Journal of Organometallic Chemistry, 248 (1983) 189–197
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHOTOCHEMICAL REACTION OF DIRHENIUM DECACARBONYL WITH TRIPHENYLPHOSPHINE

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(Received October 15th, 1982; in revised form December 27th, 1982)

Summary

The CO substitution reaction of $Re_2(CO)_{10}$ by triphenylphosphine was investigated photochemically under vacuum. In contrast to the previous studies, three sterically crowded, triply substituted dirhenium complexes, i.e. 1-*axial*-2′,4′-*diequatorial*-$Re_2(CO)_7(PPh_3)_3$, 1-*axial*-2,2′-*diequatorial*-$Re_2(CO)_7(PPh_3)_3$ and 2,2′4′-*triequatorial*-$Re_2(CO)_7(PPh_3)_3$, were isolated and characterized. A fourth compound, which was tentatively assigned as $Re_2(CO)_6(PPh_3)_4$, was also isolated. Contrary to the Mn system, the $[Re(CO)_n(PPh_3)_{5-n}]^{\cdot}$ radical, which is believed to be the intermediate of the photochemical substitution reaction, could not be detected by EPR spectroscopy. The subtle differences in substitution chemistry between rhenium carbonyl and manganese carbonyl complexes are the manifestation of the delicate balance of metal–metal bond strength and the steric repulsion introduced by the bulky phosphorus-containing ligands.

Introduction

The chemical properties of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ would be expected to be similar, especially as far as ligand substitution is concerned. Many experimental results support this proposition. For example, consider the thoroughly studied substitution reaction of CO by triphenylphosphine:

$$M_2(CO)_{10} + n\,PPh_3 \xrightarrow{\Delta} M_2(CO)_9PPh_3,\ M_2(CO)_8(PPh_3)_2,\ \text{etc}$$

$M = Mn, Re$

The well characterized products are monosubstituted complexes: *axial*-$Mn_2(CO)_9(PPh_3)$ [1–5], *axial*-$Re_2(CO)_9(PPh_3)$ [1,5–8], and disubstituted complexes: *diaxial*-$Mn_2(CO)_8(PPh_3)_2$ [2,9,10], *diaxial*-$Re_2(CO)_8(PPh_3)_2$ [6,7,8]. In these early studies, there were other less well characterized and sometimes controversial products being reported. The mechanism for the thermal reaction generating the mono- and di-substituted products has been established as being a dissociative

0022-328X/83/$03.00

mechanism [2–5,9,11,12] for both the Mn and Re compounds. The photolysis of $M_2(CO)_{10}$ in the presence of carbon tetrachloride generates $M(CO)_5Cl$ for both Mn [13] and Re [13,14] carbonyl complexes. The photochemical reactions of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in solution have been found to go through zerovalent, metal-centered radical intermediates [15,16,17]. These zerovalent radicals can be spin trapped by nitrosodurene [18,19] for both metals. The spin-trapped adducts, thoroughly studied by EPR spectroscopy, exhibit similar behavior. Thus, there is a strong resemblance between the chemical properties of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.

However, in the course of studying 17-electron metal-centered organometallic radicals, which may be important intermediates in catalytic [20–23] as well as organometallic reactions [15,24–27], we found that there are subtle differences between the properties of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. For example, it was shown that the $[Mn(CO)_3L_2]^{\cdot}$ [15,28] radical, where L is various phosphines and phosphites, can be produced from the photochemical reaction of $Mn_2(CO)_{10}$ and L. Under vacuum, the Mn^0 radicals are stable in an inert solvent for several days. On the contrary, under identical reaction conditions, the Re^0 radicals are not detected. Instead, the photochemical reaction yielded sterically crowded dirhenium complexes. The different behavior of the Mn^0 and Re^0 radicals was investigated in this work.

Experimental

Materials

Dirhenium decacarbonyl was used as obtained from Strem Chemicals. Triphenylphosphine was recrystallized from absolute ethanol before use. Solvents used were purified according to standard methods. Triethylphosphine, triisobutylphosphine and tricyclohexylphosphine were used as obtained from Strem Chemicals or Aldrich Chemicals.

Spectroscopic measurements

IR spectra were recorded on a Perkin-Elmer model 580 IR spectrometer. ^1H and ^{31}P NMR spectra were obtained on a JEOL JNM-FX-100 spectrometer with ^1H frequency at 99.6 MHz and ^{31}P frequency at 40.3 MHz. The standard for ^{31}P is 85% H_3PO_4 and a negative chemical shift indicates down-field shift as opposed to the convention in ^1H and ^{13}C NMR spectroscopy. Mass spectra were recorded on a JEOL JMS-D-100 spectrometer with a beam energy of 12 eV. The mass spectrometer was optimized to detect the mass range below 900, thus the parent peak of most compounds studied in this work was not detectable.

Photochemical reaction of $Re_2(CO)_{10}$ and triphenylphosphine

The heptane solution, which contained 0.4 m*M* $Re_2(CO)_{10}$ and 2.0 m*M* PPh_3, was subjected to photolysis, under vacuum, using a 450 W medium pressure mercury lamp. The carbon monoxide gas generated from phosphine substitution was pumped away periodically (every 30 min irradiation). There was precipitate formation during photolysis. The reaction was stopped when no further carbon monoxide evolution could be detected. The temperature of the reaction was kept under 60°C. After evaporating off the heptane solvent, the yellowish residue was redissolved in hexane/benzene (1/1). Separation was achieved by using preparative TLC (Merck Kieselgel 60 pF 254). Besides the well characterized *diaxial*-$Re_2(CO)_8(PPh_3)_2$ (40%

yield), four new compounds were isolated. Their spectroscopic data and physical properties are listed below.

Compound I, $Re_2(CO)_7(PPh_3)_3$. Yellow crystalline solid. Yield: 35%. Decomposition temperature: 160°C. ν(C≡O) in $CHCl_3$: 2050w, 2022w, 1959s, 1920s, 1897s cm^{-1}. ^{31}P NMR (in C_6D_6): -17.0 ppm (singlet), -9.9 ppm (singlet), integrated intensity ratio 1 : 2. Mass spec.: 804, 802, 800, ($I - 2PPh_3 - CO$), 776, 774, 772 ($I - 2PPh_3 - 2CO$), 748, 746, 744 ($I-2PPh_3-3CO$), 720, 718, 716 ($I - 2PPh_3 - 4CO$), 692, 690, 688 ($I - 2PPh_3 - 5CO$), 664, 662, 660 ($I - 2PPh_3 - 6CO$), 636, 634, 632 ($I - 2PPh_3 - 7CO$), 795, 793 ($Re(CO)_3(PPh_3)_2$), 767, 765 ($Re(CO)_2(PPh_3)_2$), 739, 737 ($Re(CO)(PPh_3)_2$), 711, 709 ($Re(PPh_3)_2$), 561, 559 ($Re(CO)_4PPh_3$), 533, 531 ($Re(CO)_3PPh_3$) 505, 503 ($Re(CO)_2PPh_3$), 477, 475 ($Re(CO)PPh_3$), 449, 447 ($Re-PPh_3$). Found: C, 53.9; H, 3.1. Calcd. for $C_{64}H_{45}O_7Re_2$; C, 54.1; H, 3.0%.

Compound II, $Re_2(CO)_7(PPh_3)_3$. White solid. Yield: 15%. Decomposition temperature: 88–90°C. ν(C≡O) (in $CHCl_3$): 2098m, 2082w, 2015w, 2010s, 1990m, 1959s, 1930s cm^{-1}. ^{31}P NMR: -21.5 ppm (singlet), -10.1 ppm (singlet), -1.3 ppm (singlet), integrated intensity ratio 1 : 1 : 1. Mass spec.: peak positions and intensities are exactly the same as for I.

Compound III, $Re_2(CO)_7(PPh_3)_3$. White solid. Yield: 5%. m.p.: 113–115°C. ν(C≡O) (in $CHCl_3$): 2038m, 2007vs, 1957s, 1927(sh), 1917s, 1889m cm^{-1}. ^{31}P NMR: -10.8 ppm (singlet), -4.8 (singlet), integrated intensity ratio 2 : 1. Mass spec.: same as for I.

Compound IV, $Re_2(CO)_6(PPh_3)_4$. Orange solid. Yield: 0.5%. Decomposition temperature: 135°C. ν(C≡O) (in $CHCl_3$): 1948s cm^{-1}. Mass spec. 804, 802, 800 [$Re_2(CO)_6PPh_3$] 776, 774, 772 [$Re_2(CO)_5(PPh_3$], 748, 746, 744 [$Re_2(CO)_4PPh_3$], 720, 718, 716 [$Re_2(CO)_3PPh_3$], 692, 690, 688 [$Re_2(CO)_2PPh_3$], 664, 662, 660 [$Re_2(CO)PPh_3$], 636, 634, 632 [Re_2PPh_3], 795, 793 [$Re(CO)_3(PPh_3)_2$], 767, 765 [$Re(CO)_2(PPh_3)_2$], 739, 737 [$Re(CO)(PPh_3)_2$], 711, 709 [$Re(PPh_3)_2$]. The $Re(CO)_4(PPh_3)$ fragment was not detected. Soluble in chloroform and benzene, but decomposes slowly.

EPR measurement mol/l

A 5 ml heptane solution of 5×10^{-3} mol/l $Re_2(CO)_{10}$ and 5×10^{-2} mol/l, PR_3 (R = Et, iso-Bu, Ph, cyclohexyl) was irradiated with a 450 W medium pressure mercury lamp under vacuum. The CO generated was pumped away intermittently. The irradiation was stopped after no more carbon monoxide was released from the substitution reaction. The solution was transferred to the quartz side arm, which was connected to the photolysis chamber. EPR measurements were carried out at several different temperatures ranging from -150°C to 80°C. However, no EPR signal was observed. The same preparation procedure was used to prepare samples for proton NMR measurement. No hydride signal was observed in the range of 0 to -20 ppm.

Results and discussion

Five compounds can be isolated as major products in the photochemical substitution reaction (eq. 1). Compounds I–IV have not been isolated before. Their molecular formulae are determined mainly based on mass spectroscopic data. From the presence of mass peaks of species containing a single rhenium atom, it could be deduced that the maximum number of triphenylphosphine ligands coordinated to a

$$\mathrm{Re_2(CO)_{10} + PPh_3 \xrightarrow[\text{heptane}]{h\nu} \underset{\text{(I)}}{Re_2(CO)_7(PPh_3)_3} + \underset{\text{(II)}}{Re_2(CO)_7(PPh_3)_3}} \quad (1)$$

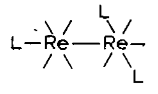
$$\mathrm{+ \underset{\text{(III)}}{Re_2(CO)_7(PPh_3)_3} + \underset{\text{(IV)}}{Re_2(CO)_6(PPh_3)_4} + \underset{\text{(V)}}{Re_2(CO)_8(PPh_3)_2}}$$

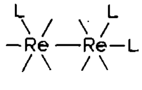
rhenium atom is two and the minimum is one. Furthermore, the presence of mass peaks containing two rhenium atoms established that the compounds are dirhenium complexes. The IR and ^{31}P NMR are consistent with the assignment. It is noteworthy that rhenium has two isotopes, ^{185}Re and ^{187}Re, with natural abundances 37.1% and 62.9%, respectively. Species containing two rhenium atoms show up in the mass spectrum as three peaks M, $M-2$ and $M-4$, with relative intensities 2.8:3.4:1. If a species contains a single Re atom and at least one PPh$_3$, besides the M, $M-2$ peaks, additional peaks at $M-1$ and $M-3$ could be observed. Their intensities are sometimes stronger than the corresponding M and $M-2$ peaks. This phenomenon can be explained on the basis of metallation reaction of the ions in the mass spectrometer. The M^+ ion has the general structure, $[\mathrm{Re(CO)}_n(\mathrm{PPh_3})_m]^+$; it may readily convert to $[\mathrm{Re(CO)}_n(\mathrm{PPh_3})_{m-1}(\mathrm{PPh_2})(\mathrm{Ph-H})]^+$ by losing a hydrogen. The (Ph – H) group then forms a chemical bond with the metal center. The above general remark on mass spectra has been confirmed on the well characterized samples: 1,1′-*diaxial*-Re$_2$(CO)$_8$(PPh$_3$)$_2$ and 1,1′-*diaxial*-Re$_2$(CO)$_8$[P(cyclohexyl)$_3$]$_2$ [29,30].

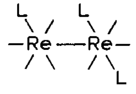
I, II and III are geometrical isomers, which contain both Re(CO)$_4$PPh$_3$ and Re(CO)$_3$(PPh$_3$)$_2$ fragments. Their structures could be elucidated based on ^{31}P NMR spectra. In 1,1′-*diaxial*-Re$_2$(CO)$_8$(PPh$_3$)$_2$, $\delta_\mathrm{P} = -17.9$ ppm, thus the axial phosphine, in the absence of a neighboring phosphine, will have δ_p close to -17.9 ppm. In I, δ_P are -17.0 ppm and -9.9 ppm, and the intensity ratio is 1:2. Hence, there is one phosphine bonded axially in the Re(CO)$_4$(PPh$_3$) fragment. To account for the mass and NMR spectra, the two PPh$_3$ must be bonded to the other Re atom at equatorial positions, most likely 2,4 mutual *trans* positions. The possibility of a mutual *cis* arrangement can be dismissed because of the strong steric repulsion between the bulky PPh$_3$ ligands. Thus I can be assigned as 2,4-*diequatorial*-1′-*axial* Re$_2$(CO)$_7$(PPh$_3$)$_3$. In II, δ_P are -21.5, -10.1 and -1.3 ppm with intensity ratio of 1:1:1. Due to the lack of signal at -17.9 ppm, the PPh$_3$ in the Re(CO)$_4$PPh$_3$ fragment must be bonded to the Re atom at the equatorial position. To account for the remaining two NMR signals, the two PPh$_3$ ligands must be bonded to the Re atom at non-equivalent positions. The only possibility is that one is at an equatorial position, while the other is axial. The -10.1 ppm signal, which is quite close to the δ_P for equatorial PPh$_3$ in I, is assigned to the equatorial PPh$_3$, while the -21.5 ppm signal is attributed to the axial PPh$_3$. This leaves the signal at $\delta_\mathrm{P} = -1.3$ ppm to be assigned to the equatorial PPh$_3$ in the Re(CO)$_4$(PPh$_3$) fragment. Thus compound II is established as 1-*axial*-2,2′-*diequatorial*-Re$_2$(CO)$_7$(PPh$_3$)$_3$. In compound III, the NMR signals are at -10.8 ppm and -4.8 ppm with an intensity ratio of 2:1. The two PPh$_3$ at -10.8 ppm must occupy the *trans*-equatorial positions at the disubstituted Re, in analogy with I. The PPh$_3$ in Re(CO)$_4$PPh$_3$ must occupy the equatorial position, because its chemical shift is at -4.8 ppm, far from the value of -17.9 ppm. This is consistent with the assignment in II, where -1.3 ppm is attributed to the equatorial phosphine of $Re(CO)_4(PPh_3)$. Hence, compound III is assigned as 2,2′,4-*triequatorial*-$Re_2(CO)_7(PPh_3)_2$. Compound IV is a dirhenium complex because its mass spectrum exhibits the mass peaks of $Re_2(CO)_6(PPh_3)$. The only monorhenium mass peaks observed are due to $Re(CO)_3(PPh_3)_2$ and its decarbonylated homolog. By comparison with the mass spectra of *diaxial*-$Re_2(CO)_8(PPh_3)_2$ and compounds I to III, compound IV is tentatively assigned to be $Re_2(CO)_6(PPh_3)_4$. The possibility of IV being a cluster compound cannot be ruled out completely.

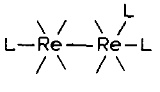
Despite extensive studies on the substitution reaction of $Re_2(CO)_{10}$ by PPh_3, I, II, III and IV have never been isolated. This may be due to the different reaction conditions. In the early studies, the reactions were carried out thermally in refluxing toluene or xylene, and the products always contained $Re_2(CO)_9(PPh_3)$ and $Re_2(CO)_8(PPh_3)_2$. Recently, the substitution reaction has been reinvestigated [31,32] in the hope of producing metal-centered radicals. Besides $Re_2(CO)_8(PPh_3)_2$, hydrides, i.e. $HRe(CO)_4(PPh_3)$ and $HRe(CO)_3(PPh_3)_2$, polynuclear cluster compounds and metallated compounds were obtained. The different reaction results are mainly due to the reaction temperature. I has a decomposition temperature of 160°C, while II decomposes at only 88–90°C. Very likely, III and IV also have low decomposition temperatures. They surely cannot be isolated from the thermal reaction. Thus, instead of I, II, III or IV, hydrides were isolated from the thermal reaction. Formation of the hydrides may be due to the hydrogen abstraction reaction, which may occur at sufficient rate only at high temperature [33]. This also explains why a hydride was not isolated in the photochemical reactions, where the reaction temperature was kept below 60°C.

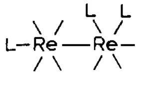
It is noteworthy that there are 6 geometrical isomers of $Re_2(CO)_7(PPh_3)_3$, if each Re has at least one PPh_3 bonded to it. They are depicted below:

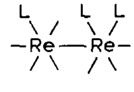

(A)


(B)


(C)


(D)


(E)


(F)

L is PPh_3, and CO ligands are omitted for clarity. E and F are expected to be unstable because of the strong repulsion between the *cis*-diequatorial PPh_3. A, B and C, were isolated in this work. It is surprising to find that D, which one would expect to be stable, has totally eluded our detection. The main product of disubstituted $Re_2(CO)_8(PPh_3)_2$ is diaxial from the substitution reaction, whether thermal or photochemical, of $Re_2(CO)_{10}$ with PPh_3. It is natural to expect that the third substituted PPh_3 would replace one of the equatorial CO in the *diaxial*-$Re_2(CO)_8(PPh_3)_2$, and D would be a major product. However, there are a few examples in the literature which indicate that D is probably less stable. Photochemical reaction of $Re_2(CO)_{10}$ with $PMePh_2$ [34] produced two triply substituted compounds: 2,2′,4-*triequatorial*-$Re_2(CO)_7(PMePh_2)_3$, which corresponds to C, and 1-*axial*-2′,4′-*diequatorial*-$Re_2(CO)_7(PMePh_2)_3$ which corresponds to A. The photochemical reactions of $Re_2(CO)_{10}$ with XMe_2Ph (X = P, As) [35] resulted in only the triply substituted 2,2′,4-*triequatorial*-$Re_2(CO)_7(XMe_2Ph)_3$, which corresponds to C. There is only one report which had tentatively assigned $Re_2(CO)_7(P(OPh)_3)_3$ [36] a D-type of structure. Nevertheless, the evidence is tenuous. Though the cone angles of $PMePh_2$ and PMe_2Ph are smaller than that of PPh_3 [37] and the steric repulsions of the phosphines in $Re_2(CO)_7(PR_3)_3$ may be different, the results certainly indicate that isomer D is not especially stable. The relative stabilities and reactivities of the triply substituted $Re_2(CO)_7(PR_3)_3$ isomers are currently under study in our group.

There is much evidence to indicate that the photochemical reactions of $Re_2(CO)_{10}$ involve radical intermediates. The absorption of a photon at 310 nm [38–40] is attributable to the σ–$\sigma^\star$ transition of the Re–Re bond, and results in efficient homolytic fission of $Re_2(CO)_{10}$. The radicals can rapidly recombine to form dimers:

$$Re_2(CO)_{10} \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} 2[Re(CO)_5]^{\cdot} \xrightarrow{L} [Re(CO)_{5-n}L_n]^{\cdot}$$

The recombination rate has been measured by flash photolysis [17] and radiolysis [14] to be as high as $3.7 \times 10^9\ M^{-1}\ s^{-1}$ and $2.7 \times 10^9\ M^{-1}\ s^{-1}$ respectively. The $[Re(CO)_5]^{\cdot}$ radical and its substituted derivatives can undergo substitution reactions, in analogy with the $[Mn(CO)_5]^{\cdot}$ radical [15,41]. Subsequent recombination results in substituted dirhenium complexes. Despite the short life time of the $[Re(CO)_5]^{\cdot}$ radical, it can be trapped by nitrosodurene [16,17] and quinones [42]. The results of photolysis [13,14] of $Re_2(CO)_{10}$ in the presence of CCl_4 also indicate that $[Re(CO)_5]^{\cdot}$ is an intermediate. From the photochemical substitution reaction [43] and photochemical reaction with H_2 [44], it has been concluded that $[Re(CO)_5]^{\cdot}$ is the reaction intermediate. Thus, the intermediacy of the Re^0 radical is beyond doubt.

However, the physical and chemical properties of the $[Re(CO)_5]^{\cdot}$ radical and its derivative are poorly characterized [45]. The reason is that the lifetimes of the radicals are short because of the rapid radical combination reaction. To lengthen the lifetime of the $[Re(CO)_5]^{\cdot}$ radical, the commonly used method of steric stabilization [46] of organic radicals is a natural choice. The strategy is to substitute bulky ligands into the coordination sphere of the Re^0 radical. The steric repulsion between the bulky ligands may be strong enough to slow down the radical combination rate. Then, the radicals can be studied by various spectroscopic tools, especially EPR. Despite extensive efforts, employing $P(cyclohexyl)_3$, $P(iso\text{-}Bu)_3$, PEt_3 and $P(OPh)_3$ as bulky ligands, the Re^0 radical was not detected by EPR. This is in contrast to the early literature reports which claimed to have observed or isolated the Re radical [7,8,34,35,47].

The steric stabilization technique has been used successfully to generate the square pyramidal $[Mn(CO)_3L_2]^{\cdot}$ radicals [16] (L is $P(n\text{-}Bu)_3$ or $P(OEt)_3$). A thorough study of this type of Mn^0 radical by EPR spectroscopy [28], where L ranges from the very bulky $P(cyclohexyl)_3$ to the less bulky PMe_3 and $P(OEt)_3$, reveals that the $[Mn(CO)_3L_2]^{\cdot}$ radicals are in equilibrium with their dimers, $Mn_2(CO)_6L_4$, and that the rate constants of radical combination depend largely on the sizes of the bulky ligand, i.e., the cone angles [44]. When L is a sterically very demanding ligand, e.g. $P(cyclohexyl)_3$, the rate of combination is negligible and the dimer is unstable. When the ligand is sterically less demanding, such as PEt_3, $P(iso\text{-}Bu)_3$ and $P(O\text{-}iso\text{-}Pr)_3$, the dimer is still unstable, but the rate constant of radical combination is high, as shown clearly by temperature-dependent EPR spectroscopy. When L is small, such as PMe_3, $P(OEt)_3$ and $P(O\text{-}n\text{-}Bu)_3$, the radical combination rate is high and the dimer, $Mn_2(CO)_6L_4$, is also stable at low temperatures with a Mn–Mn bond energy approximately 13 kcal/mol.

The question of why $[Mn(CO)_3L_2]^{\cdot}$ can be observed while the corresponding rhenium radicals cannot, may be answered from both thermodynamics and from kinetics. In the metal carbonyl compounds, the Mn–Mn bond energy is 23 kcal/mol, but the Re–Re bond energy is 50 kcal/mol [49]. And the metal–metal bond lengths [50,51,52] differ by only 4% in the metal carbonyls: 2.9038 Å for Mn–Mn and 3.0413 Å for Re–Re. Hence, the steric repulsion induced by the bulky substituents will be roughly the same in the corresponding Mn and Re compounds. When L is PMe_3, the Mn–Me bond energy is reduced from 23 kcal/mol in $Mn_2(CO)_{10}$ to 13 kcal/mol in $Mn_2(CO)_6L_4$, a difference of 9 kcal/mol. When L is $P(cyclohexyl)_3$, the $Mn_2(CO)_6L_4$ is not stable, and the repulsion energy is higher than the Mn–Mn bond energy of 23 kcal/mol, probably somewhere around 25–30 kcal/mol. Thermodynamically, the repulsion energy induced by the bulky ligands L in $Re_2(CO)_6L_4$ is not strong enough to cause rupture of the Re–Re bond, assuming the stereochemistries of the Mn and Re carbonyl derivatives are the same. This is also the reason for the isolation of the sterically crowded $Re_2(CO)_7(PPh_3)_3$ isomers and $Re_2(CO)_6(PPh_3)_4$. Only sterically less demanding ligands can be incorporated into $Mn_2(CO)_7L_3$ ($L = PF_3$ [53], or $P(OEt)_3$ [15]). Coincidently, the structure [54] of the triply substituted $P(OEt)_3$ derivative cannot be 1,1′-*diaxial*-2-*equatorial*-$Mn_2(CO)_7(P(OEt)_3)_3$ (isomer form D), as observed in the dirhenium complexes. The stable $Mn_2(CO)_6L_4$-type of compounds are unknown, the steric repulsion is probably too strong to be stable at room temperature. Kinetically, the combination rate of $[Re(CO)_5]^{\cdot}$ to form dimer is higher than that of $[Mn(CO)_5]^{\cdot}$ [42,55] by a factor of about 4, deduced from both flash photolysis and radiolysis studies. It is reasonable to expect that the combination rate of $[Re(CO)_{5-n}L_n]^{\cdot}$ will be also faster than that of $[Mn(CO)_{5-n}L_n]^{\cdot}$. Thus, even if some Re^0 radicals are generated in photoreactions, they will rapidly combine to form dimers, and no EPR signals could be detected.

Conclusion

Some of the products of photochemical reactions of $Re_2(CO)_{10}$ with triphenylphosphine are highly substituted $Re_2(CO)_7(PPh_3)_3$ isomers and $Re_2(CO)_6(PPh_3)_4$. These sterically crowded compounds could not be isolated in the corresponding $Mn_2(CO)_{10}$ system. The differences are mainly due to the metal–metal bond energies. The delicate balance between steric repulsion and bond energy dictates the outcome of the photochemical reaction. For example, if phosphites are used as ligands, $Mn_2(CO)_7(P(OEt)_3)_3$ is the thermally stable product with highest degree of substitution. The $Mn_2(CO)_6(P(OEt)_3)_4$ is in equilibrium with the $[Mn(CO)_3(P(OEt)_3)_2]^{\cdot}$ radical, which is quite reactive. However, in the Re system, using the sterically more demanding ligand $P(OPh)_3$, $Re_2(CO)_7(P(OPh_3))_3$ can be isolated. Preliminary results in our laboratory indicate that $Re_2(CO)_6P(OPh_3))_4$ and $Re_2(CO)_4(P(OPh_3))_6$ can be isolated and they are stable in air. More dramatically, $Re_2(P(OMe)_3)_{10}$, with the ultimate degree of substitution, has been synthesized, via Re^{II} reduction in the presence of $P(OMe)_3$ with CO excluded [56]. It is indicative that the Re^0 radicals are difficult to stabilize with bulky phosphine or phosphite ligands in contrast to the Mn^0 radicals. It is simply because the steric repulsion is not strong enough to cause rupture of the Re–Re bond.

Acknowledgement

We are grateful for financial support of this research by the National Research Council of the Republic of China.

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    2   3   2'  3'
     \ /     \ /
1 —— Re ———— Re —— 1'
     / \     / \
    4   5   4'  5'
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