$[AgSe_4]_n^{n-}$ chains in the unit cell with the Ph_4P^+ ions acting as spacers. Figure 2 shows two views of an individual chain. Each chain can be thought of as a corrugated ribbon. The mode of polymerization of $AgSe_4$ unit is such that a selenium atom which is coordinated to a Ag atom in the ring also acts as a ligand for a second Ag atom of a neighboring $AgSe_4$ unit. Each $AgSe_4$ ring can be generated from its adjacent one by a 2-fold screw operation parallel to the crystal *b*-axis. The coordination geometry of the Ag atom is trigonal planar with two markedly different intra-ring Ag–Se(1) and Ag–Se(4) bonds of 2.672 (2) and 2.553 (2) Å, respectively, and an inter-ring Ag–Se′(1) bond of 2.545 (2) Å. It is interesting to note the unusual feature of the bridging inter-ring Ag–Se bond being considerably shorter than the corresponding intra-ring bond in the $AgSe_4$ unit. The bonding geometry around the bridging Se(1) atom is trigonal pyramidal. The conformation of the $AgSe_4$ ring is best described as an "envelop" with the Se(2) atom lying 2.21 (4) Å above the Se(1)/Ag/Se(4)/Se(3) plane. The Se–Se distances within the Se_4^{2-} ligand are as follows: Se(1)–Se(2), 2.360 (3); Se(2)–Se(3), 2.339 (3); Se(3)–Se(4), 2.358 (4)Å; and they are similar to those found for $(PPN)_2Se_4{\cdot}4CH_3CN$.[16]

This bridging mode of the Se_4^{2-} ligand in I is uncommon in metal/polychalcogenide chemistry, but it is encountered in the dimeric $[Ag(S_6)]_2^{2-}$,[17] and trimeric $[Cu(S_x)]_3^{3-}$.[18] It is conceivable that the latter two are members of a whole family of compounds with the general formula $[M(Q_x)]_n^{n-}$ (M = group I metals, Q = chalcogen). In this context $[Ag(Se_4)]_n^{n-}$ may be considered an end member. The stabilizaton of polymers via a vis oligomers is probably determined by a combination of counterion and size of the chalcogenide ligands with short chain chalcogenides stabilizing the former. The existence of two other members of this family, the polymeric NH_4CuS_4[19] and $KCuS_4$,[20] is certainly consistent with this contention. It should be noted, however, that the structural motif found in $[(Ph_4P)AgSe_4]_n$ is distinct from that of NH_4CuS_4 or $KCuS_4$ which are composed of double $[Cu(S_4)]_n^{n-}$ chains. In these chains Cu^+ is found in a distorted tetrahedral environment, while the S_4^{2-} units bridge three copper atoms.

The structure of I is unique and has no parallel in chalcogenide chemistry. One-dimensional transition-metal/polychalcogenide compounds such as I are rare, particularly those prepared at ambient temperature. NH_4CuS_4[19] and $(Ph_4P)_2Hg_2Te_5$[21] are two such examples. Other materials containing anionic one-dimensional metal/polychalcogenide chains include $K_4Ti_3S_{14}$[22] and $Na_2Ti_2Se_8$,[23] which feature bridging Q_2^{2-} (Q = S, Se) units.

Preliminary examination of the charge transport[24] and optical[24] properties along the needle axis of single crystals of I indicates wide bandgap/narrow bandwidth semiconducting behavior. A steep optical absorption threshold occurs at 384 nm suggesting a bandgap of 3.2 eV.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles of all atoms (9 pages); a listing of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

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Catalysis of Closed-Shell Reactions by Complexation with Metal Radical Cations

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One-electron oxidation of organic substrates is one of the few physical processes that can produce similar rate accelerations to those found in enzymatic systems. Bauld,[1] Haselbach,[2] Roth,[3] and Dinnocenzo,[4] among others, have demonstrated this for a variety of Woodward–Hoffmann-type reactions. Ab initio molecular orbital calculations[5] have been widely used to investigate these reactions. The electronic flexibility gained by the presence of a singly occupied orbital often leads to low activation energies, as found in many neutral radical reactions,[6] and the inclusion of a positive charge, which favors one- and three-electron bonding,[7] often leads to even more facile reactions. This latter effect was recently demonstrated theoretically for the addition of the methyl radical to ethylene.[8] The calculated barrier is lowered significantly by complexation of the olefin with the lithium cation, an effect that is expected to be general for radical reactions involving odd-electron bonds in the transition state.[9] However, this catalysis by complexation with a metal cation is not limited to introducing charge into a radical reaction. In principle, it is also possible to introduce both charge and radical character into a closed-shell reaction by complexation with a doublet metal cation. This communication reports model ab initio molecular orbital calculations[10,11] designed to test this hypothesis.

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[10] All calculations used the Convex version of the GAUSSIAN 82 program (Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L. GAUSSIAN 82; Carnegie-Mellon University: 1982) on a Convex C120. Geometry optimizations were performed at the unrestricted Hartree–Fock level with the 3-21G basis set (Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797) for carbon, hydrogen, beryllium, and magnesium and small Huzinaga split-valence basis sets for Zn and Ca.[11] The stationary points were characterized by diagonalization of the force constant matrix calculated at this level of theory. Energy calculations used the 6-31G* (Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654) basis set for C, H, Be, and Mg and larger split-valence Huzinaga basis sets for Ca and Zn.[11] The fourt-order Møller–Plesset correction for electron correlation including single, double, triple, and quadruple excitations (MP4SDTQ: Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Binkley, J. S.; Pople, J. A. *Int. J. Quant. Chem.* **1975**, *9*, 229 and references therein. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quant. Chem. Suppl.* **1976**, *10*, 1 and references therein. Frisch, M. J.; Krishnan, R.; Pople, J. A. *Chem. Phys. Lett.* **1980**, *75*, 66) was included for the energy calculations. The core orbitals were not included in the calculation of the MP4 correction. Calculations including calcium and zinc used five real d-orbitals for all atoms, rather than the six Cartesian d-functions used in the standard 6-31G* basis set.

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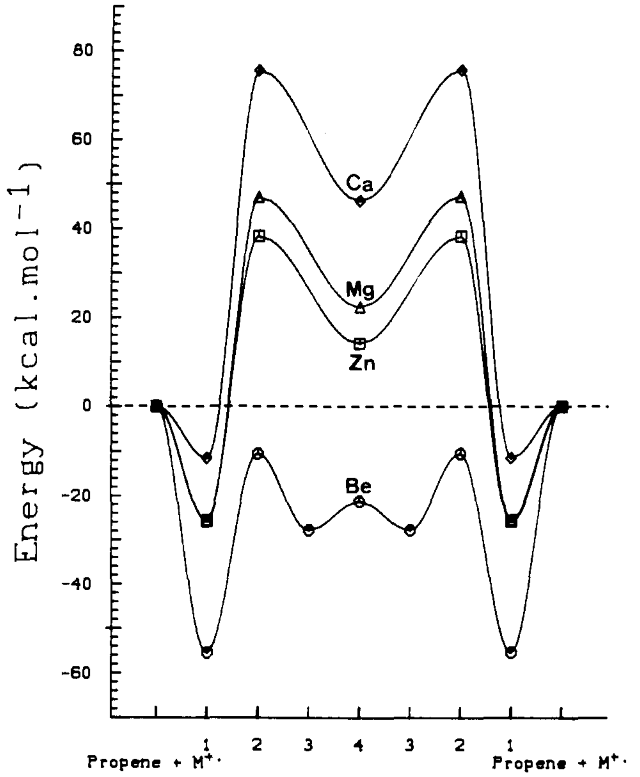


Figure 1. Schematic reaction curves for the $M^{\bullet+}$ catalyzed 1,3-hydrogen shift in propene. The points on the reaction coordinate correspond to structures **1**–**4**. The energy scale is that given in Table I.

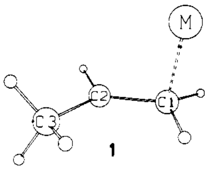
The 1,3-hydrogen shift in propene has been found by ab initio calculations to proceed via an *antarafacial* transition state whose energy is close to the dissociation limit (the best calculations suggest a barrier of 93 kcal mol^{-1}),[12] but the radical cation reaction is found to be *suprafacial* with an activation energy of about 30 kcal/mol.[13,14] Our original Hartree–Fock calculations[13] suggested C_s trimethylene$^{\bullet+}$ to be the transition state for this 1,3-shift, but MP2 optimization[14] proved this structure to be a shallow minimum between two transition states for consecutive 1,2-shifts. The large change in the reaction profile upon oxidation makes this simple reaction an ideal model for investigating possible catalysis mechanisms. Although it cannot be expected that the type of catalysis proposed above should be more effective than "hole catalysis", and therefore that experimentally accessible activation energies for the propene 1,3-shift will not be achieved, it was decided to investigate this reaction because of the wealth of information already available about the neutral and radical cation reactions. The purpose of this investigation is to establish the principle of this novel type of catalysis, rather than to propose an experimentally viable reaction system. Reactions such as the ethylene dimerization (see below) are certainly better suited for experimental investigations.

Table I. Total[a] and Relative[b] Energies and Selected Geometrical Parameters[c] for **1–4**

	Be	Mg	Ca	Zn
		$M^{\bullet+}$ + Propene		
total energy	−131.77988	−316.85720	−793.36287	−1894.55635
rel energy	0.0	0.0	0.0	0.0
$\Delta_{IP} + E_a^+$	55.3	92.4	137.3	70.3
		1		
total energy	−131.79660	−316.89822	−793.38130	−1894.59706
rel energy	−55.3	−25.7	−11.5	−25.5
C_1C_2	1.372	1.346	1.332	1.355
C_2C_3	1.486	1.497	1.507	1.494
C_1M	1.886	2.483	2.972	2.086
CCC	125.0	125.6	124.9	125.0
C_2C_3M	105.3	93.9	95.1	109.3
		2		
total energy	−131.79660	−316.78200	−793.24208	−1894.49536
rel energy	−10.5	47.2	75.8	38.3
E_a (**1** → **2**)	44.8	72.9	84.5	61.0
C_1C_2	1.400	1.410	1.412	1.407
C_2C_3	1.529	1.536	1.548	1.520
C_1M	1.762	2.194	2.581	1.973
C_2H_1	1.169	1.160	1.149	1.164
C_3H_1	1.641	1.768	1.820	1.735
CCC	122.4	120.5	118.3	121.3
C_2C_1M	121.7	126.7	134.8	127.6
		3		
total energy	−131.82411			
rel energy	−27.7			
C_1C_2	1.634			
C_2C_3	1.535			
C_1M	1.660			
C_2M	2.230			
		4		
total energy	−131.81361	−316.82143	−793.28903	−1894.53369
rel energy	−21.2	22.4	40.4	14.2
point group	C_{2v}	C_{2v}	C_s	C_{2v}
CC	1.549	1.525	1.521	1.539
CM	1.901	2.434	2.917	2.134

[a] As described in ref 10 and 11 (Hartrees). [b] kcal mol^{-1} relative to propene + $M^{\bullet+}$. $\Delta_{IP} + E_a^+$ as shown in Scheme I. [c] Bond lengths in Å, angles in deg.

Geometry optimizations revealed four stationary points on the propene/$Be^{\bullet+}$ 1,3-shift reaction path and three for the other metals. The propene/metal cation complex **1** is the only minimum of this type located. The possible isomer in which the metal cation is more closely associated with the central carbon atom rearranges spontaneously to **1**. The reaction then proceeds via the C_1 1,2-hydrogen shift transition state **2** to give the radical cation **3** in the beryllium case, **3** is a partly opened metallacyclobutane radical cation that can undergo a 1,3-beryllium shift via **4**. For beryllium, **4** is a transition state, but for the other metals **3** does not exist and **4** is the minimum energy structure for the metallacyclobutane radical cation. This difference in the details of the reaction profile between beryllium and the larger metals is probably a consequence of the short C–Be bonds. Table I shows some geometrical parameters and the total and relative energies of **1**–**4**. Note that for Be, the intermediate **3** and for Mg and Zn the intermediate



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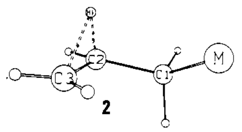

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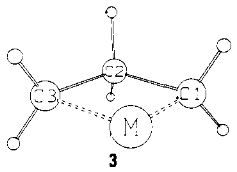

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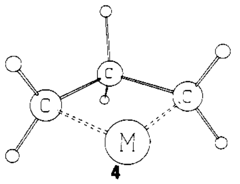

4

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(11) The calcium and zinc basis sets were taken from the following: Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984. The individual basis sets used were as follows. Optimizations used the 3333/33 basis set (p 101) split 21 for the 4s and with a single p-polarization function (33321/331) for calcium and a 33321/3331/3 basis set for zinc obtained in the same way from the 3333/333/3 basis set (p 198). Energy calculations used a 43321/421 calcium basis set obtained from the 4333/42 basis (p 102) and a 53321/531/5 zinc basis obtained from the 5333/53/5 basis (p 203).

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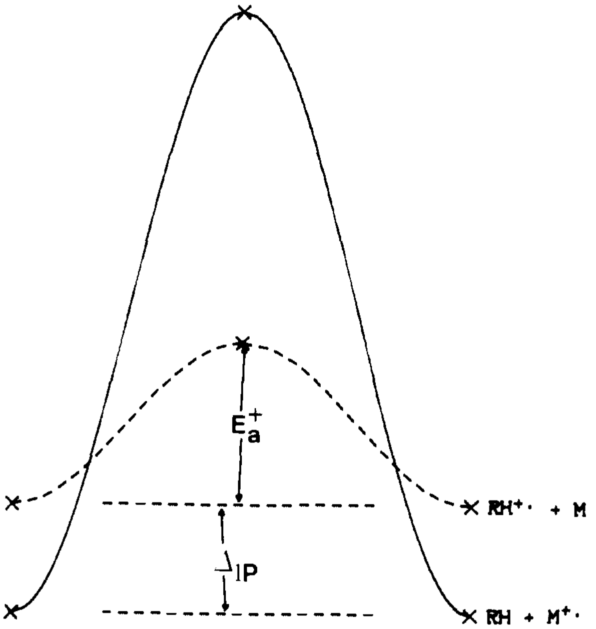
Scheme I. Schematic Reaction Curves Showing the Redox Isomers of the RH + M$^{\bullet+}$ System



4 have a plane of symmetry through the C_3H_6 unit and that, therefore, the stereochemistry of the 1,3-shift is no longer defined. Figure 1 shows schematic reaction profiles illustrating the course of the 1,3-hydrogen shift reaction for the different metals.

The propene Be$^{\bullet+}$ complex $\mathbf{1}_{Be}$ is surprisingly stable. Symmetrical first row–first row odd-electron bonds typically have dissociation energies between 40 and 50 kcal mol^{-1},[7] and the ethylene Li$^+$ complex investigated previously[8] is bound by about 23 kcal mol^{-1}. The stability of the complexes **1** decreases in the order Be > Mg $\simeq$ Zn > Ca, as would be expected from the ionization potentials of the metals and the fact that odd-electron bond energies decrease on descending the periodic table.[7] The 1,2-shift transition states **2** lie 45 (Be) to 85 (Ca) kcal mol^{-1} higher in energy than the complexes **1**. The net activation energy (propene + M$^{\bullet+}$ $\rightarrow$ **2**) is negative for Be, 40–50 kcal mol^{-1} for Zn and Mg, and close to 80 kcal mol^{-1} for Ca. The 1,2-shift transition states **2** are the highest points on the reaction profile as the 1,3-beryllium shift in $\mathbf{3}_{Be}$ has an activation energy of only 6.5 kcal mol^{-1}. Although the activation energies (**1** $\rightarrow$ **2**) are substantial, there is nevertheless a significant catalysis of the overall 1,3-hydrogen shift by Be, Zn, and Mg.

The general principles of this type of catalysis are shown in Scheme I below. The two curves represent schematic reaction profiles for the total energies of the two redox isomers of the reacting system, RH + M$^{\bullet+}$ and RH$^{\bullet+}$ + M (for simplicity, it is assumed that there is little or no interaction between the organic moiety, RH, and the metal, M, although this will normally not be the case). The high activation energy for the reaction of neutral RH (solid line) compared to that of the radical cation reaction (dashed line) leads to a crossing of the two reaction profiles on approaching the transition state. This results in an internal electron transfer from RH to M as the system approaches the transition state and a net activation energy of $\Delta_{IP} + E_a^+$, where Δ_{IP} is the difference in activation energy between RH and the metal, and E_a^+ is the activation energy of the radical cation reaction. Table I shows that the calculated activation energies are, in fact, close to $\Delta_{IP} + E_a^+$ for Be and Zn. The complexation energy differences between the reactant and the transition state with the metal are ignored in this simplified treatment. Magnesium whose ionization potential is close to that of the transition state, to which it should thus complex strongly,[7] therefore gives a significantly lower activation energy than $\Delta_{IP} + E_a^+$. Note that for calcium Δ_{IP} is larger than the activation energy of the neutral reaction, so that the two curves never cross. The small degree of catalysis observed in this case is due to differences in complexation energy along the reaction path. The type of catalysis observed for Be, Mg, and Zn should be general and independent of the orbital characteristics of the metal and the organic substrate for all "hole-catalyzed" reactions. Interestingly, Ghosh and Kevan[15] have recently identified a Pd$^{\bullet+}$ ethylene complex as the immediate precursor for ethylene dimerization on NaPd-X zeolites. Ethylene dimerization, similar to the 1,3-hydrogen shift in propene, is a reaction that proceeds in the radical cation case but not for the neutral system.[1]

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Dehydrohalogenation of *vic*-Dibromoethanes Catalyzed by Iron

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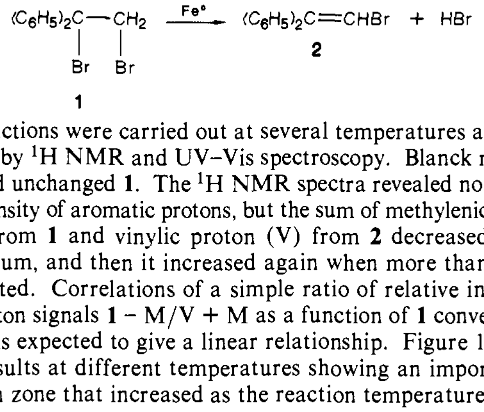
We describe here the dehydrobromination of 1,2-dibromo-1,1-diphenylethane in CCl_4 solution with freshly reduced powdered iron with a 2–7μ particle diameter as catalyst (eq 1).



$$\underset{\mathbf{1}}{(C_6H_5)_2\underset{Br}{\underset{|}{C}}-\underset{Br}{\underset{|}{C}}H_2} \xrightarrow{Fe^\circ} \underset{\mathbf{2}}{(C_6H_5)_2C{=}CHBr} + HBr \qquad (1)$$

Reactions were carried out at several temperatures and monitored by ^{1}H NMR and UV–Vis spectroscopy. Blanck reactions yielded unchanged **1**. The ^{1}H NMR spectra revealed no changes in intensity of aromatic protons, but the sum of methylenic protons (M) from **1** and vinylic proton (V) from **2** decreased until a minimum, and then it increased again when more than 95% of **1** reacted. Correlations of a simple ratio of relative intensities of proton signals **1** – M/V + M as a function of **1** conversion (**1** – M) is expected to give a linear relationship. Figure 1 collects the results at different temperatures showing an important deviation zone that increased as the reaction temperatures diminished.

Figure 2 shows typical visible spectra of the reaction mixture, and Table I presents the relative absorbance intensities of the bands. The maximum occurred at the same values of **1** conversion as the deviation zone by ^{1}H NMR, suggesting a common mechanism for both results. The wavelengths observed are close to those of Fe^{III}-Br compounds[2] and those attributed to halogen $\rightarrow$ metal charge transfer.[3]

These observations could not be explained merely on the basis of the proposed dehydrohalogenation mechanisms: (i) homolysis of a carbon–halogen bond, followed by a β-hydrogen elimination and (ii) a β-hydrogen elimination from an initial carbenium ion.[4] Other β-elimination reactions are the known decomposition of metal–alkyl complexes leading to olefin formation.[5] Our results can be best understood if similar complexes were formed on the

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[1] Grateful recipient of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina.

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