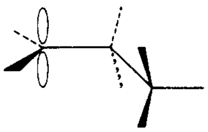
electron in ψ_0. In order to obtain a better understanding of spin-polarization effects, we have converted the delocalized MO's into quasilocalized equivalent MO's by the Foster–Boys procedure;[7] each term of the perturbation expansion is then described as the result of a well-defined local excitation.

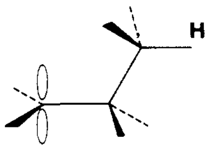
We shall first describe the stable conformation found for this propyl radical. Assuming a planar-trigonal carbon (angle HCC = 120°) for the radical site, fixed bond angles, and fixed bond lengths (CH = 1.093 Å, CC = 1.534 Å), the lowest energy is found for a conformation where the two α hydrogens are in the plane of the three carbon atoms, the methyl group being staggered ($E_{\text{staggered Me}} = -117.572018$ au).

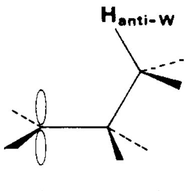


The rotation barrier of the methyl group is 4.8 kcal ($E_{\text{eclipsed Me}} = -117.564385$ au). According to epr results,[1,2] this conformation, in which both H_α are in the carbon plane but with the methyl group in free rotation, is predicted to be the most stable one. In this conformation, *ab initio* calculated hyperfine splittings are -34.34 G for α hydrogens and come exclusively from spin polarization. As shown previously for the ethyl radical,[8] β-hyperfine splittings in that conformation (+23.58 G) result from the combined effect of direct (+13.50 G) and indirect (+10.08 G) mechanisms. Delocalization has no appreciable contribution to the splittings of freely rotating γ hydrogens in this conformation, but spin polarization leads to an average value of -0.21 G on each γ atom. These results are in agreement with experimental determinations[2] of both geometry and hyperfine splittings (exptl: $a_{H\alpha} = -22.14$ G; $a_{H\beta} = +30.33$ G; $a_{H\gamma} = \pm 0.27$ G).

These calculations throw some light on the problem of long-range interactions; in this connection conformations of higher energies, in which the methyl group eclipses the p_z orbital containing the unpaired spin, are of structural interest. In one of these conformations ($E_w = -117.571544$ au), a "W-plan arrangement"[9a] of the bonds between the γ proton and the p_z orbital can be found. This situation is usually taken as being responsible for strong long-range interactions.[9]

On the contrary, the anti-W arrangement is associated with small hyperfine interactions; its energy is $E_{\text{anti-W}} = -117.564053$ au.





The present investigations confirm the above statements. In various conformations, the contribution of spin polarization to γ-proton splittings is weak and negative, the contribution of spin delocalization being negligible. However, on the anti-W hydrogen, delocalization (+1.11 G) and spin-polarization (−0.91 G) contributions are opposite in sign and of the same order of magnitude; they cancel to give a small value. On the W hydrogen, delocalization (+2.64 G) and spin-polarization (+1.73 G) contributions are both positive and relatively large; this gives a large positive hyperfine splitting (+4.37 G) for H_γ in the W conformation.

This *ab initio* calculation clearly shows that long-range interactions are critically dependent on stereochemical conditions; in the first-order perturbation, 90% of the total spin polarization always comes from the excitation of the CH bond under consideration ($\phi_d = CH_\gamma$; $\phi_{v^*} = CH_{\gamma^*}$ in eq 4). The change in sign of the spin polarization at H_γ is directly correlated with the change in sign of the bielectronic integral $\langle \phi CH_\gamma \text{-} \phi_u | \phi_u \phi CH_{\gamma^*} \rangle$, the remaining terms in eq 4 being practically independent of the conformation as a consequence of localization.

The strong long-range interactions in γ position result from an appropriate arrangement of bonds permitting a cumulative effect of delocalization and spin-polarization contributions. This is well illustrated in a number of epr studies, especially on bicyclic radicals where geometrical requirements are satisfied by a rigid molecular framework.[9,10]

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(7) J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, 32, 300 (1960).

(8) Y. Ellinger, A. Rassat, R. Subra, G. Berthier, and P. Millie, *Chem. Phys. Lett.*, 11, 362 (1972).

(9) (a) G. A. Russell in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, pp 87–150; (b) H. Lemaire, A. Rassat, and P. Rey, *Chem. Phys. Lett.*, 2, 573 (1968).

(10) (a) D. Kosman and L. M. Stock, *J. Amer. Chem. Soc.*, 91, 2011 (1969); (b) J. Gloux, M. Guglielmi, and H. Lemaire, *Mol. Phys.*, 19, 833 (1970); (c) R. Marx and L. Bonazzola, *Mol. Phys.*, 19, 899 (1970); (d) A. Rassat and J. Ronzaud, *J. Amer. Chem. Soc.*, 93, 5041 (1971).

(11) Part of the Science Thesis of R. S., 1972.

Y. Ellinger, A. Rassat, R. Subra[11]*
Laboratoire de Chimie Organique Physique
Départment de Recherche Fondamentale du Centre d'Etudes
Nucléaires de Grenoble, Cedex 85
F 38041 Grenoble, France

G. Berthier
Laboratoire de Chimie Quantique
75, Paris, France

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Activation of Homogeneous Catalysts by Polymer Attachment

Sir:

The attachment of homogeneous catalysts to polystyrene–divinylbenzene copolymer produces a new class of catalysts with many of the best properties of both heterogeneous and homogeneous catalysts.[1] These catalysts also showed selectivity toward substrates of different molecular bulk[2] and polarities.[3]

We now wish to report that catalysts can be significantly activated by such attachment. A basic requirement for homogeneous catalysis by a transition metal complex is the presence of an open coordination site. In most cases, attempts to open a coordination site on a metal result in the polymerization of the complex, and the production of bridged species in which the required site of unsaturation is blocked.[4] Attach-

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(1) R. H. Grubbs and L. C. Kroll, *J. Amer. Chem. Soc.*, 93, 3062 (1971).

(2) M. Capka, P. Suobda, M. Cerny, and J. Hetflejе, *Tetrahedron Lett.*, 4787 (1971), and references therein.

(3) R. H. Grubbs, L. C. Kroll, and E. M. Sweet, *J. Macromol. Sci., Chem.*, in press.

(4) J. P. Collman, *Accounts Chem. Res.*, 1, 137 (1968).

ment of a saturated complex that is a potential catalyst to a rigid support, followed by the reductive elimination of a ligand, should produce higher concentrations of monomeric coordinately unsaturated species than is obtained in solution.[5]

Collman and his coworkers[5] have found that 2% divinylbenzene–styrene copolymers are mobile enough to allow ligands attached to the polymer beads to act as chelates. Consequently, this polymer is not rigid enough to prevent dimerization of attached unstable species.

We have found, however, that treatment of the chlorobis(cyclooctadiene)rhodium(I) dimer with a 3-equiv excess of polystyryl–diphenylphosphine prepared from 20% divinylbenzene–styrene macroreticular copolymer (600 Å av pore size)[6] releases only 1.4 mol of cyclooctadiene per mole of complex absorbed. A similar reaction performed with phosphenated 2% divinylbenzene–styrene copolymer produces 2.0 mol of cyclooctadiene per mole of absorbed metal. The 2% cross-linked material gives the same results as the treatment of 1 mol of the cyclooctadiene dimer with 3 equiv of triphenylphosphine. The 20% cross-linked material yields the same results as the treatment of 1 mol of the cyclooctadiene rhodium dimer with 1 mol of triphenylphosphine. It is apparent that there is much less chelation, *i.e.*, less mobility of the polymer structure, in the 20% cross-linked than in the 2% cross-linked copolymer.

Titanocene has been suggested as a reactive intermediate in the reduction of olefins,[7] acetylenes, and nitrogen.[8] Brintzinger[8] has recently demonstrated that titanocene is rapidly converted into an inactive polymeric compound. We have therefore used the principles outlined above to produce a highly activated titanocene catalyst. Titanocene dichloride ($TiCp_2Cl_2$) was attached to 20% cross-linked macroreticular copolymer by the procedure shown in Scheme I.

Starting with 13.6% (1.13 mequiv/g) substitution of chloromethyl groups,[9] a polymer containing 0.79 mequiv of $TiCp_2Cl_2$ per gram of beads (20% by wt) was obtained. Visible and far-infrared spectra obtained from mulled samples of the metallocene-substituted polymer were comparable with spectra recorded for the benzyl–titanocene monomer (benzyl-Cp)$CpTiCl_2$. On treatment with excess butyllithium or sodium naphthalide, the salmon pink titanocene dichloride polymer was converted to a highly reactive gray polymer which catalyzed the reduction of olefins and acetylenes (see Table I).[7]

Treatment of titanocene dichloride or benzyltitanocene dichloride with 2 equiv of butyllithium produced a gray catalyst that was only 0.15 times as active per milliequivalent of metal in the reduction of cyclohexene as was the polymer-attached metallocene (Table II). This contrasts with the observation that the activity of the rhodium-attached catalysts are only 0.06 times[3] as reactive as an equivalent amount of homogeneous reagent. We attribute the faster reduction rate of the polymer-attached catalyst to the presence of a higher concentration of monomeric species. This conclusion is supported by esr studies.

Scheme I

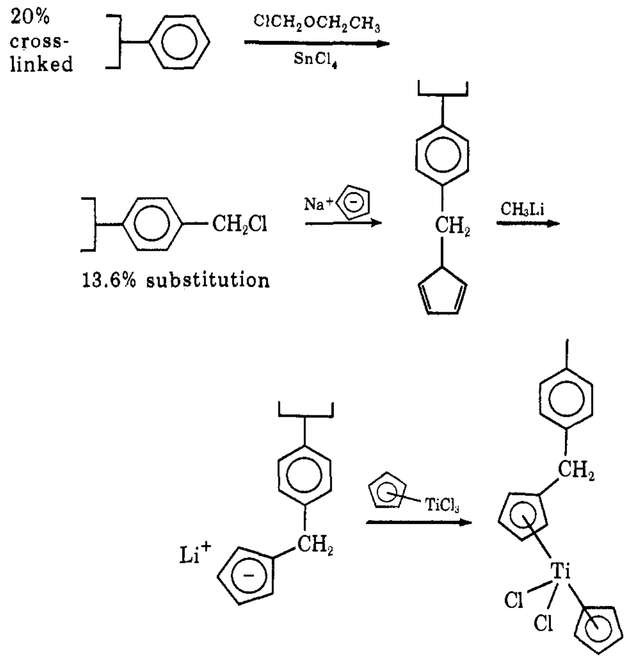

Table I. Rates of Reduction with Polymer Attached Titanocene

Olefin (~0.5 *M* in hexane)	Rate of reduction, ml of H_2/min (1 atm of H_2)
40 mg of Catalyst (in 10 ml of hexane)	
1,3-Cyclooctadiene	1.81
1,5-Cyclooctadiene	1.54
Styrene	2.05
3-Hexyne	1.26 (hexane)
1-Hexene	1.80
1-Hexyne	Polymer
Cholestenone	0
Vinyl acetate	0
420 mg of Catalyst	
Diphenylacetylene	3.6 2 (eq)
Cyclohexene	8
1-Methylcyclohexene	0.92
1,2-Dimethylcyclohexene	0

Table II. The Reduction Rate of Various Olefins with Attached and Homogeneous Titanocene Species

mequiv of cat.	Olefin	Solvent	Rate of reduction
	Benzyltitanocene Dichloride		
0.2	Cyclohexene	Hexane	1.9 ml of H_2/min
0.2	1-Methylcyclohexene	Hexane	No uptake in 115 min less than 9×10^{-3} ml/min
	Polymer–Titanocene Dichloride		
0.032	Cyclohexene	Hexane	1.8 ml of H_2/min
0.32	1-Methylcyclohexene	Hexane	0.09 ml/min
0.032	1-Hexene	Hexane	1.7 ml of H_2/min
0.032	1-Hexene	THF	0.92 ml of H_2/min
	Titanocene Dichloride		
0.2	Cyclohexene	Hexane	2.1 ml of H_2/min
0.2	Cyclohexene	THF	0

Stepwise addition of 1 and 2 equiv of sodium naph-

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(5) J. P. Collman, *et al.*, *J. Amer. Chem. Soc.*, **94**, 1789 (1972).

(6) Obtained from The Dow Chemical Co., Midland, Mich.

(7) Y. Tajima and E. Kunioka, *J. Org. Chem.*, **33**, 1689 (1968).

(8) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1219 (1972), and references therein.

(9) K. W. Pepper, H. M. Paisley, and M. A. Young, *J. Chem. Soc.*, 4097 (1953).

thalide to polymer-bound titanocene dichloride resulted in the formation of species with two distinctly different esr signals of comparable intensity near $g = 2$.[10] These data suggest that both stages of reduction yield paramagnetic species. Treatment of monomeric benzyltitanocene with sodium naphthalide under identical conditions yields solutions containing a rapidly disappearing paramagnetic species and mediocre catalytic ability. These observations support the suggestion that dimerization of the reduced titanocene complexes has been avoided by polymer attachment.

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(10) H. H. Brintzinger, *J. Amer. Chem. Soc.*, **89**, 6871 (1967).

(11) On leave from The Dow Chemical Co., Midland, Mich.

Robert H. Grubbs,* Carl Gibbons,[11] LeRoy C. Kroll
Wesley D. Bonds, Jr., C. H. Brubaker, Jr.
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823

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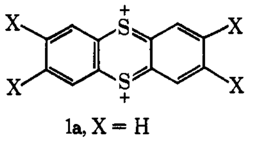
2,3,7,8-Tetramethoxythianthrene Dication. An Isolable Thianthrene Dication

Sir:

There is considerable theoretical interest in potentially aromatic compounds formally derived from aromatic hydrocarbons or ions (or perhaps better said Hückel systems)[1] in which one or more carbon atom is replaced by one or more heteroatom. Thianthrene dication **1a** is one such system. If d orbitals are neglected then thianthrene dication is derived from anthracene because the number of atomic orbitals capable of forming π molecular orbitals and the number of electrons to be accommodated in these orbitals are the same in both systems.[2] However, if sulfur uses pd^2 hybrid atomic orbitals[2,3] then thianthrene dication is derived from dibenzo[*a*,*e*] cyclooctatetraene dication.



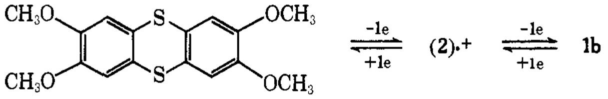
1a, X = H
b, X = OCH_3

Thianthrene dication is of interest not only for theoretical reasons but also because it has been suggested as an intermediate in the reactions of thianthrene cation radical with nucleophiles.[4] This suggestion, however, has been challenged recently.[5]

Dissolution of thianthrene sulfoxide in concentrated sulfuric acid gives rise reportedly[6] to the dication **1a**. The evidence for this contention is the observed *i* factor of 5 and the isolation of ^{18}O-labeled thianthrene sulfoxide after pouring a solution of the dication onto ice prepared from ^{18}O-labeled water. No direct evidence for dication **1a** has been presented nor has dication **1a** been isolated.

This communication reports the isolation of a substituted thianthrene dication and the evidence for the assigned structure. The dication of 2,3,7,8-tetramethoxythianthrene (**1b**) could be prepared from 2,3,7,8-tetramethoxythianthrene[7] in any of three ways: (1) anodic oxidation, (2) oxidation by perchloric acid, and (3) oxidation by oxygen in the presence of aluminum chloride.

Cyclic voltammetric studies on 2,3,7,8-tetramethoxythianthrene in purified acetonitrile[8] 0.1 *M* in tetra-*n*-butylammonium perchlorate show three oxidation waves with half-wave potentials at +0.54, +0.79, and +1.20 V *vs.* silver|saturated silver nitrate (acetonitrile). The first oxidation is reversible at moderate scan rates (0.435 V/sec) but, unlike the case of thianthrene,[9] the second oxidation process is also reversible at the moderate scan rate. The scan rate independent separations of the anodic and cathodic waves for both processes (both 60 mV) suggest[10] that each step involves the transfer of one electron. These reversible oxidation processes may be accounted for by the reaction shown in eq 1.



2 (1)

Controlled potential electrolysis of 2,3,7,8-tetramethoxythianthrene in acetonitrile 0.1 *M* in tetra-*n*-butylammonium perchlorate was complicated by the limited solubility of the products. However, this problem was eliminated by use of nitromethane[11] as solvent and anhydrous magnesium perchlorate (at saturation) as supporting electrolyte. With these conditions, the waves due to the two reversible oxidation processes observed in acetonitrile overlapped. Nevertheless, sufficient separation was obtained in an epr cavity cell equipped with a platinum gauze electrode so that two waves were observed at half-wave potentials of +0.6 and +0.8 V *vs.* silver|saturated silver nitrate (nitromethane). Electrolysis at the potential of the first wave produced a green solution which gave an epr signal. At high resolution a complex spectrum whose *g* value and hyperfine splitting were consistent with that expected for the resonance of the cation radical of

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(1) D. Lloyd and D. R. Marshall, *Angew. Chem., Int. Ed. Engl.*, **11**, 404 (1972).

(2) (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961; (b) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966.

(3) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

(4) (a) H. J. Shine and Y. Murata, *J. Amer. Chem. Soc.*, **91**, 1872 (1969); (b) Y. Murata and H. J. Shine, *J. Org. Chem.*, **34**, 3368 (1969); (c) J. J. Silber and H. J. Shine, *ibid.*, **36**, 2923 (1971); (d) H. J. Shine and J. J. Silber, *J. Amer. Chem. Soc.*, **94**, 1026 (1972).

(5) V. D. Parker and L. Eberson, *ibid.*, **92**, 7488 (1970), but see also L. Marcoux, *ibid.*, **93**, 537 (1971) for limitations of the rotating disk electrode technique.

(6) (a) H. J. Shine and D. R. Thompson, *Tetrahedron Lett.*, 1591 (1966); (b) H. J. Shine in "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience, New York, N. Y., 1967, Chapter 6.

(7) K. Fries, H. Koch, and H. Stukenbrock, *Justus Liebigs Ann. Chem.*, **478**, 162 (1929).

(8) C. K. Mann in "Electroanalytical Chemistry," A. J. Bard, Ed., Vol. 3, Marcel Dekker, New York, N. Y. 1969.

(9) (a) C Barry, G. Cauquis, and M. Maurey, *Bull. Soc. Chim. Fr.*, 2510 (1966); (b) W. Schroth, R. Borsdorf, R. Herzschuh, and J. Seidler, *Z. Chem.*, 10, 147 (1970).

(10) (a) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964); (b) R. S. Nicholson and I. Shain, *ibid.*, **37**, 178 (1965).

(11) J. D. Voorhies and E. J. Schurdak, *ibid.*, **34**, 939 (1962).