PHOTOCHEMICAL REACTION OF DIRHENIUM DECACARBONYL WITH TRIPHENYL PHOSPHITE

C.S. YOUNG, S.W. LEE and C.P. CHENG *

Department of Chemistry, National Tsing Hua University, Hsinchu (Taiwan 300)

(Received May 9th, 1984)

Summary

The photochemical carbonyl substitution reaction of $Re_2(CO)_{10}$ with $P(OPh)_3$ was studied under vacuum. Using mass, ^{31}P NMR, and IR spectroscopic data, four well-characterized new products, in addition to a mononuclear hydride *mer*-$HRe(CO)_3[P(OPh)_3]_2$, were obtained: 1-*ax*-2',4'-di-*eq*-$Re_2(CO)_7[P(OPh)_3]_3$; 1,1'-di-*ax*-2,2'-di-*eq*-$Re_2(CO)_6[P(OPh)_3]_4$; 2,2',4,4'-tetra-*eq*-$Re_2(CO)_6[P(OPh)_3]_4$ and 1,1'-di-*ax*-2,2',4,4'-tetra-*eq*-$Re_2(CO)_4[P(OPh)_3]_6$. The isolated highly substituted metal carbonyl products are the isomers with favorable steric repulsive interactions among the triphenyl phosphite ligands.

Introduction

17-*e* organometallic radicals have been established to be particularly reactive. The radicals can undergo carbonyl substitution [1–3], halogen abstraction [4], hydrogenation [1,5,6], radical coupling (recombination) [7,8] and hydrogen activation [9]. The organometallic radicals can also initiate polymerization and alkane halogenation reactions [10]. One of the most convenient methods of generating the radicals is the homolytic cleavage of the metal–metal bond of dinuclear carbonyl compounds and their substituted derivatives. Well-characterized persistent organometallic radical systems include $Fe[P(OMe)_3]_3(\eta^3$-alkenyl) [11,12], $Co[P(OMe)_3]_4$ [13], $Mn(CO)_3L_2$ [14–16] (L = PR_3, $P(OR)_3$, CO) and $Mn(\eta$-$C_4H_6)_2L$ (L = PR_3, Co) [17].

In extending our work on ·$Mn(CO)_3L_2$, where L is phosphine or phosphite, to the congener species ·$Re(CO)_3L_2$, it was found [18] that the rhenium radical could not be detected by EPR following the identical procedure used for preparing the manganese radical. The different behavior of the similar Mn and Re radicals is attributable to the following two factors. First, the Re–Re bond is stronger than the Mn–Mn bond in their respective carbonyl compounds [19,20]. The steric repulsion introduced by the bulky ligand L is not strong enough to cause the cleavage of the Re–Re bond, whereas it is sufficient to breakup the Mn–Mn bond. Second, the

rhenium-centered radicals are kinetically more prone to the radical-radical recombination reaction than the manganese centered radical [21,22]. Recently, Brown et al. [23] were successful in detecting the $\cdot$Re(CO)$_3$[P(cyclohexyl)$_3$]$_2$ radical by EPR, where the tricyclohexylphosphine has a very large cone angle [24] of 170°.

Since the rhenium-centered radicals have the thermodynamic and kinetic tendency to form the dirhenium compounds one would expect that dirhenium compounds highly substituted by phosphine or phosphite can be isolated in contrast to the dimanganese systems. Indeed, stable trisubstituted dirhenium compounds [25]; i.e., 1-*ax*-2′,4′-di-*eq*-Re$_2$(CO)$_7$(PPh$_3$)$_3$, 2,2′,4-tri-*eq*-Re$_2$(CO)$_7$(PPh$_3$)$_3$ and 1-*ax*-2,2′-di-*eq*-Re$_2$(CO)$_7$(PPh$_3$)$_3$, were isolated in the photochemical reaction of Re$_2$(CO)$_{10}$ with PPh$_3$ [18]. They exhibit interesting stereochemistry. For example, 1-*ax*-2′,4′-di-*eq*-Re$_2$(CO)$_7$(PPh$_3$)$_3$ is the major product among the trisubstituted isomers; the isomer expected to be the major product 1,1′-di-*ax*-2-*eq*-Re$_2$(CO)$_7$(PPh$_3$)$_3$ does not exist in the products. Hoping to shed some light on the stereochemistry of the highly substituted dirhenium complexes, the photochemical reaction of Re$_2$(CO)$_{10}$ with P(OPh)$_3$, which has a smaller cone angle (128°) than PPh$_3$ (145°), was carried out. The results of the reaction are reported here.

Experimental section

Materials

Dirhenium decacarbonyl and triphenyl phosphite were obtained from Strem Chemical Co. and used directly without further purification. Solvents used were purified according to the standard method.

Spectroscopic measurements

IR spectra were recorded on a Perkin–Elmer model 580 IR spectrometer. ^{31}P NMR were obtained on a Bruker WP-80-DS FT NMR, using 85% phosphoric acid as external standard. A positive chemical shift indicates downfield shift in conformity with the convention used in ^{1}H and ^{13}C NMR. ^{1}H NMR were obtained on a JEOL JNM-FX-100 spectrometer. Mass spectra were recorded on JEOL JMS-D-100 spectrometer with beam energy of 12 eV. The mass spectrometer was optimized to detect the species with mass below 1000. Thus, the parent peak of most compounds studied in this work was not observed. Elemental analysis results were obtained on a Perkin–Elmer FM, C-H-N model 185 analyzer. The elemental analysis data for Re were obtained by neutron activation analysis method.

Photochemical reaction of Re$_2$(CO)$_{10}$ and triphenyl phosphite

The 20 ml hexane solution of 0.2 mM Re$_2$(CO)$_{10}$ and 2.4 mM P(OPh)$_3$ was subjected to photolysis, under vacuum, using a 450 W medium pressure mercury lamp which was placed inside a water jacket to filter out the IR radiation. The carbon monoxide generated in the triphenyl phosphite substitution reaction was pumped away periodically (every 30 min of irradiation). The photolysis was stopped when no further carbon monoxide evolution was detected on a Pirani vacuum gauge. After 10 h of irradiation, the hexane solvent was pumped away, and a yellowish green oily residue was obtained. The residue was redissolved in hexane/benzene/ chloroform (4/1/1) mixed solvent. Separation was achieved by employing preparative TLC (Merck Kieselgel 60 PF 254). Eight compounds were isolated, but only five

of them can be unambiguously identified. Their physical properties and spectro-scopic data are listed below.

Compound I, $Re_2(CO)_6[P(OPh)_3]_4$. White crystalline solid. Yield 15%. M.p. 135°C. R_f: 0.55 (in hexane/benzene (6/1) mixed solvent). Air stable, slightly soluble and stable in hexane. Also soluble in benzene and chloroform, but decomposes slowly. $\nu(C\equiv O)$ in $CHCl_3$: 2070vw, 2043vs, 1975s, 1943s. ^{31}P NMR in C_6D_6: 141.46 (doublet, J 47.7 Hz), 100.70 (doublet, J 47.7 Hz), integrated intensity ratio 1/1. $^{31}P\{^1H\}$ spectrum is identical to non-decoupled spectrum. No hydride ^1H NMR signal was observed. Mass spectra ($M = Re(CO)_3[P(OPh)_3]_2$): 891, 889, [M]; 890; 888 [$M - H$]; 862, 860 [$M - CO - H$]; 834, 832 [$M - 2CO - H$]; 806, 804 [$M - 3CO - H$]; 721, 719 [$M - Ph - OPh$]. Analysis: Found: C, 53.09; H, 3.37; Re, 20.90. $C_{78}H_{60}O_{18}P_4Re_2$ calcd.: C, 52.60; H, 3.37; Re, 21.20%.

Compound II, $HRe(CO)_3[P(OPh)_3]_2$. White crystalline solid. M.p. 162°C. R_f: 0.5 (in hexane/benzene (6/1) mixed solvent). Yield 20%. Stability and solubility properties are the same as compound I. $\nu(C\equiv O)$ in $CHCl_3$ (cm^{-1}): 2060w, 2040w, 1968s. ^{31}P NMR in C_6D_6 (ppm): 121.26 (doublet, J 28.1 Hz). Under proton noise decoupling, doublet collapses into singlet. ^1H NMR (ppm): 7.20(s), 7.15(s), 7.08(s), -6.67 (triplet, J 28.1 Hz). Mass spectra ($M = HRe(CO)_3[P(OPh)_3]_2$): 892, 890 [$M$]; 890, 888 [$M - 2H$]; 862, 860 [$M - CO - 2H$]; 834, 832 [$M - 2CO - 2H$]; 806, 804 [$M - 3CO - 2H$]; 721, 719 [$M - H - Ph - OPh$]. Analysis: Found: C, 52.63; H, 3.43; Re, 19.98. $C_{39}H_{31}O_9P_2Re$ calcd.: C, 52.60; H, 3.46; Re, 20.90%.
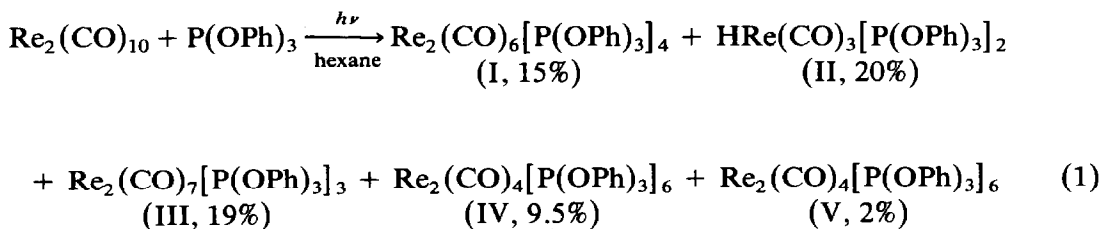
Compound III, $Re_2(CO)_7[P(OPh)_3]_3$. Yellow crystalline compound. M.p. 175°C. R_f: 0.45 (in hexane/benzene (6/1) mixed solvent). Yield 19%. Air stable, soluble and stable in chloroform and benzene. $\nu(C\equiv O)$ in CH_3Cl: 2100vw, 2070vw, 2000m, 1975vs, 1960vs, 1905s. ^{31}P NMR in C_6D_6 (ppm): 115.24(s), 104.67(s), integrated ratio 1/2. Mass spectra ($M = Re(CO)_3[P(OPh)_3]_2$, $M' = Re(CO)_4[P(OPh)_3]$): 891, 889 [M]; 890, 888 [$M - H$]; 886, 862, 860, 858, 856 [$M - CO - nH$]; 835, 834, 833, 831, 829 [$M - 2CO - nH$]; 805, 803 [$M - 3CO$]; 609, 607 [M']; 608, 606 [$M' - H$]; 580, 578 [$M' - CO - H$]; 552, 550 [$M' - 2CO - H$]; 524, 522 [$M' - 3CO - H$]. Analysis: Found: C, 49.73; H, 3.04; Re, 25.20. $C_{61}H_{45}O_{16}P_3Re_2$ calcd.: C, 49.68; H, 3.05; Re, 24.80%.

Compound IV, $Re_2(CO)_4[P(OPh)_3]_6$. White crystalline solid. Yield 9.5%. M.p. 200°C. R_f: 0.42 (in hexane/benzene (6/1) mixed solvent). Air stable. Soluble but unstable in benzene and chloroform. $\nu(C\equiv O)$ in $CHCl_3$: 1990s, 1920s. ^{31}P NMR (ppm): 142.60 (triplet, J 45.60 Hz), 101.3 (doublet, J 45.60 Hz), integrated ratio 1/2. ^{31}P proton noise decoupled spectrum is identical to non-decoupled spectrum. No hydride ^1H NMR signal was observed. Mass spectra ($M = Re(CO)_2[P(OPh)_3]_3$): 863, 861 [$M - P(OPh)_3$]; 835, 833 [$M - P(OPh)_3 - CO$]; 807, 805 [$M - P(OPh)_3 - 2CO$]; 786, 784 [$M - P(OPh)_3 - Ph$]; 758, 756 [$M - P(OPh)_3 - Ph - CO$]; 730, 728 [$M - P(OPh)_3 - Ph - 2CO$]; 692, 690 [$M - (OPh)_3 - Ph - OPh - H$]. Analysis: Found: Re, 16.01. $C_{112}H_{90}O_{22}P_6Re_2$ calcd.: Re, 15.87%.

Compound V, $Re_2(CO)_6[P(OPh)_3]_4$. White crystalline compound. M.p. 160°C. Yield 2%. R_f: 0.33 (hexane/benzene (6/1) mixed solvent). Air stable. Soluble but unstable in benzene, chloroform and methylene chloride. $\nu(C=O)$ in $CHCl_3$: 1990vs, 1940s. ^{31}P NMR (ppm): 102.8 (s). Mass spectra ($M = Re(CO)_3[P(OPh)_3]_2$): 891, 889 [M]; 890, 888 [$M - H$]; 862, 860 [$M - H - CO$]; 834, 832 [$M - H - 2CO$]. Analysis: Found: C, 52.48; H, 3.40; Re, 19.93. $C_{78}H_{60}O_{18}P_4Re_2$ calcd.: C, 53.60; H, 3.37; Re, 20.90%.

Results

The photochemical reaction of $Re_2(CO)_{10}$ with $P(OPh)_3$ in hexane produces five well-characterized compounds as shown in eq. 1:

$$Re_2(CO)_{10} + P(OPh)_3 \xrightarrow[\text{hexane}]{h\nu} \underset{\text{(I, 15\%)}}{Re_2(CO)_6[P(OPh)_3]_4} + \underset{\text{(II, 20\%)}}{HRe(CO)_3[P(OPh)_3]_2}$$

$$+ \underset{\text{(III, 19\%)}}{Re_2(CO)_7[P(OPh)_3]_3} + \underset{\text{(IV, 9.5\%)}}{Re_2(CO)_4[P(OPh)_3]_6} + \underset{\text{(V, 2\%)}}{Re_2(CO)_4[P(OPh)_3]_6} \qquad (1)$$

Except compound III, the other four compounds have never been isolated and characterized despite previous studies of this system under thermal reaction conditions [26–28].

Determinations of the molecular formulas of these compounds are based mainly on mass spectroscopic data. Because of the limitations of our spectrometer and the high molecular mass, the molecular ion of only compound II could be detected. Only the fragments resulting from the Re–Re bond scission of the parent dirhenium compounds could be observed. The molecular formulas were then deduced from the fragments. While this procedure of analysis may appear questionable, there are convincing reasons to believe that the formulas are correct: (a) In the mass spectra of all dirhenium carbonyl compounds and phosphine substituted derivatives studied in our laboratory, the monorhenium fragments and their decarbonylated homologues have the predominant mass peaks. (b) The proposed formulas are consistent with the IR, and ^{31}P NMR spectroscopic data (vide infra).

The Re-containing species that appear in the mass spectrum of compound I can be accounted for by the presence of $Re(CO)_3[P(OPh)_3]_2$ and its decarbonylated and/or dehydrogenated species. Thus, compound I has the simple formula $[Re(CO)_3[P(OPh)_3]_2]_2$. In the ^{31}P NMR spectrum, identical to the $^{31}P\{^1H\}$ spectrum, there are phosphorus peaks at 141.46 and 100.70 ppm. The two phosphorus atoms are mutually coupled with coupling constant of 47.70 Hz. The only reasonable assignment for compound I is $1,1'$-di-ax-$2,2'$-di-eq-$Re_2(CO)_6[P(OPh)_3]_2$. One would expect to observe three carbonyl stretching absorptions from the above structure, if no interaction between the carbonyl stretchings of different Re metal centers is assumed. Indeed, three strong CO absorption bands were detected.

The presence of mass peaks at 892, 890, indicates that compound II is $HRe(CO)_3[P(OPh)_3]_2$. The two phosphorus nuclei are equivalent in the NMR at 121.26 ppm. They are also coupled to the hydride proton with coupling constant J 28.1 Hz. The fact that three carbonyl stretching bands (two weak bands at 2060 and 2040 cm^{-1}, and one strong band at 1968 cm^{-1}) were observed, is indicative of a C_{2v} symmetry at the Re center. Thus, the structure of compound II is $trans$-mer-$HRe(CO)_3[P(OPh)_3]_2$. An analogous phosphine complex $HRe(CO)_3(PPh_3)_2$ [5,6] has been reported.

In compound III, the mass peaks due to $Re(CO)_3[P(OPh)_3]_2$ and $Re(CO)_4P(OPh)_3$ were detected in the mass spectrum. This leads to the assignment that compound III is $Re_2(CO)_7[P(OPh)_3]_3$. In the ^{31}P NMR spectrum, two singlet peaks were observed at 115.24 and 104.67 ppm with integrated ratio of $1/2$. From the integrated ratio, it
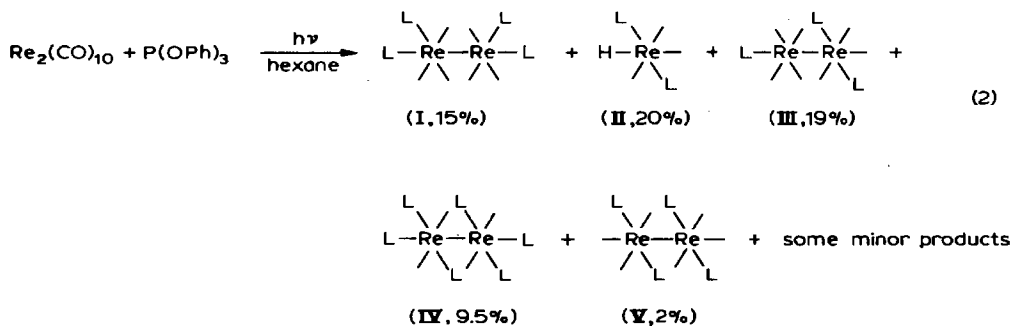
could be deduced that the signal at 115.24 ppm is due to the phosphorus of the $Re(CO)_4[P(OPh)_3]$ fragment, and the signal at 104.67 is due to the two equivalent phosphorus atoms of the $Re(CO)_3[P(OPh)_3]_2$ fragment. By comparing with the ^{31}P chemical shift of δ 117.8 ppm seen for $1,1'$-di-ax-$Re_2(CO)_8[P(OPh)_3]_2$ [28], it is reasonable to assign the phosphite in the $Re(CO)_4P(OPh)_3$ fragment to the axial position. The two equivalent phosphites in $Re(CO)_3[P(OPh)_3]_2$ may occupy the cis- or $trans$-equatorial positions. One would expect that, in the cis geometry, there would be three strong IR carbonyl stretching bands, and in the $trans$ geometry, there would be one strong and two weak bands. Taking into account of the one strong band and one weak band from the C_{4v} carbonyl stretching of $Re(CO)_4P(OPh)_3$, the experimental IR spectrum is consistent with the $trans$ geometry in the $Re(CO)_3[P(OPh)_3]_2$ fragment. Furthermore, the $trans$ arrangement is also favored based on the steric considerations. Thus, the structure of compound III is assigned as 1-ax-$2',4'$-di-eq-$Re_2(CO)_7[P(OPh)_3]_3$.

In compound IV, the $Re(CO)_2[P(OPh)_3]_3$ mass peak was observed, and no other distinct rhenium carbonyl peak was detected. Thus, the compound is $\{Re(CO)_2$-$[P(OPh)_3]_3\}_2$. There are two ^{31}P peaks at 142.63 (triplet) and 101.30 ppm (doublet). The integrated ratio of the two peaks is 1 to 2. The only reasonable assignment is that one phosphite is at the axial position with δ 142.63 ppm, and two equivalent phosphites are at the equatorial positions with δ 101.30 ppm. It is very likely that the phosphites are located mutually $trans$ because the ^{31}P chemical shift is very close to that of the $trans$ structure in compound III, and the steric consideration favors the mutual $trans$ arrangement. Hence, compound IV is assigned to be $1,1'$-di-ax-$2,2',4,4'$-tetra-eq-$Re_2(CO)_4[P(OPh)_3]_6$.

The mass spectrum of compound V is almost the same as that of compound I, except for minor intensity differences. The formula of compound V is $Re_2(CO)_6$-$[P(OPh)_3]_4$. Its ^{31}P NMR spectrum exhibits a single peak at 102.8 ppm (singlet). Thus, the two phosphites are equivalent. There are two strong carbonyl absorption bands in the IR, indicative of a $trans$ structure; otherwise, there should be three carbonyl bands. Hence, the structure of compound V is assigned as $2,2',4,4'$-tetra-eq-$Re_2(CO)_6[P(OPh)_3]_4$.

Discussion

The results of the photochemical reaction of $Re_2(CO)_{10}$ with $P(OPh)_3$ are summarized in eq. 2.

where L represents $P(OPh)_3$, and carbonyl ligands are omitted for clarity. There are three minor products, which we were unable to identify

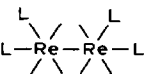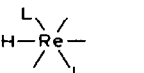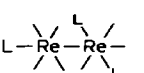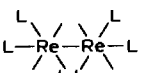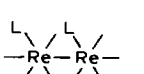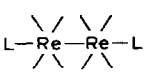The ^{31}P NMR chemical shifts of the compounds listed in Table 1, show three trends. First, $\delta(P)$ of the equatorial phosphite ligands are in the range of 100.7 to 104.7 ppm, upfield from free $P(OPh)_3$ by about 24 ppm. The environment of the Re, whether there are *trans-eq-* or/and *cis-ax*-$P(OPh)_3$, seems to exert negligible effect on the chemical shift of equatorial triphenyl phosphite. Nevertheless, the presence of hydride alters the chemical shift significantly. Second, the chemical shift of axial triphenyl phosphite is strongly influenced by the presence of *cis*-equatorial triphenyl phosphite ligands. $\delta(P)$ of *ax*-$Re(CO)_4P(OPh)_3$ is 116 ± 1 ppm, the presence of *cis-eq*-$P(OPh)_3$ causes $\delta(P)$ a downfield shift by 26 ppm, which is surprisingly independent of the number of *cis-eq.* triphenyl phosphite. Third, $J(P-P)$ between axial and equatorial triphenyl phosphites bound to the same Re center is 46.6 Hz. This coupling was not observed in the similar PPh_3 substituted dirhenium compounds.

There was only one triply substituted isomer, 1-*ax*-2',4'-di-*eq*-$Re_2(CO)_7[P(OPh)_3]_3$, being isolated in the photochemical reaction of $Re_2(CO)_{10}$ with $P(OPh)_3$. In the thermal reaction, Cox et al. [27,28] isolated a triply substituted isomer, which was tentatively assigned to be 1,1'-di-*ax*-2'-*eq*-$Re_2(CO)_7[P(OPh)_3]_3$. Its carbonyl stretching bands are identical to compound III isolated in this work. It should be correctly assigned as 1-*ax*-2',4'-di-*eq*-$Re_2(CO)_7[P(OPh)_3]_3$.
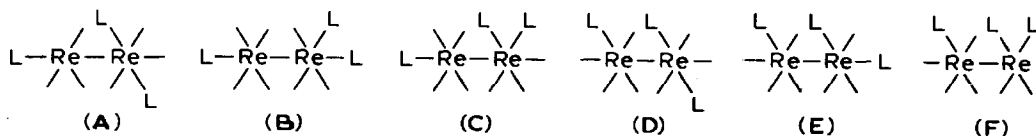
If each Re center is coordinated at least, by one $P(OPh)_3$, there are six possible isomers of $Re_2(CO)_7[P(OPh)_3]_3$:

TABLE 1

^{31}P NMR CHEMICAL SHIFT DATA FOR THE COMPOUNDS I–V

Compound [a]	δ [b] (ppm in C_6D_6)		Coupling constant (Hz)
	δ_{axial}	δ_{eq}	
(I)	141.46	100.7	J(PP) 47.7
(II)	(121.26)		J(PH) 28.1
(III)	115.24	104.67	
(IV)	142.63	101.3	J(PP) 45.6
(V)		102.8	
[c]	117.8		
	(126.75)		

[a] L represents $P(OPh)_3$, carbonyl ligands are omitted for clarity. [b] Chemical shifts were measured using 85% H_3PO_4 as reference. Downfield shifts are indicated by positive chemical shifts. [c] See Ref. 28.

L—Re—Re— L—Re—Re—L L—Re—Re— —Re—Re— —Re—Re—L —Re—Re

(A)   (B)   (C)   (D)   (E)   (F)

Isomer **C** and **F** are expected to be least stable because of the strong repulsion between the *cis-eq* triphenyl phosphites. In isomer **B** and **E**, the repulsion between the equatorial-axial triphenyl phosphites could be reduced by folding back of all equatorial ligands toward the other Re center as shown in the structure of $Re_2(CO)_{10}$ [29,30], where the average $Re–Re–C_{eq}$ angle is 86°. From the steric repulsion alone, isomer **A** which was isolated in this work, is expected to be the most stable isomers. In the triphenylphosphine system, $1-ax-2',4'-di-eq-Re_2(CO)_7(PPh_3)_3$, which corresponds to isomer **A**, is also the most abundant triple substituted product in the photochemical reaction [18]. In the photochemical reaction of $PMePh_2$ [31] with $Re_2(CO)_{10}$, both isomer **A** and isomer **D** were isolated. The relative yield depends on the mole ratio of the reactants, and photoreaction condition. In the PMe_2Ph and $AsMe_2Ph$ system [32] $2,2',4-tri-eq-Re_2(CO)_7L_3$, which correspond to isomer **D**, are the sole triply substituted photoreaction products. Since the cone angles of $PMePh_2$ (136°) and PMe_2Ph (122°) are not far from those of PPh_3 (145°) and $P(OPh)_3$ (128°), the different stereochemical behavior might be attributable to the electronic effect. Indeed, the electronic parameter ν as defined by Tolman [24], indicates that the donor strength of the ligands is decreasing in the order $PMe_2Ph > PMePh_2 > PPh_3 > P(OPh)_3$. Certainly kinetic effect will affect the product distribution, but the stability consideration can account for the distribution qualitatively in this situation.

We had isolated two tetrasubstituted compounds, i.e., $1,1'-di-ax-2,2'-di-eq-Re_2(CO)_6[P(OPh)_3]_4$ (15%) and $2,2',4,4'-tetra-eq-Re_2(CO)_6[P(OPh)_3]_4$ (2%). The mixed isomer $1-ax-2,2',4-tri-eq-Re_2(CO)_6[P(OPh)_3]_4$ was not isolated. The stereochemistry of one rhenium center seems to exert some influence on the other rhenium center. It is possible to rationalize this product distribution based on steric repulsive interaction. There are two main types of steric repulsive interactions: (a) the interaction between the axial phosphite and the equatorial phosphite bonded to the same rhenium; (b) the interaction of the equatorial phosphite with the two equatorial phosphites and carbonyl groups bonded to the other rhenium. Let's suppose the repulsive interaction energy be E_a and E_b for the type (a) and (b) interactions. Examining simple molecular model, even under the most favorable conformation, there is significant steric repulsion in type (b) interaction. In type (a) interaction, the strong steric interaction between the *cis* phosphites may be lessened by bending the equatorial phosphite to make the PReP angle larger than 90°. This ligand bending behavior is conspicuous in the structure of $Re_2(CO)_{10}$. And it is very likely to be presented in type (a) interaction. Thus, it is not unreasonable to expect that E_b may be larger than E_a. The total repulsive energy in $1,1'-di-ax-2,2'-di-eq$ isomer is $2E_a$, in $2,2',4,4'-tetra-eq$ isomer is $2E_b$, and the mixed isomer $1-ax-2,2',4-tri-eq$ is $E_a + E_b$. With the $E_a < E_b$ condition, one expects that $1,1'-di ax-2,2'-dieq$ isomer is the most stable isomer as observed in the product yield. However, the mixed $1-ax-2,2',4'-tri-eq$ isomer was not isolated despite of more favorable steric repulsion energy than the tetra-equatorial isomer. The explanation may rest on the fact that the phosphite ligand at 2 position in the mixed isomer is subjected to strong steric repulsion from the other three phosphite ligands. This posphite ligand is in a particularly unfavora-

bly congested position, it is likely to dissociate or rearrange.

Hexakis-triphenylphosphite substituted complex, $1,1'$-di-*ax*-$2,2',4,4'$-tetra-*eq*-$Re_2(CO)_4[P(OPh)_3]_6$, is the highest substituted dirhenium compound obtained in this work. It is, conceivably, the least sterically congested isomer of all hexakis-substituted isomers. And it is also the highest phosphorus ligand substituted compound obtained through thermal or photochemical carbonyl substitution of $Re_2(CO)_{10}$ so far. Seven and higher triphenyl phosphite substituted dirhenium carbonyl compounds will be difficult to prepare based on steric consideration. These highly substituted dirhenium compounds are also difficult to form kinetically, if a radical mechanism is the major reaction pathway. It has been established that the substitution reactivity of a series of Mn^0 radicals follows the pattern $\cdot Mn(CO)_5 > \cdot Mn(CO)_4 L > \cdot Mn(Co)_3 L_2$ [34]. It is likely that the same reactivity pattern also exists in the rhenium radicals. Thus, the highly substituted rhenium radicals and the radical combined product: $Re_2(CO)_{10-n}[P(OPh)_3]_n$ ($n \geq 7$), would be difficult to form.

From the results of rhenium isotope crossover experiment [35], one would expect that the radical mechanism should be a major reaction pathway in the photochemical reaction between $Re_2(CO)_{10}$ and $P(OPh)_3$. However, besides the $\cdot Re(CO)_5$ radical, the CO dissociated species $Re_2(CO)_9$ [36] could be detected in photolyzing the $Re_2(CO)_{10}$ solution. It has been shown that $Re_2(CO)_9$ is not a major intermediate in the photochemical ligand substitution reaction. Because there is no data available on the photochemical properties of $Re_2(CO)_{10-n}L_n$, we are not certain whether the CO dissociated intermediate $Re_2(CO)_{9-n}L_n$ is a viable intermediate in forming the highly substituted dirhenium complex photochemically.

In the above discussion, the steric repulsion between the phosphites is invoked to account for the observed reaction product pattern. A careful examination of the disubstituted dirhenium compounds, in addition to the triply substituted dirhenium compounds (see above), indicates that the electronic effect also controls the stereochemistry. The dirhenium compounds, $Re_2(CO)_8 L_2$, isolated in the photochemical or thermal reactions are $1,2$-$Re_2(CO)_8(NRH_2)_2$ (R = Me, Et), $2,2'$-di-*eq*-$Re_2(CO)_8(Py)_2$, $2,2'$-di-*eq*-$Re_2(CO)_8(CH_3CN)_2$ [33], $2,2'$-di-*eq*-$Re_2(CO)_8(PMe_2Ph)_2$ [32], $2,2'$-di-*eq*-$Re_2(CO)_8(PMe_2Ph_2)_2$ [31], $1,1'$-di-*ax*-$Re_2(CO)_8(PPh_3)_2$ [5,6] and $1,1'$-di-*ax*-$Re_2(CO)_8[P(OPh)_3]_2$ [27,28]. The donor strength [37] of the ligand L is decreasing from NRH_2 (R = Me, or Et), to the $P(OPh)_3$, the geometry changes from $1,2$-disubstitution, to $2,2'$-di-*eq*, and finally to $1,1'$-di-*ax*. Thus, when different ligands are used in the substitution reactions, the influence of electronic effect on the stereochemistry can not be neglected.
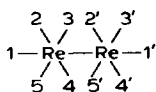
Acknowledgement

References

1 D.R. Kidd and T.L. Brown, J. Am. Chem. Soc., 100 (1978) 4095.

2 S.B. McCullen and T.L. Brown, J. Am. Chem. Soc., 104 (1982) 7496.

3 Q.-Z. Shi, T.G. Richmond, W.C. Trogler and F.J. Basolo, J. Am. Chem. Soc., 104 (1982) 4032.

4 M.S. Wrighton and D.S. Ginley, J. Am. Chem. Soc., 97 (1975) 4246.

5 D.J. Cox and R. Davis, Inorg. Nucl. Chem. Lett., 13 (1975) 301.

6 D.J. Cox and R.J. Davis, J. Organomet. Chem., 186 (1980) 339.

7 R.W. Wegman, R.J. Olsen, D.R. Gard, L.R. Faulkner and T.L. Brown, J. Am. Chem. Soc., 103 (1981) 6089.

8 W.K. Meckstroth, R.T. Wlaters, W.R. Waltz, A. Wojcicki and L.M. Dorfman, J. Am. Chem. Soc., 104 (1982) 1842.

9 B.H. Byer and T.L. Brown, J. Am. Chem. Soc., 97 (1975) 3260.

10 R. Davis, I.F. Groves and C.C. Roland, J. Organomet. Chem., 239 (1982) C9.

11 S.D. Ittel, P.J. Krusci and P. Meakin, J. Am. Chem. Soc., 100 (1978) 3264.

12 R.L. Harlow, R.J. McKinney and S.D. Ittel, J. Am. Chem. Soc., 101 (1979) 7496.

13 E.L. Muetterties, J.R. Bleeke, Z.-Y. Yang, and V.W. Day, J. Am. Chem. Soc., 104 (1982) 2940.

14 D.R. Kidd, C.P. Cheng and T.L. Brown, J. Am. Chem. Soc., 100 (1978) 4103.

15 C.P. Cheng, A.H. Cheng and P.J. Shyong, Proc. Nat. Sci. Coun. B., (1982) 298.

16 J.A. Howard, J.R. Morton and K.F. Preston, Chem. Phys. Lett., 83 (1981) 226.

17 R.L. Harlow, P.J. Krusic, R.J. McKinney and S.S. Wreford, Organometallics, 1 (1982) 1506.

18 S.W. Lee, L.T. Wang and C.P. Cheng, J. Organomet. Chem., 248 (1983) 189.

19 H.J. Svec and G.A. Junk, J. Am. Chem. Soc., 89 (1967) 2936.

20 G.A. Junk and H.J. Svec, J. Chem. Soc. A, (1970) 2102.

21 T. Foster, K.S. Cheng and K.S. Wan, J. Organomet. Chem., 184 (1980) 113.

22 W.L. William, O. Heckelberg, L.M. Dorfman and A. Wojcicki, J. Am. Chem. Soc., 100 (1978) 7259.

23 H.W. Walker, G.B. Ratinger, R.L. Belford and T.L. Brown, Organometallics, 2 (1983) 776.

24 C.A. Tolman, Chem. Rev., 77 (1977) 313.

25 The numbering system is shown below:

1,1′ are the axial positions and 2, 2′3, 3′, 4, 4′5, 5′ are the equatorial positions. The rotational isomers are ignored throughout this work.

26 A.G. Osborne and M.H.B. Stiddard, J. Organomet. Chem., 3 (1965) 340.

27 D.J. Cox and R. Davis, Inorg. Nucl. Chem. Lett., 13 (1977) 669.

28 D.J. Cox and R. Davis, J. Organomet. Chem., 186 (1980) 347.

29 L.F. Dahl, E. Ishishi and R.E. Rundle, J. Chem. Phys., 26 (1957) 1750.

30 M.R. Churchill, K.N. Amoh and H.J. Wasserman, Inorg. Chem., 20 (1981) 1609.

31 J.T. Molewyn-Hughes, A.W.B. Garner and N. Gordon, J. Organomet. Chem., 26 (1971) 373.

32 E. Singleton, J.T. Molewyn-Hughes and A.W.B. Garner, J. Organomet. Chem., 21 (1970) 449.

33 D.R. Gard and T.L. Brown, Organometallics, 1 (1982) 1143.

34 S.B. McCullen, H.W. Malker and T.L. Brown, J. Am. Chem. Soc., 104 (1982) 4007.

35 A.M. Stolzenberg and E.L. Muetterties, J. Am. Chem. Soc., 105 (1983) 822.

36 L.J. Rothberg, N.J. Cooper, K.S. Peters, and V. Vaida, J. Am. Chem. Soc., 104 (1982) 3536.

37 V. Gutamn, Coordination Chemistry in Non-Aqueous Solutions, Springer Verlag, New York, 1968.