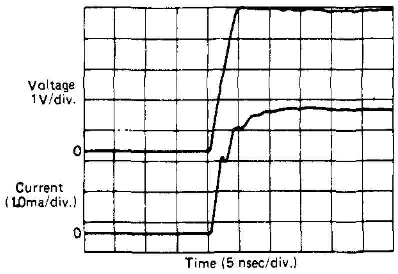

Figure 2. Transient response to a fast rise time rectangular pulse.

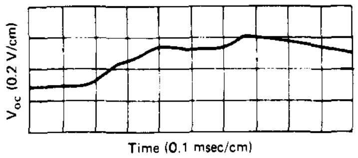

Figure 3. Spontaneous open-circuit potential generated in a Cu/Cu-TNAP/Al sample at room temperature.

applied to the sample to reduce any current oscillations which appear when the applied voltage was set near V_{th}. The fast combined delay and switching time observed in this experiment indicate that the transition between states of different conductivity is not induced by thermal effects.[6]

To obtain information pertaining to the nature of the mechanism of the phase transition, an experiment was designed to determine if the system generates an open-circuit potential or electromotive force (emf) in switching from the high to the low conductivity state since the appearance of a spontaneous emf would indicate that an electrochemical reaction was resonible for switching phenomena.[7] In this experiment, (1) an applied voltage in excess of the threshold voltage was used to place a Cu-TNAP sample into a high conductivity state where this state was such that it would remain intact for a short time after the applied voltage was removed; (2) the sample was then externally short circuited to eliminate any capacitive effects; and finally (3) a high input impedance storage oscilloscope was used to measure open-circuit voltage when the sample spontaneously returned to its original high impedance state. The oscilloscope was set to trigger whenever a voltage exceeding a few millivolts appeared across the sample. The results are shown in Figure 3 where the spontaneous open-circuit voltage measured by the oscilloscope is reproduced and is seen to have a maximum value of ~0.3 V.

The open-circuit voltage of 0.3 V observed in this experiment does show that the mechanism by which the phase transition occurs is due to a field induced solid-state reversible electrochemical redox reaction involving the metal charge-transfer salts. It is postulated that this redox reaction produces mixed-valence species or complex salts. A similar switching phenomena is reported in copper and silver TCNQ.[8] Further work to examine other charge-transfer salts[9] and their possible application to solid-state electronics is in progress.

Acknowledgments. We thank Dr. J. C. Murphy for valuable discussions and comments on this work. We are grateful to Mr. M. Maxfield for supplying neutral TNAP material. We thank Mr. J. W. Leight and Mr. R. A. Murphy for their technical assistance. We gratefully acknowledge support by the National Science Foundation (DMR76-84238) and the Department of the Navy (N00024-78-C-5384).

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(9) We are currently investigating thin films of the acceptors TCNQ, TCNE, TCNQ-F_4, TCNQ-$(OCH_3)_2$, TCNQ-$(CH_3)_2$, and TCNQ-$(CH_2CH_3)_2$.

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Competitive Oxidation Processes in the Reaction between (Dicyclopentadienyl)zirconium Bis(phosphine) Complexes and Alkyl Halides

Sir:

Comprehensive kinetic and stereochemical studies of the oxidative addition of alkyl halides to low-valent group 8 complexes have established several mechanisms for these reactions including direct S_N2 attack, radical chain, and nonchain electron-transfer pathways.[1] In contrast, few examples of net carbon-halogen addition to early transition metal complexes are known and, consequently, no systematic investigation involving these species has been reported. We recently found[2] that ligand-induced elimination of alkane from the zirconocene alkyl hydrides provides a straightforward synthesis of Cp_2Zr^{II} bis(phosphine) complexes, species whose ease of preparation and high reactivity toward oxidation make them valuable for elucidation of fundamental processes involving complexes of early transition metals in low-oxidation states. In this context we have investigated the oxidation of Cp_2XrL_2 (L = PPh_2Me or PMe_2Ph) by RX (RX = alkyl halide) and find that both the formal oxidative addition product, Cp_2ZrRX, and the dihalide, Cp_2ZrRX_2, can be formed. Alkyl chlorides, bromides and iodides all react readily with Cp_2ZrL_2 (see Table I). As expected, we find the qualitative ordering of reactivity for alkyl halides to be RI > RBr > RCl. Surprisingly, though, we noted that these halides ranked in order of *selectivity* of reaction with Cp_2ZrL_2 in the *same* way, in opposition to conventional intuition which predicts an inverse relationship between rates and selectivity of reactions. We have set forth a mechanistic scheme to account for these observations (Scheme I) and wish to present our results which are in support of this scheme.

Formation of both Cp_2ZrRX and Cp_2ZrX_2 occurs by multistep processes and involves intermediary organic radicals. These contentions are supported by the following observations. (a) For a given halide primary, secondary and tertiary alkyl halides react with Cp_2ZrL_2 at comparable rates (although product ratios of Cp_2ZrRX:Cp_2ZrX_2 formed from these halides are not the same). (b) The reaction between Cp_2ZrL_2 and *erythro*-1-bromo-3,3-dimethylbutane[3] gives the alkyl zirconium species which has been completely racemized. This was demonstrated unambiguously by ^1H NMR analysis of the corresponding carbonylated product.[3] Excess alkyl bromide recovered at the end of the reaction was unracemized. (c) Reaction between Cp_2ZrL_2 and 6-chloro-1-hexene yielded both acyclic and cyclic products. To a solution of 0.42 mmol of $Cp_2Zr(PPh_2Me)_2$ and 2.4 mmol of PPh_2Me in 7 mL of

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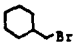
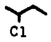
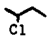
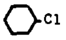
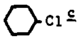
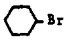
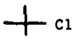
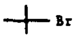
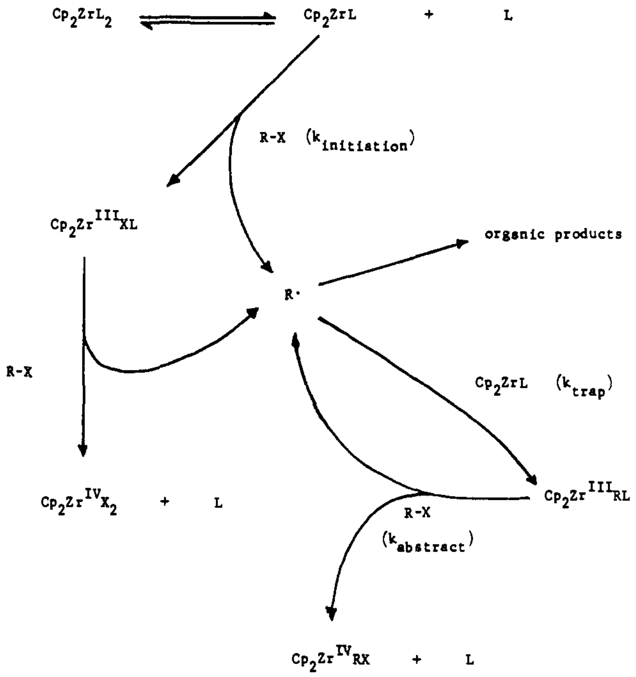
Table I. Oxidation of Cp_2Zr^{II} Bis(phosphine)[a] by RX

Substrate	Cp_2ZrRX	Cp_2ZrX_2	Combined Yield (%)	Equivalents of RX
	100	0	100	5
	100	0	96	1.6
	0	0	decomp	4
	90.5	9.5	100	11
	100	0	100	6
	87	13	87	8.5
	88[b]	12	83	7
	82	18	95	4
	42	58	96	3.5
	29	71	100	12
	56	44	95	3.7
	60	40	96	3.9
	56	44	98	17.5
	56	44	100	19
[c]	83	17	98	20
	72	28	97	20
	0	100	98	14
	0	100	100	8

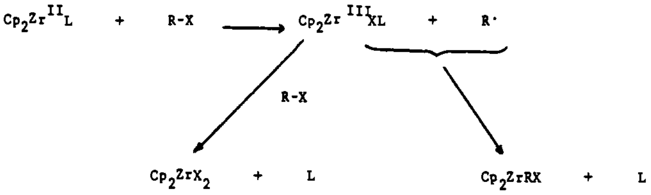
[a] All reactions except (b) and (c) were carried out in C_6D_6 with PPh_2Me in NMR tubes. [b] Reaction terminated at 85% completion. Product hydrolysis showed a mixture of methylcyclopentane and 1-hexene in a ratio of 3.63:1. [c] With PMe_2Ph.

C_6H_6 was added 3.0 mmol of 6-chloro-1-hexene. The reaction mixture was stirred at room temperature for 45 min; reaction volatiles were then removed to leave a dark red oil.[4] ^1H NMR analysis (C_6D_6) of this product showed the presence of alkyl zirconium chloride and zirconocene dichloride in the ratio of 88:12. The composition of the alkylzirconium species was determined to be a mixture of cyclized and uncyclized alkyls by VPC analysis of alkane hydrolysis products [methylcyclopentane (57%) and 1-hexene (15.5%)]. The formation of substantial cyclized alkyl zirconium compound is consistent with a mechanism involving free 5-hexenyl radical.[5] This species is known[6] to cyclize at a rate of ~10^5/s. A cage recombination route can be ruled out by noting the high relative yield of cyclized alkylzirconium complex. The ratio of cyclized to uncyclized organozirconium compounds suggests that capture of hexenyl radical by a zirconium species is competitive with its cyclization.[5] Volatiles formed prior to hydrolysis were methylcyclopentane (7%), 1-hexene (2%), and methylenecyclopentane (1%). Attempts to substantiate the occurrence of a chain process by direct means were unsuccessful, as common radical quenching agents[7] (such as galvinoxyl) reacted with Cp_2ZrL_2. (d) The reaction between Cp_2ZrL_2 and *tert*-butyl chloride gives only Cp_2ZrCl_2, isobutane, and isobutene. When this reaction was followed by ^1H NMR, pronounced CIDNP effects were observed in the signals of the organic products. The A/E phase of the signal is consistent with a diffusive encounter of *tert*-butyl radicals.[8] Isobutane and isobutene were formed in a ratio of 2:1 in 188% yield (based on Zr). CIDNP effects were also observed in the reactions of Cp_2ZrL_2 and *tert*-butyl bromide, *sec*-butyl chloride, *sec*-butyl bromide, and *sec*-butyl iodide.

Scheme I



Scheme II



Partitioning between oxidative addition and formation of dihalide depends on the structure of the alkyl halide employed. Primary straight-chain chlorides, bromides and iodides favor oxidative addition, while *tert*-butyl chloride and bromide produce dihalide exclusively. Secondary halides gave product mixtures.

The product ratio (Cp_2ZrRX:Cp_2ZrX_2) is also sensitive to the steric bulk of the phosphine. Thus, $Cp_2Zr(PPh_2Me)_2$ reacted with excess cyclohexyl chloride to give the oxidative adduct and zirconocene dichloride in a ratio of 68:32. However, when PMe_2Ph (which has a cone angle 14° smaller than that of PPh_2Me)[9] was used, this ratio increased to 83:17.

Rate studies show an inverse dependence on added phosphine concentration and a direct first-order dependence on the concentration of alkyl halide for the disappearance of Cp_2ZrL_2. Thus at 26 °C a 0.036 M solution Cp_2ZrL_2 in C_6D_6 reacted with 11 equiv in bromobutane in the presence of 12 equiv excess of PPh_2Me to produce Cp_2ZrRBr with an observed second-order rate constant of 5.4×10^2 M^{-1} s^{-1}. This value is ~10 times greater than that rate recorded for the Rh(I) macrocycle reported to be one of the most reactive species towards oxidative addition of alkyl halide known prior to this report.[10,11]

We propose that the ratio of oxidative adduct to Cp_2ZrX_2 byproduct formed depends on relative rates of chain initiation and propagation. Initiation gives Cp_2ZrXL which can yield only dihalide by attack on a 2nd equiv of RX. To produce Cp_2ZrRX, both capture of R· by Cp_2ZrL and attack of the Zr(III) species thus formed upon RX must occur. We have noted that product distribution depends on R· and on the cone angle of L in ways which sterically influence the capture step in obvious fashion. As well, attack of the Zr(III) species on RX must be rapid to ensure a large supply of R· to consume starting Zr(II) species in competition with initiation.

Variation in the *halide* species used in oxidation reactions proved to be the most intriguing parameter affecting product distributions (see Table I). Reactions between $Cp_2Zr(PPh_2Me)_2$ and 2-halobutanes illustrate this selectivity pattern: 2-iodobutane reacted rapidly to produce $Cp_2Zr($*n*-butyl$)I$ as the major product,[14] while the analogous chloride reacted more slowly to generate zirconocene dichloride as the predominant species. To elucidate this phenomenon, reactions between $Cp_2Zr(PPh_2Me)_2$ and *sec*-butyl chloride, bromide, and iodide were qualitatively followed by ^1H NMR. We note that reaction occurs immediately on mixing the zirconium species with each of these halides. For the iodide rapid growth of oxidative adduct is recorded; for the bromide, somewhat slower growth is observed; and, for the alkyl chloride, much slower growth is noted. Variation in formation rates for Cp_2ZrRX as a function of halogen atom *abstracted* is reminiscent of results reported for tin radicals[15] or for Cr(II) species.[16] These observations exclude significant participation of a recombination scheme such as the one shown in Scheme II: Here alkyl iodides would be expected to yield the *greatest* relative amount of Cp_2ZrX_2 and alkyl chlorides the least.

We conclude that whereas propagation depends dramatically on R·, L, and X, initiation is apparently not highly sensitive to variation in X.[17,18] It seems then that it is this discrepancy in discrimination profiles (iodides vs. bromides vs. chlorides) between these two competing routes, both of which involve attack of a metallic species upon an alkyl halide, which determines the overall outcome of these competitive oxidation processes.

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(17) Initiation as a function of R· and L was not studied.
(18) Initiation may proceed by electron transfer in alkyl halide complexes of Zr(II). Electrochemical potentials for alkyl halides complexed to this or similar species have not been measured.

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Additions and Corrections

Statistical Phase Space Theory of Polyatomic Systems. Application to the Unimolecular Reactions $C_6H_5CN^{\cdot+} \rightarrow C_6H_4^{\cdot+} + HCN$ and $C_4H_6^{\cdot+} \rightarrow C_3H_3^+ + {\cdot}CH_3$ [*J. Am. Chem. Soc.*, **99,** 1705 (1977)]. By WALTER J. CHESNAVICH and MICHAEL T. BOWERS,* Department of Chemistry, University of California, Santa Barbara, California 93106.

The right-hand side of eq 6 should be divided by σ_a. Also, eq 7 should read

$$R_{\mathcal{J}}(\mathrm{b}\rightarrow\mathrm{a}) = \frac{S_r'}{\sigma_b} \iint \bar{k}_{\mathcal{J}}(\mathcal{E}_r{}^b,\mathcal{E}_t)\rho_t(\mathcal{E}_t)\rho_r(\mathcal{E}_r{}^b) \times \rho_b(E - \mathcal{E}_0 - \mathcal{E}_{tr}{}^b)\, d\mathcal{E}_t d\mathcal{E}_{tr}{}^b \quad (7)$$

eq 8 should read

$$k_{\mathcal{J}}(E)_a = \frac{S_r'}{\sigma_b S_r \rho_a(E - \mathcal{E}_r{}^a)} \iint \bar{k}_{\mathcal{J}}(\mathcal{E}_r{}^b,\mathcal{E}_t)\rho_b(\mathcal{E}_t) \times \rho_r(\mathcal{E}_r{}^b)\rho_b(E - \mathcal{E}_0 - \mathcal{E}_{tr}{}^b)\, d\mathcal{E}_t d\mathcal{E}_{tr}{}^b \quad (8)$$

and equation (9a) should read

$$\bar{k}_{\mathcal{J}}(\mathcal{E}_r{}^b,\mathcal{E}_t) = \mathcal{P}_b(\mathcal{E}_\mathrm{l}.\mathcal{E}_r{}^b,\mathcal{J})/2\pi\hbar\rho_t(\mathcal{E}_t)\rho_r(\mathcal{E}_r{}^b) \quad (9a)$$

where $\rho_r(\mathcal{E}_r{}^b)$ is the density of rotational states of the separated fragments at rotational energy $\mathcal{E}_r{}^b = \mathcal{E}_{tr}{}^b - \mathcal{E}_t$. Equation 10a is correct as published.

In eq 10b–14, in the text surrounding these equations, and in Figures 2, 3, and 5, the quantity E should be replaced by E_v, the vibrational energy of the parent ion "a" except as follows; E should be replaced by $E_v + \mathcal{E}_r{}^a$ in the right-hand side of eq 10b, in both sides of eq 11 and 12, and in the first argument of $\mathcal{P}_{\mathcal{J}}$ in eq 14. These replacements are based on the standard assumption that the rotational angular momentum and rotational constant of the parent neutral are unaltered by the ionization process. Also the right-hand side of eq 10b should be divided by the rotational partition function of the parent molecule, and the right-hand side of eq 14 should be divided by a (numerically determined) normalization constant.

For clarification, S_r' always equals $2\mathcal{J}$, and $\mathcal{P}_b(\mathcal{E}_t,\mathcal{E}_r{}^b,\mathcal{J})$, $\Gamma_b(\mathcal{E}_{tr},\mathcal{J})$, $\bar{k}_{\mathcal{J}}(\mathcal{E}_r{}^b,\mathcal{E}_\mathrm{l})$, $k_{\mathcal{J}}(E)_a$, and $k_{\mathcal{J}}(E,\mathcal{E}_t)_a$ are functions of both $\mathcal{J}$ and its projection on a space-fixed axis. Furthermore, if the parent molecule is treated as a spherical top, then $k_{\mathcal{J}}(E)_a$ and $k_{\mathcal{J}}(E,\mathcal{E}_t)_a$ are also functions of the projection of $\mathcal{J}$ on a body-fixed axis and $g_{\mathcal{J}}$ in eq 10b equals $(2\mathcal{J})^2$. Also, note that $\int \bar{k}_{\mathcal{J}}(\mathcal{E}_r{}^b,\mathcal{E}_t)2\mathcal{J}_t\, d\mathcal{J} = k_L$, where k_L is the Langevin capture rate constant.

Finally, a minor error was found in our RRKM computer program which, when corrected, required minor changes (~10%) in the transition state frequencies in order to reproduce the RRKM curves plotted in Figures 3 and 5.

None of the errors or misprints affect in any way the general conclusions of this paper.

Catalytic Decarbonylation of Aldehydes [*J. Am. Chem. Soc.*, **100,** 7083 (1978)]. By D. H. DOUGHTY and L. H. PIGNO-