Part I. Studies of the Substitution and Formation Reactions of Rhenium Carbonyl *o*-Semiquinone Compounds

Part II. Molecular Mechanics Studies of the Steric Interactions in Chromium Pentacarbonyl Phosphine Compounds

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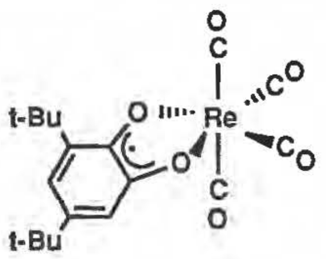
Part I

Many reports on the synthesis and properties of rhenium carbonyl complexes containing a singly-reduced *o*-quinone (i. e. *o*-semiquinone) ligand such as **1** and **2** have appeared [1-9]. These air-sensitive compounds can be prepared by 310 nm irradiation of a solution containing $Re_2(CO)_{10}$ and the free quinone ligand. Rhenium carbonyl *o*-semiquinone compounds undergo substitution reactions with a wide variety of two-electron donor ligands such as phosphites [1,4,6,10,12], phosphines [1,2,4,5,8-11], arsines [1,4,10], stibenes [1,4,10], and amines [1,2,4,10] to form the monosubstituted derivatives.



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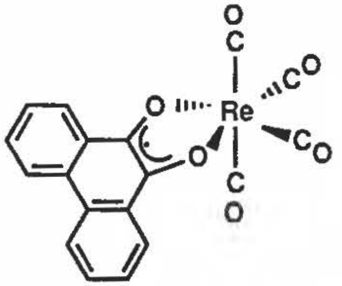

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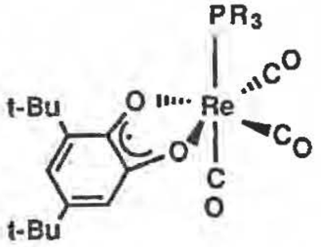

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Although a couple of attempts at studying the substitution kinetics of **1** have been reported, there is no agreement on the form of the rate law, much less on the values of rate constants. Creber and Wan[10] investigated the kinetics of the reaction of **1** with PPh_3, $AsPh_3$, $SbPh_3$, and $P(OPh)_3$. The authors suggested a dissociative mechanism with the loss of a CO ligand as the rate determining step along with a small contribution from a dissociative interchange pathway. Cheng et. al. [5] also studied the kinetics of the reaction of **1** with PPh_3. The observed rate constant was found to increase with increasing PPh_3 concentration, consistent with an associative mechanism.

In our hands, the thermal substitution reactions of **1** with $P(n\text{-}Bu)_3$ was found to occur so rapidly at room temperature that it was necessary to employ stopped-flow methods. Preliminary kinetic runs were carried out using crude, unpurified solutions of **1** in hexane. Both the time required for the reaction to go to completion at a given phosphine concentration and the general shape of the absorbance vs. time curves were found to vary widely from one stock solution of **1** to another. In addition, the reproducibility within each set of curves was not high. Because these preliminary results suggested that the reaction is quite sensitive to the presence of impurites, great efforts were extended to develop a method of obtaining adequate amounts of pure **1**.

Purification of **1** was accomplished using high performance liquid chromatography [13]. Preliminary kinetic runs using a toluene solution of HPLC-purified **1** were carried out. The absorbance vs. time traces showed an induction period, during which time there is very little disappearance of **1**, followed by a fast reaction to form the monophosphine substituted derivative. Because attempts to upscale to a preparative scale column were unsucessful, alternate synthetic routes to **1** were explored.

Minimally-sufficient quantities of **1** became available when it was discovered that **1** is formed from the thermal reaction of $Re(CO)_5Cl$ and the quinone radical anion and that the unreacted starting materials can be removed from the solution by anaerobic flash chromatography. Stopped-flow experiments using CH_2Cl_2 solutions of **1** purified by anaerobic flash chromatography were carried out at various concentrations of $P(n\text{-}Bu_3)$. For concentrations of $P(n\text{-}Bu)_3$ that were 3.0×10^{-3} M and higher, a first-order rate expression provided the best fit to the observed traces. The k_{obs} values show a strong dependence on the concentration of $P(n\text{-}Bu)_3$. For concentrations of $P(n\text{-}Bu)_3$ that are below 2.0×10^{-3} M, rate constants could not be obtained because the absorbance vs. time curves are not regular. The observed kinetics data show considerable variability, both within and among individual data sets.

The kinetic results suggest that the phosphine substitution reaction occurs via an electron-transfer chain (ETC) catalysis mechanism, initiated by an adventitious electron donor. Cyclic voltammetry studies of **1** and its monophosphine derivatives suggest that the chain-propagating electron transfer step will occur. Unfortunately, experimental difficulties in preparing adequate amounts of **1** of extremely high purity prevented a thorough testing of the ETC catalysis mechanism. For this reason, further substitution kinetic experiments were not pursued.

The photochemical formation of the rhenium carbonyl *o*-semiquinone complexes is of interest because the overall reaction can be viewed as both an electron transfer and a CO displacement. The photochemical formation of these complexes has been interpreted as a two-step process [1,3,6-8,12]. The first step involves the oxidative addition of one of the quinone oxygen atoms to the photogenerated $\cdot Re(CO)_5$ radical, with concomitant electron transfer from the metal to the quinone, forming a monodentate intermediate . In a second step, the intermediate undergoes an intramolecular CO substitution reaction to form the chelated product, **1**. A more recent study suggests that **1** may also be formed from the CO-loss product, $Re_2(CO)_9$ [14]. Although these previous experiments provide some clues to the formation mechanism, no reliable kinetics data have been obtained for the various steps in the reaction.

To investigate the photochemical formation reaction, laser and xenon flash photolysis experiments were carried out on solutions containing $Re_2(CO)_8L_2$ (L = CO, phosphine) and 3,5-di-t-butylbenzoquinone. The reaction of $\cdot Re(CO)_4L$ with 3,5-di-t-butylbenzoquinone is very fast; the large magnitude of the bimolecular rate constants suggest that the reaction is close to the diffusion-controlled limit. More than one process leading to **1** or **3** is seen in the xenon flash photolysis experiments under argon; one of the processes is absent and the yield of **1** or **3** is reduced under one atmosphere of CO. These results are consistent with a mechanism in which both $\cdot Re(CO)_4L$ and $Re_2(CO)_7L_2$ lead to **1** or **3**. The rate constants for the ring closure reactions in the mechanism are sensitive to the nature of L.

Part II

Because the steric effects of phosphines are so important in understanding the chemistry of organometallic systems, considerable effort has been extended to develop a quantitative measure of the amount of space required by various phosphines. The most commonly used quantitative measure of the amount of space occupied by a phosphine ligand is the so-called "cone angle," Θ, as defined and measured by Tolman [15]. While several groups have modified the cone angle concept in an attempt to circumvent some of the limitations of

Tolman's approach [16], almost all efforts to evaluate the steric requirements of phosphines have been based on the same cone angle idea.

In the hope that the method would lead to the development of a new and more realistic measure of the steric requirements of various phosphine ligands, molecular mechanics methods [17] were used to investigate the steric interactions of phosphine ligands with the prototypical metal center, $Cr(CO)_5$. In order to carry out the calculations, it was necessary to establish appropriate force field parameters for the metal carbonyl fragment, and to properly account for the effects of complex formation on the stain-free bond angles about the metal and phosphorus atoms. The x-ray crystal structure of $Cr(CO)_5PMe_3$ was determined to aid in the establishment of strain-free bond distances and angles. The agreement of the key bond distances and angles in the x-ray crystal structure and the molecular mechanics minimum energy structure of $Cr(CO)_5PMe_3$ is excellent, suggesting that the force field parameters choosen are appropriate.

The computed molecular mechanics minimum energy structures of 19 different trialkylphosphines and their $Cr(CO)_5$ complexes were determined. With some ligands, such as $P(i\text{-}Pr)_3$, the overall conformation of the ligand does not change dramatically upon complex formation. However, in many instances, such as with $P(n\text{-}Bu)_3$ and PCy_3, the ligand confromation is substantially different in the $Cr(CO)_5$ complexes as compared to that of the unbound phosphine. Consistent with these qualitative observations, the P-C bond distances and C-P-C angles in both the complexes and the free ligands generally increase as the substituent groups becomes increasingly bulky. In addition, the C_{ax}-Cr-C_{rad} angles decrease and the Cr-P distance increases as the ligand becomes larger in the $Cr(CO)_5$ complexes.

Variations in the energy change upon complex formation for the process $PR_3 + Cr(CO)_5 \longrightarrow Cr(CO)_5PR_3$, denoted ΔE, were calculated. With the exception of $Cr(CO)_5P(i\text{-}Bu)_3$, the ΔE_{total} values are more or less independent of cone angle up to about 145°. At larger cone angles, the ΔE_{total} values increase steadily with increasing cone angle. The trend seen in the plot of ΔE_{total} vs. Tolman's cone angle is due almost entirely to changes in the bond stretching component, ΔE_{bonds}; no regular trends are seen in the variations of ΔE_{angles}, $\Delta E_{torsions}$ and ΔE_{VDW}, the other components of ΔE_{total}, with Tolman's cone angle. There is an absence of a regular trend in ΔE_{VDW} as a function of cone angle because the van der Waals potential function contains both attractive and repulsive components which tend to cancel one another as the ligand becomes bulkier.

To test the hypothesis that ΔE_{total} constitutes an effective measure of the steric requirements of trialkylphosphine ligands, rate data for various reactions have been analyzed in terms of a two-parameter free energy relationship, $\ln k = a\delta + b\theta + c$. In 11 out of 13 cases, better or equivalent correlation coefficients are obtained when ΔE_{total} is used as the steric parameter, suggesting that ΔE_{total} may be an appropriate measure of the steric requirements of phosphines. However, when reaction rate data sets containing mixtures of phosphines and phosphites are analyzed in terms of the above free energy relationship using ΔE_{total} as a steric parameter, the correlation coefficients are much poorer than when Tolman's cone angle is used [18]. The use of ΔE_{total} as a steric parameter in linear free energy relationships is thus limited to a particular class of ligands. This is because the relative importances of the components comprising ΔE_{total} differ from one class of ligands to another and because the calculated van der Waals energy includes a contribution from an attractive term, the relative importance of which also varies from one class of ligands to another.

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