The results in Table I clearly indicate that the efficiency of energy transfer is reduced by increased α-methyl substitution around the carbonyl group. Thus it may be concluded that the energy transfer occurs *via* a close interaction of the excited benzene molecule and the carbonyl group. Also, from the magnitude of the cross section it can be concluded that the transfer occurs with a high efficiency in the case of the simple ketones. Viscosity measurements of molecular diameters[8] indicate that a hard-sphere collision cross section of about 25 Å^2 is appropriate for the benzene–acetone system. Therefore the energy transfer would appear to have a maximum efficiency of approximately 0.4. If, however, only the π systems of the interacting species determine the effective molecular diameter, a "collision" diameter of 3.5–4 Å is quite reasonable and indicates that the transfer process has a unit efficiency for the simple ketones. The conclusion concerning the efficiency of energy transfer is in line with other work[7,9] but the conclusion regarding transfer distance contrasts with that of Birks, Saltee, and Leite[10] on the system naphthalene–biacetyl in the liquid phase, where they conclude that singlet transfer occurs by an electron transfer mechanism over an 11-Å interaction distance. It is possible, of course, that the mechanism is entirely different in the two phases or in the two systems. We are examining solutions of the benzene–ketone systems in order to ascertain the effect of phase.

Again, we reiterate that the presence of measurable steric effects may provide a useful means of examining electronic energy transfer processes in sufficient detail to obtain basic knowledge about the nature of the interactions. Further work on other systems with this goal in mind is in progress in our laboratory.

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Five-Coordinate Rhodium(I) Complexes Containing Small Molecules and a Chelating Triphosphine Ligand[1]

Sir:

Recent extensive studies on tertiary phosphine complexes of the platinum group metal halides have demonstrated many diverse and interesting reactions involving (1) homogeneous catalysis,[2] (2) oxidative addition,[3] (3) coordination of elemental molecules,[4] (4) the Lewis basicity of metal complexes,[5] and (5) stabilization of small molecular fragments.[6] Many of these reactions which utilize the Wilkinson compound,[7] $Rh(Ph_3P)_3Cl$, often yield complexes where one or more of the phosphine ligands is displaced, *e.g.*, in $Rh(Ph_3P)_2COCl$. We became interested in designing a triphosphine ligand that would make the rhodium atom more basic than in $Rh(Ph_3P)_3Cl$ and simultaneously minimize the tendency of one or more phosphine donors to be displaced in chemical reactions. The chelating triphosphine $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ fits these criteria and it was synthesized; however, our initial experiments with this ligand indicated that one of the phosphine donors often bridged to another rhodium atom, thereby producing polynuclear rhodium complexes. In order to relieve the implied chelate-ring strain, the tritertiary phosphine with trimethylene linkages, $C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2$ (L), was prepared. This ligand should facilitate coordination of all three phosphorus atoms in a monomeric, square-planar complex of the type RhP_3Cl, which would possess a donor set similar to the Wilkinson compound.

Addition of a benzene solution of L to a suspension of $[Rh(C_8H_{12})X]_2$ (X = Cl, Br, I) in refluxing ethanol readily produces the corresponding square-planar complexes, RhLX, in high yields ($\sim$80%). The yellow chloride complex, RhLCl, is stable for months in air, whereas the iodide complex, RhLI, changes color in air over a period of several months from orange to brown.

The chloride complex, RhLCl (**1**), reacts with a variety of small molecules to form the five-coordinate, nonionic adducts RhLCl·A where A = BF_3, CO, $HgCl_2$, SO_2, O_2, and S_2.[8] Tensiometric titrations of **1** with BF_3 show sharp breaks at the 1:1 stoichiometry, and the infrared spectrum of the isolated solid shows a strong broad band at *ca.* 1060 cm^{-1}, indicative of a coordinated BF_3 group.[9] The monocarbonyl complex, RhLCl·CO, shows a single CO infrared peak both in solution (CH_2Cl_2, 1956 cm^{-1}) and in the solid state (Nujol, 1957 cm^{-1}); in the more polar solvent, CH_3NO_2, where conductance measurements show some ionization, there is an additional peak of medium intensity. The latter peak at *ca.* 2020 cm^{-1} signifies the presence of the cation $[RhL(CO)]^+$ as discussed below. For comparison, ν(CO) in RhLI·CO occurs at 1937 cm^{-1} (Nujol), indicating greater Rh → CO back bonding when chloride is replaced with iodide.

A microcrystalline light-brown dioxygen complex, **1**·O_2, is formed rapidly when O_2 is bubbled through a benzene suspension of **1**. This RhLCl·O_2 compound is one of the most stable rhodium–dioxygen complexes

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(1) Presented at the 3rd Central Regional Meeting of the American Chemical Society, Cincinnati, Ohio, June 1971, and in the Symposium on Five-Coordinate Complexes, at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstracts, No. INORG 96.

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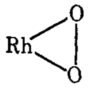
known. For example, it is stable indefinitely in air, and it does not lose O_2 by pumping at 80° and 0.05 Torr. However, it does react rapidly with other chemicals such as sulfur dioxide. Bubbling SO_2 through a suspension of $RhLCl \cdot O_2$ in benzene immediately converts the dioxygen complex into the yellow sulfate complex of Rh(III), $RhLCl \cdot SO_4$. The infrared spectrum of the latter complex exhibits strong peaks at 1250, 1240, 1147, and 640 cm^{-1}, characteristic of a bidentate sulfate group,[10] while the 862-cm^{-1} peak due to the symmetric



unit[11] in $RhLCl \cdot O_2$ has disappeared. If one performs the SO_2 and O_2 reactions in the reverse manner, *i.e.*, by bubbling O_2 through a benzene solution of $RhLCl \cdot SO_2$, no sulfate complex is formed within 1 hr at 25°. Thus, the addition sequence of reagents is very important in forming the $RhLCl \cdot SO_4$ complex. Collman found that the $Ir(Ph_3P)_3Cl \cdot O_2$ complex also reacts with SO_2 much faster than the corresponding SO_2 complex reacts with molecular oxygen.[12]

The disulfur complex $\mathbf{1} \cdot S_2$ was isolated by treating a benzene slurry of **1** with a benzene solution of cyclooctasulfur. This reaction could conceivably convert two of the three phosphine donors in L to phosphine sulfide groups. In fact, the analytical data and the infrared spectrum, which shows a new peak at 546 cm^{-1}, would be consistent with a complex containing two coordinated phosphine sulfide groups. However, such a complex can be excluded on the basis of the mass spectrum of $RhLCl \cdot S_2$, which shows the peak of highest relative abundance at $m/e = 700$ (*i.e.*, $RhL^{35}Cl$) and no peaks attributable to phosphine sulfide fragments. Thus, the S_2 group is not incorporated into the triphosphine ligand, and we propose that $\mathbf{1} \cdot S_2$ contains a symmetrically, π-bonded S_2 ligand similar to the recently prepared iridium complex $[Ir(diphos)_2S_2]Cl \cdot CH_3CN$ (diphos = bis(diphenylphosphino)ethane).[6,13] The RhLCl compound has cleaved the S_8 ring during the reaction and stabilized the S_2 fragment, which does not exist at room temperature.

Five-coordinate cationic complexes of the general formulas $[RhLCl \cdot A]^+$ (A = H, NO, N_2Ph) may be isolated by treating RhLCl with cationic reagents such as H^+, NO^+, and $N{\equiv}NPh^+$. For example, the cationic hydride $[RhLClH]^+$, which has νRh–H at 2198 cm^{-1} (Nujol), was isolated by treating RhLCl with aqueous 50% HBF_4. The nitrosyl cation $[RhLClNO]^+$ is obtained from RhLCl and $NO^+BF_4^-$ in a benzene–methanol mixture. The NO stretching frequency (1699 cm^{-1}) is in the range for a bent Rh–N–O linkage.[14] The phenyl diazonium cation, $C_6H_5N_2^+$, reacts with **1** to form the phenylazo complex $[\mathbf{1} \cdot N_2C_6H_5]BF_4$. The red-orange crystals separate from the methanol reaction solution at or slightly below room temperature; however, if this slurry is warmed to *ca.* 50°, the red-orange crystals redissolve and the solution turns golden yellow. The hydride $[\mathbf{1} \cdot H]BF_4$ can be isolated from this yellow solution in good yield. Anisole, $C_6H_5OCH_3$, was identified by glc as a major product of this decomposition.

Four- and five-coordinate cations of the types $[RhL(solvent)]^+$, $[RhLCO]^+$, $[RhL(solvent)A]^+$, and $[RhL(CO)_2]^+$ can be obtained by chloride displacement from RhLCl in polar solvents. Several of these four- and five-coordinate cations are interconvertible, depending on the reaction conditions. For example, the dicarbonyl $[RhL(CO)_2]PF_6$ is isolated from a 1:1 dichloromethane–acetone mixture when the solution is saturated with CO; however, the monocarbonyl $[RhLCO]PF_6$ is isolated if the solution is treated with CO and then purged with N_2. The infrared spectrum of freshly prepared solid $[RhL(CO)_2]PF_6$ shows two strong, sharp peaks at 2037 and 1980 cm^{-1}. The compound loses carbon monoxide over a period of weeks in the solid state and rapidly with effervescence in solution to give the monocarbonyl cation $[RhLCO]^+$, which has one infrared peak in the CO region at 2026 cm^{-1} (CH_2Cl_2). If a solution containing $[RhLCO]^+$ is saturated with CO at 1 atm and 25°, the $[RhL(CO)_2]^+$ cation can be isolated.

On the basis of the increased stability and reactivity patterns of these four- and five-coordinate rhodium complexes of the chelating triphosphine $C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2$ as compared to other tertiary phosphine–rhodium systems, it is concluded that the RhLCl complex offers tremendous potential for future study because (1) in general, it functions as a stronger Lewis base; (2) it forms qualitatively more stable adducts of small molecules (*cf.* the increased stability of the O_2, SO_2, and BF_3 adducts); and (3) it simplifies the stoichiometry of the products, as all three phosphine groups remain bonded in the resulting complexes.

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Enzymic Formation of Squalene Homologs from Farnesyl Pyrophosphate Homologs

Sir:

The effect of structural modification of 2,3-oxidosqualene on the enzymic cyclization has been studied in some detail.[1] The substrate specificity of the "head-to-tail" condensation catalyzed by farnesyl-PP[2] synthetase has also been studied.[3,4] However, the specificity of the "tail-to-tail" condensation of farnesyl-PP, *i.e.*, the formation of squalene, has not yet been reported. We describe here the finding that 12-methyl-

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