobaloxime and related types.^{2,3}

We now wish to report that dimethyl derivatives of titanocene, zirconocene, and hafnocene⁴ readily undergo photolysis with homolytic cleavage of the methyl-metal bond. By this process, the metal is reduced to a lower oxidation state and the methyl radicals so produced



M = Ti, Zr, Hf

undergo further reactions. These photolytic reactions are solvent dependent. In pentane, for example, photolysis of group IVb metallocene dimethyl compounds results in formation of the corresponding metallocenes and the generation of methane. Infrared spectra (Nujol) of the organometallic products from each reaction are virtually identical and exhibit only absorptions which are characteristic of π -cyclopentadienyl-metal complexes.^{5,6} It is important to note that titanocene prepared by our photochemical method does *not* show any absorption frequencies in the vicinity of 1230 cm^{-1} which have previously been attributed to bridging metal-hydrogen-metal bonds in the "so-called" titanocene prepared by other methods.⁷ Furthermore, the carbon-hydrogen bending vibrations at 800 and 1015 cm^{-1} for our titanocene appear as sharp, unsplit bands and give strong evidence for only π -bonded cyclopentadienyl rings being present.^{7,8} ESR studies in tetrahydrofuran solution at low temperatures combined with proton nmr studies⁹ give evidence that these metallocenes are diamagnetic under the conditions measured. The elemental analyses of these organometallic products are in agreement with the empirical formulas $\text{C}_{10}\text{H}_{10}\text{M}$ in each case. Preliminary mass spectral studies indicate that photochemically produced titanocene is not as volatile as is titanocene prepared by other methods.⁷ At 180° , however, a spectrum can be obtained which is similar to that of the previously reported titanocene.⁷ The most intense titanium-containing peak at m/e 178 can represent either $[\text{C}_{10}\text{H}_{10}\text{Ti}]^+$ or a doubly charged dimer ion. Additional molecular weight studies are in progress.

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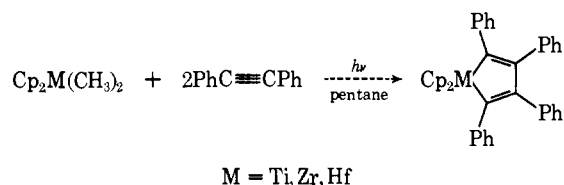
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(9) The proton nmr spectra of all three metallocenes in C_6D_6 solution at room temperature exhibit broad absorptions due to cyclopentadienyl protons between τ 4-5 ppm. Temperature-dependent nmr studies are in progress and will be reported later.

Titanocene produced by this photochemical process can be obtained in yields of >90% during photolysis periods of 2–3 hr, while zirconocene and hafnocene are obtained in lower yields and require correspondingly longer periods of irradiation. Titanocene prepared in this manner appears black in the solid state, in contrast to the green color of titanocene prepared by other methods.^{10,11} Zirconocene and hafnocene obtained by the photolytic method are dark brown and gray, respectively, in contrast to the dark purple colors described for these metallocenes prepared by the sodium-naphthalene reduction of the corresponding metallocene dichlorides.^{5,12} All three metallocenes are pyrophoric in air, the hafnium analog being especially so.

When the dimethyl derivatives of titanocene, zirconocene, and hafnocene are photolyzed in solution in the presence of acetylenes, metallocycles are the major products. Photolysis in the presence of diphenylacetylene, for example, produces the corresponding metallocycles in yields of 35–50%. All metallocycles were characterized by elemental analysis, mass spectrometry, and proton nmr spectrometry. The green



titanium and the orange zirconium metallocycles have been previously described;^{5,13–15} however, the present photochemical route offers a very convenient new route to these products. The yellow hafnocycle has not yet been characterized, and attempts to prepare it by other methods have been largely unsuccessful.⁵ Under the photochemical conditions employed, the methyl radicals react not only to produce methane but also undergo reaction with the diphenylacetylene present to yield a variety of other compounds, including *cis*- and *trans*-methylstilbenes (identified by proton nmr and mass spectrometry).¹⁶

The previously reported⁴ bis(indenyl)metal dimethyl derivatives of titanium, zirconium, and hafnium show reactivities similar to their π -cyclopentadienyl analogs under photochemical conditions. Thus, photolysis of bis(indenyl)zirconium dimethyl in pentane proceeds with the liberation of methane and formation of the black pyrophoric product, bis(indenyl)zirconium. In contrast to the broad absorptions of the cyclopentadienyl ring protons in zirconocene, this new indenyl complex exhibits sharp, distinct signals for the protons of the five-membered and the six-membered rings at τ 3.8–4.2 and 2.4–3.2 ppm, respectively. Photolysis of

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the bis(indenyl)metal dimethyl compounds in the presence of acetylenes likewise leads to metallocycles containing indenyl substituents.

In solution, all these bis(cyclopentadienyl) and bis(indenyl) derivatives of titanium, zirconium, and hafnium show very high reactivities toward carbon monoxide, nitric oxide, nitrogen, hydrogen, and olefins as well as toward acetylenes. For example, *black* titanocene reacts with carbon monoxide in solution at room temperature and atmospheric pressure to form $\text{Cp}_2\text{Ti}(\text{CO})_2$ in essentially quantitative yield. Zirconocene and hafnocene also react with carbon monoxide under these conditions, and further studies along these lines are in progress. Black titanocene also reacts with hydrogen chloride in benzene solution to form Cp_2TiCl_2 as the major product and with molecular nitrogen in tetrahydrofuran solution at room temperature to form a dark purple, nitrogen-containing complex which can be isolated as a solid. It is possible that black titanocene obtained in our studies may be similar to a metastable form of titanocene prepared in solution but not isolated by Brintzinger, *et al.*^{8,17} Several of these photochemically produced metallocenes have also been found to be highly active catalysts for the polymerization of α -olefins. Further investigations concerning the structures and chemical behavior of these compounds as well as extensions to other σ -organotransition metal systems are in progress and will be described in subsequent publications.

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Intermolecular Insertion Reactions of Phosphoryl Nitrenes

Sir:

Nitrene insertion has been used in affinity labeling of enzymes.¹ It is also an attractive reaction for application in remote oxidation,² in which it could be directed to the functionalization of unactivated positions in a molecule by geometric proximity constraints. However, most nitrenes undergo intramolecular rearrangement processes³ rather than insert into nearby C–H bonds. Even those nitrenes derived from the class⁴ referred to as “starre” azides, which supposedly are resistant to intramolecular rearrangement, nonetheless

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