

Progress Report (1/1/92-11/1/92)

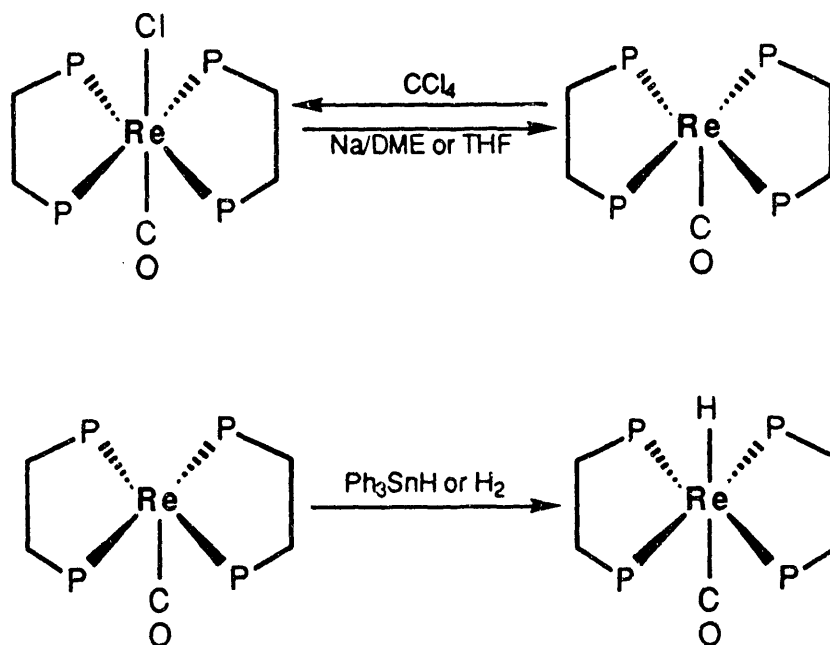
Homolytic Activation of Hydrocarbons and Hydrogen by Persistent Metal Radicals
(DE-FG06-92ER14254; formerly DE-FG02-90ER14122)

DOE/ER/14254--1

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DE93 010775

The main focus of the work to date has been in the development of synthetic methodology to build upon and generalize the earlier isolation of zerovalent rhenium radicals of the type $\text{Re}(\text{CO})_3(\text{PR}_3)_2$. We have found that reduction of rhenium halides such as $\text{Re}(\text{diphos})_2(\text{CO})\text{Cl}$ with metallic sodium gives highly colored species which have EPR signals demonstrating a strong coupling to $\text{Re}(I=5/2)$. Regeneration of starting material occurs upon reaction with CCl_4 . These materials react with hydrogen gas or Ph_3SnH to give the corresponding hydrides. Attempts to isolate pure samples of these radicals have not been successful, and extensive efforts to obtain diffraction quality crystals have so far been fruitless.



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Labeling experiments with D_2 and with deuterated phosphine ligands establish that the source of the hydride in the products is the hydrogen and not the ligands. Most of the thermal reactions of the radicals were carried out in benzene, and no reaction with the solvent was observed. The radical samples prepared in DME(dimethoxyethane) contain some residual DME which cannot be removed even by prolonged evacuation. Control experiments at high temperature establish that the radicals abstract hydrogen atoms from the DME, to form the corresponding hydride. None of the radicals studied could be induced to react with methane.

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As previously reported, we have found that rhenium radicals such as $\text{Re}(\text{CO})_3(\text{PR}_3)_2$ ($\text{R} = \text{Cy}$ and $i\text{Pr}$) react readily with hydrogen but fail to react with methane. We have carried out MM2 calculations on these molecules using the structure derived from X-ray crystallography results for $\text{R}=\text{Cy}$. The results indicate that the sixth coordination site in these molecules is very crowded, hindering close approach of the methane substrate. Less sterically demanding phosphine ligands such as PPh_3 do not afford persistent radicals, instead the Re-Re bonded dimers were obtained. The problem is to design a ligand system with sufficient steric bulk to prevent dimerization, but leave enough room around the sixth coordination site for close approach by the substrate. We have attempted to meet these apparently conflicting requirements by synthesis of a new phosphine ligand. The preparation of (*p-t*-BuPh) $_3\text{P}$ has been completed and we are currently working to prepare the radical $\text{Re}(\text{CO})_3(\text{P}(\text{C}_6\text{H}_5\text{-}i\text{-Bu})_3)_2$. Molecular mechanics calculations have been carried out on this hypothetical radical, which indicate that it is not capable of forming a Re-Re bonded dimer.

In other work, we have discovered some limitations on our original synthesis of radicals from $(\eta^5\text{-CPh}_3)\text{Re}(\text{CO})_3$. Reaction of two equivalents of a sterically demanding phosphine with $(\eta^5\text{-CPh}_3)\text{Re}(\text{CO})_3$ affords $\text{Re}(\text{CO})_3(\text{PR}_3)_2$ and Ph_3C . In the course of an investigation of the mechanism of this reaction, we have now found that the outcome of this reaction is dependent on the concentration of the entering phosphine. At high concentrations of the phosphine ligand, the expected radical product is formed, and is the exclusive rhenium containing product. At lower concentrations, a monophosphine complex is the predominant product. This species has been isolated and fully characterized in the case of $\text{P}(i\text{-Pr})_3$ as $(\eta^3\text{-CPh}_3)\text{Re}(\text{P}(i\text{-Pr})_3)(\text{CO})_3$ (including an x-ray crystal structure). Curiously, this complex is completely inert to further substitution by additional phosphine ligands, indicating that it is not an intermediate on the reaction pathway for radical formation. This result is not encouraging for our planned synthesis of biradicals, since high concentrations of a bifunctional phosphine ligand are to be avoided, in order to prevent polymerization reactions.

In attempts to develop a more versatile radical preparation, we have investigated the preparation of rhenium(I) alkyls of the form $\text{Re}(\text{CO})_3(\text{PR}_3)_2\text{-R}$ ($\text{R} = \text{Me}$ and benzyl). These complexes are readily obtained by thermally induced carbonyl substitution starting from the parent alkyls $\text{Re}(\text{CO})_5\text{-R}$. The methyl complexes serve as useful authentic samples of the products of the proposed methane activation reactions. As expected, the methyl complexes are found to be extremely thermally stable. The benzyl complexes were prepared with the expectation that thermolysis would lead to cleavage of the Re-C σ bond, to afford bibenzyl and the Re radicals. In fact, the benzyl complexes were found to also be very thermally stable, undergoing negligible reaction in refluxing toluene over the course of seven days. While these alkyl groups have not lead to the desired chemistry, the potential of this approach has not been exhausted. It is known that sigma bonded cycloheptatrienyl complexes of rhenium are relatively

unstable with respect to metal-carbon σ bond cleavage. We intend to prepare complexes of the form $\text{Re}(\text{CO})_3(\text{PR}_3)_2(\eta^1\text{-C}_7\text{H}_7)$. Thermolysis should afford $\text{Re}(\text{CO})_3(\text{PR}_3)_2$ and bitropyl under very mild conditions.

In our ongoing effort to prepare biradicals, we have prepared the rigid spanning bidentate ligand $\text{Ph}_2\text{P}-(p\text{-C}_6\text{H}_4)\text{-PPh}_2$, but have found that this ligand does not lead to persistent radicals. Diamagnetic solids of very limited solubility were obtained, presumably due to metal-metal bond formation as previously observed for PPh_3 reactions. Additional steric encumbrance is apparently required to make this approach succeed. To this end, we plan to prepare the para tertiary-butyl substituted analog to this ligand, which should avoid this problem.

Research Plan for 1993

As noted above, we expect that the thermolysis of $\text{Re}(\text{CO})_3(\text{PR}_3)_2(\eta^1\text{-C}_7\text{H}_7)$ will provide a versatile entry to the rhenium radical species, free of the side reactions that complicate our current approach. With the long-range goal of hydrocarbon activation, we will attempt to react each of the new radical species that we obtain with methane and other hydrocarbons.

An important goal remains the preparation and reactivity studies of biradical species. Suitable spanning bidentate ligands have been prepared, but limitations of the current synthetic method indicate that polymerization is a problem. The modified ligand (para-*t*-BuPh) $_2$ P-(para-C $_6$ H $_4$)-P(para-*t*-BuPh) $_2$ has been prepared in small quantities from (para-*t*-BuPh) $_2$ PCl and para dilithio benzene. We are currently working to optimize the yield of this rather unsatisfactory preparation and to prepare biradicals employing this ligand.

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