

FREE RADICAL INTERMEDIATES IN THE REACTION BETWEEN DECACARBONYLDIRHENIUM AND TRIPHENYLPHOSPHANE

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Summary

The reaction between $\text{Re}_2(\text{CO})_{10}$ and PPh_3 in refluxing xylene has been re-examined. The main products are 1,2-diaxial $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ and *mer-trans*- $\text{HRe}(\text{CO})(\text{PPh}_3)_2$. A range of other products have been isolated by chromatographic procedures and their production rationalised. The previously reported isolable paramagnetic products have not been confirmed, but evidence is presented for their formation as unstable intermediates.

It is now recognised that species which fall under the broad definition of transition metal organo-metallic free radicals play an important role in this area of chemistry [1]. Thus, it has been well established that certain oxidative addition reactions proceed by mechanisms involving free radical intermediates [1] and such species have recently been demonstrated in some-hydrogenation reactions [2], substitution reactions of group VII metal carbonyl compounds [3,4] and alkylation reactions of metal carbonylate anions and hydrides [5]. Despite these studies, there still remains a paucity of isolable paramagnetic low valent transition metal organometallic compounds outside the early transition elements. Stable 17-electron transition metal species have been reported by a number of workers, however, some of these have subsequently been shown to be diamagnetic complexes [6,7]. While radicals such as $\text{Mn}(\text{CO})_3\text{L}_2$ ($\text{L} = \text{PBU}_3$, $\text{P}(\text{OEt})_3$) have recently been shown to have considerable stability in solution [8], the only 17-electron species for which a solid state crystal structure has been determined is $\text{Mn}(\text{CO})(\eta^4\text{-C}_4\text{H}_6)_2$ [9].

Our interest in such species as reactive intermediates has led us to reinvestigate the preparation of $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2]$ [10,11]. A preliminary account of this study has appeared elsewhere [12].

Experimental

All reactions were performed under dry deoxygenated nitrogen. Solvents were purified and dried by standard techniques and were degassed by repeated freeze-pump-thaw cycles immediately prior to use. Preparative TLC separations were performed on silica gel (Merck type PF₂₅₄), 0.3 mm thickness on glass plates (20 cm × 20 cm). The following solvent systems were used for elution: system I, 3 parts of 80–100 petroleum ether to 1 part of ethyl acetate; system II, 9.5 parts of 80–100 petroleum ether to 0.5 parts of ethyl acetate. The plates were washed with methanol prior to use.

Infrared spectra were recorded on Perkin Elmer 157 and 457 spectrometers as solutions in chloroform unless otherwise stated. PMR spectra were recorded on a Perkin Elmer R32 spectrometer operating at 90 MHz and 35°C. When necessary, the FT attachment was employed. Mass spectra were recorded on an AEI MS9 operating at 70 eV and 100–150°C. Microanalyses were performed by Butterworths Ltd., Teddington, Middlesex.

The reaction of Re₂(CO)₁₀ with PPh₃

Re₂(CO)₁₀ (0.33 g; 0.57 mmol) and PPh₃ (1.25 g; 4.77 mmol) were dissolved in xylene (15 ml) and heated under reflux for 48 h. After this time the solvent was removed under vacuo yielding an orange residue. This was dissolved in boiling benzene (10 ml) and cooled to 60°C. Hexane was then added, to just induce crystallisation, and the mixture was cooled in ice. The cream powder was collected and recrystallised from benzene–hexane to give white flakes, (0.24 g; 45.3% based on *mer-trans*-HRe(CO)₃(PPh₃)₂; m.p. 210°C(d); $\nu(\text{C}\equiv\text{O})$: (benzene and chloroform) 1935s cm⁻¹; PMR (δ , ppm): -5.06 (t, 18Hz, 1 proton), 7.39 (m, 30 protons); mass spec. (m/e): 794 (M^+), 766 ($M - \text{CO}$), 738 ($M - 2 \text{CO}$), 710 ($M - 3 \text{CO}$); anal. found: C, 59.09; H, 3.86; C₃₉H₃₁O₃P₂Re calcd.: C, 58.93; H, 3.80%).

The orange filtrate was concentrated to an oily residue. This was extracted with benzene (2 × 10 ml) and the solid residue, from evaporation of the hexane, crystallised from ether to give colourless crystals (29 mg; 5.1% based on Re(CO)₃(PPh₃)(C₆H₄PPh₂); m.p. 203°C; $\nu(\text{C}\equiv\text{O})$: 2018s, 1993m, 1900m cm⁻¹; mass spec. (m/e) 792 (M^+), 764 ($M - \text{CO}$), 736 ($M - 2 \text{CO}$), 708 ($M - 3 \text{CO}$)).

If the above reaction was stopped after 16 h, the solvent removed, the residue dissolved in hot benzene and precipitation induced by addition of hexane, a white powder was obtained. This was recrystallised from benzene–hexane to yield white plates (0.318 g; 20% based on Re₂(CO)₈(PPh₃)₂; m.p. 239–241°C; $\nu(\text{C}\equiv\text{O})$: 2010w, 1960vs cm⁻¹; PMR (δ , ppm): 7.40 (m); anal. found: C, 47.75; H, 2.70; C₄₄H₃₀O₈P₂Re calcd.: C, 47.20; H, 2.68%).

On occasions, precipitation from both 16 h and 48 h reactions led to a mixture of HRe(CO)₃(PPh₃)₂ and Re₂(CO)₈(PPh₃)₂ depending upon the composition of the benzene–hexane solvent system and the rate of cooling.

Other products could be isolated from the above reactions of Re₂(CO)₁₀ and PPh₃, by the following procedure. The solvent was removed in vacuo and the residue taken up in a minimal volume of chloroform. This solution was applied to 36 preparative TLC plates and eluted with mixture I. The separated bands were removed from the silica with chloroform which, in turn, was removed

TABLE 1
THE SEPARATED PRODUCTS FROM THE REACTION OF $\text{Re}_2(\text{CO})_{10}$ AND PPh_3

Band	Physical Data	Identity
1a	mass spec. inconclusive (trace quantity)	
1b	mass. spec. highest mass ion, m/e : 1016 ($\text{H}_2\text{Re}_3(\text{CO})_7\text{PPh}_3^+$)	polynuclear product
2a	m/e : 884, 884 - 28 <i>n</i> (<i>n</i> = 1-9) $\nu(\text{C}\equiv\text{O})$: 1963s, 1912m, 1897m, 1880(sh) cm^{-1}	eq. $\text{Re}_2(\text{CO})_9\text{PPh}_3$
2b	$\nu(\text{C}\equiv\text{O})$: 2010w, 1960vs cm^{-1}	$\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$
2c	m/e : 792, 764, 736, 708; $\nu(\text{C}\equiv\text{O})$: 2018s, 1933m, 1900m	$\text{Re}(\text{CO})_3(\text{PPh}_3)(\text{C}_6\text{H}_4\text{PPh}_2)$
2d	m/e 794: 766, 738, 710 $\nu(\text{C}\equiv\text{O})$: 2009s, 1960s, 1900s	<i>fac</i> - $\text{HRe}(\text{CO})_3(\text{PPh}_3)_2$
3	m/e : 794, 766, 738, 710; $\nu(\text{C}\equiv\text{O})$: 1935s cm^{-1}	<i>mer-trans</i> - $\text{HRe}(\text{CO})_3(\text{PPh}_3)_2$
4	m/e : 572, 544, 516, 488; $\nu(\text{C}\equiv\text{O})$: 1966s, 1978vs, 1993s 2081m cm^{-1} (comparison with authentic sample)	<i>cis</i> - $\text{HRe}(\text{CO})_4\text{PPh}_3$
5	m/e : 262, IR and TLC comparison with authentic sample	PPh_3
6	m/e : 650, IR and TLC comparison with authentic sample	$\text{Re}_2(\text{CO})_{10}$

under vacuo. Six bands were resolved by this procedure. These were examined by infrared and mass spectroscopy, results of which are shown in Table 1.

Separation of the components of bands 1 and 2 were effected by re-elution using mixture II, the identification of which is also shown in Table 1.

$\text{Re}_2(\text{CO})_{10}$ (0.325 g, 0.5 mmol) and PPh_3 (0.131 g, 0.5 mmol) were dissolved in xylene (15 ml) and heated under reflux for 19 h. After this time the solvent was removed in vacuo and the residue applied to preparative TLC plates. Elution with mixture I yielded one major component that was isolated as above as off-white crystals (0.15 g; 33.7% based on *ax*- $\text{Re}_2(\text{CO})_9\text{PPh}_3$; $\nu(\text{C}\equiv\text{O})$: 2100s, 2080w, 2030w, 2000vs, 1940s cm^{-1} ; mass spec. (m/e): 884 (M^+), 884 - 28 *n* (*n* = 1-9); anal. found: C, 36.67; H, 1.7; $\text{C}_{27}\text{H}_{15}\text{O}_9\text{PRe}_2$ calcd.: C, 36.67; H, 1.7%).

The reaction of mer-trans-HRe(CO)₃(PPh₃)₂ and PPh₃

A mixture of $\text{HRe}(\text{CO})_3(\text{PPh}_3)_2$ (0.3 g, 0.38 mmol) and PPh_3 (0.3 g, 1.1 mmol) was heated in a sealed evacuated tube for 3 h at 230°C, during which time the melt adopted a tan colour. The tube was cooled, opened and contents dissolved in benzene to give an orange solution. This was filtered to remove a little insoluble material and absolute ethanol added. On cooling, a cream powder was precipitated. Recrystallisation from benzene-hexane gave white flakes (55 mg) identified as $\text{HRe}(\text{CO})_3\text{PPh}_3$ from melting point, mixed melting point and infrared and mass spectra.

Preparation of cis-HRe(CO)₄PPh₃ and its reaction with PPh₃

Freshly distilled $\text{HRe}(\text{CO})_5$ was allowed to react with excess PPh_3 in benzene at room temperature for 3 h. This was then concentrated in vacuo to yield a

mixture of *cis*-HRe(CO)₄PPh₃ and PPh₃ which was separated by preparative TLC (mixture I) to give *cis*-HRe(CO)₄PPh₃ as white crystals ($\nu(\text{C}\equiv\text{O})$: 2081m, 1993s, 1978s, 1966s cm⁻¹; anal. found: C, 47.88; H, 3.06, C₂₂H₁₆O₄PRe calcd.: C, 47.14; H, 2.85%).

This sample of *cis*-HRe(CO)₄PPh₃ was then allowed to react with PPh₃ in boiling xylene and the reaction followed by infrared spectroscopy. After 24 h the mono-phosphine hydride was completely consumed and the only product was *mer-trans*-HRe(CO)₃(PPh₃).

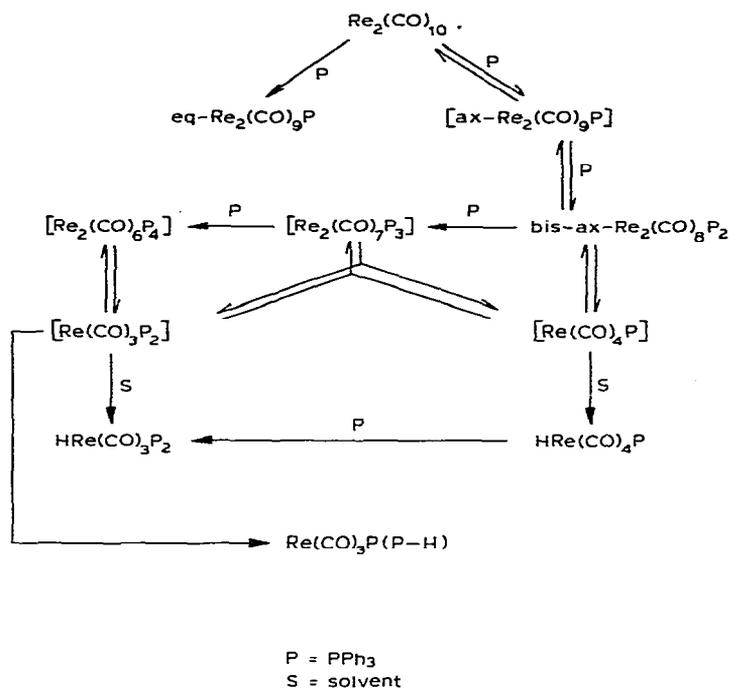
Results and discussion

A number of previous studies of the reaction between Re₂(CO)₁₀ and PPh₃ have been published. Nyman [10] reported that heating the reagents in refluxing xylene yielded [Re(CO)₃(PPh₃)₂]. This was found to be paramagnetic and was assigned a trigonal bipyramidal structure on the basis of a single infrared bands at 1934 cm⁻¹. Freni et al [11] employed similar conditions, but isolated paramagnetic [Re(CO)₃(PPh₃)₂] which was assigned a square pyramidal structure on the basis of dipole moment and infrared measurements. There is one other brief report of this molecule [13]. There has also been a kinetic study of the reaction [14] which led to a detailed scheme accounting for the formation of PPh₃ containing dimeric products. A further kinetic study of the reaction of Re₂(CO)₈(PPh₃)₂ with PPh₃ [15] suggests that the reaction may proceed via a number of mononuclear species, but none of these was isolated.

We have re-examined the preparative scale reaction between Re₂(CO)₁₀ and PPh₃ and have adhered to the conditions previously employed [11]. We have been unable to isolate any paramagnetic products, but have found a wide range of diamagnetic compounds. The major products are 1,2-Re₂(CO)₈(PPh₃)₂ and *mer-trans*-HRe(CO)₃(PPh₃)₂. These may be isolated as pure components or as a mixture depending on the conditions of crystallisation. The other products are listed in Table 1 and were isolated by preparative TLC. These were identified by standard techniques. We suggest that these compounds are formed in the reaction sequence shown in the Scheme. The evidence for this is given below.

It has been found that the reaction can proceed by either one of two possible routes. Both pathways have common steps up to the formation of 1,2-Re₂(CO)₈(PPh₃)₂. This presumably arises via a stepwise substitution of Re₂(CO)₁₀, however, no *ax*-Re₂(CO)₉(PPh₃), previously reported by Poë et al [15], was isolated from this reaction. The form of Re₂(CO)₉PPh₃ isolated shows an infrared spectrum quite different to that of the axial isomer (comparison with an authentic sample) and has been assigned to the equatorially substituted isomer. That the axial isomer is not isolated is presumably a reflection of the relative reactivities of the two forms. The equatorial isomer is expected to be less reactive towards further substitution on the basis of both *cis* labilisation [16] and steric effects. Reactions carried out in daylight yield the full range of products shown in Table 1, however when light is rigorously excluded from the reaction, HRe(CO)₄(PPh₃) is not obtained. On this basis we suggest that homolytic fission of 1,2-Re₂(CO)₈(PPh₃)₂ is a purely photo-induced process and that formation of [Re(CO)₃(PPh₃)₂], the precursor of HRe(CO)₃(PPh₃)₂ and Re(CO)₃(PPh₃)(C₆H₄PPh₂), does not proceed by phosphane substitution into [Re(CO)₄

SCHEME 1



Compounds in square brackets were not isolated

PPh_3]. In order to account for the range of products formed by reactions performed in the dark, we invoke the intermediacy of $\text{Re}_2(\text{CO})_7(\text{PPh}_3)_3$ and $\text{Re}_2(\text{CO})_6(\text{PPh}_3)_4$ (Scheme 1), although we have been unable to isolate either from the reaction mixture. Such sterically crowded molecules might be expected to be rather unstable, however the latter has been reported in the literature [11,17], by two preparative procedures. The first of these involves thermal reaction between $\text{Re}_2(\text{CO})_{10}$ and PPh_3 (1 : 5 ratio) and, indeed, the isolated product shows the same infra-red spectrum as that reported for the expected dimer (1930s in C_6H_6) but PMR and mass spectrometry confirm it to be *mer-trans*- $\text{HRe}(\text{CO})_3(\text{PPh}_3)_2$. The alternative procedure involving a solid state reaction between $\text{Re}_2(\text{CO})_{10}$ and PPh_3 in a sealed tube yielded no products in our hands.

The radical intermediates, $[\text{Re}(\text{CO})_4\text{PPh}_3]$ and $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2]$ undergo reaction with the solvent to yield the hydrides. We were unable to confirm this by deuteration experiments in the case of xylene, however others [18] have shown the source of hydrogen in a similar reactions of $\text{Mn}_2(\text{CO})_{10}$, yielding $\text{HMn}(\text{CO})_3(\text{PPh}_3)_2$, is not the phosphane and the $\{\text{Mn}(\text{CO})_3[\text{P}(\text{O}^i\text{Pr})_3]_2\}$ radical, generated under mild conditions, has been shown to activate the C—H bond in methanol [19]. $\text{Re}_2(\text{CO})_{10}$ also reacts with PPh_3 in wet xylene to yield $\text{HRe}(\text{CO})_3(\text{PPh}_3)_2$ and in this case deuteration has shown water to be the hydrogen source. Thus, although every effort has been made to exclude water from the reaction, this hydrogen source cannot be totally ruled out. Separate experiments have also shown that $\text{HRe}(\text{CO})_4\text{PPh}_3$ reacts with PPh_3 to yield HRe -

$(\text{CO})_3(\text{PPh}_3)_2$ and this route cannot be excluded for reactions performed in daylight. As we have been unable to observe any isomerisation of either *mer-trans*- or *fac*- $\text{HRe}(\text{CO})_3(\text{PPh}_3)_2$ under the reaction conditions, we suggest isolation of both isomers is indicative of fluxional character for their precursor, $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2]$.

The metalated complex $\text{Re}(\text{CO})_3(\text{PPh}_3)(\text{C}_6\text{H}_4\text{PPh}_3)$ is included as arising from $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2]$, but it may arise by dissociation of a dimeric molecule such as $\text{Re}_2(\text{CO})_7(\text{PPh}_3)_3$ with elimination of $\text{HRe}(\text{CO})_4\text{PPh}_3$ in a manner similar to that suggested by Alper [20] for the reaction between $\text{Re}_2(\text{CO})_{10}$ and thiobenzophenones.

Some confirmatory evidence for the early substitution steps in the reaction scheme is provided by the following observations. Reactions of PPh_3 with either *ax*- $\text{Re}_2(\text{CO})_9\text{PPh}_3$ or *1,2*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ yielded the same product distribution as that arising from the decacarbonyl. When a xylene solution of *1,2*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ is maintained at room temperature in daylight, *cis*- $\text{HRe}(\text{CO})_4(\text{PPh}_3)$ is slowly formed. In a boiling xylene solution, with the total exclusion of light and in the absence of added PPh_3 , *1,2*- $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ undergoes total decomposition. Separate experiments in both the presence and absence of PPh_3 at lower temperatures have shown the reaction proceeds in the same manner in the former, however, no $\text{HRe}(\text{CO})_5$ is observed in the latter, although the experiments were conducted below the decomposition point of this compound. This indicates that homolytic fission of the parent carbonyl is not an important process in this reaction and that phosphane substitution precedes radical formation.

Direct evidence for the intermediacy of free radicals comes from the following observations. The rate of reaction is slowed considerably by the admission of oxygen. The free radical trapping agent, galvinoxyl, was decolourised when added to the reaction mixture, the reaction being inhibited. Control reactions performed under similar conditions did not lead to decolourisation and inhibition. The reaction mixture initiated polymerisation of a 1 : 1 mixture of methyl methacrylate and styrene, a reaction known to proceed by a free radical mechanism [21]. Finally, Poë et al [15] have reported the observation of an incompletely defined ESR signal during reaction between $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ and PPh_3 .

A polynuclear complex was isolated from the reaction in quantities sufficient only for mass spectral analysis. The ion of highest mass observed corresponds to $\text{H}_2\text{Re}_3(\text{CO})_7(\text{PPh}_3)^+$ and as this is clearly not the molecular ion this product is incompletely characterised and is therefore not placed in the reaction scheme.

In summary, this study shows the close, and expected, parallel between the reaction of $\text{Re}_2(\text{CO})_{10}$ and PPh_3 and that of $\text{Mn}_2(\text{CO})_{10}$ and PPh_3 [6], in that the formation of the products can best be accounted for by invoking the production of radical intermediates. The kinetic studies of certain aspects of this reaction [15] are broadly in agreement with our findings. We have been unable to confirm the isolable radicals previously reported and believe the main product observed in the kinetic study [15] and by Nyman [10] to be *mer-trans*- $\text{HRe}(\text{CO})_3(\text{PPh}_3)_2$ rather than $\text{Re}(\text{CO})_3(\text{PPh}_3)_2$. We have been unable to confirm the isomeric form of $\text{Re}(\text{CO})_3(\text{PPh}_3)_2$ reported elsewhere [11], as we have found nothing with an analogous infrared spectrum to that observed earlier.

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