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Substituted metal carbonyls

XX *. Unexpected formation of two diphenylphosphine complexes from the oxidation of pentacarbonylrhenate by chlorodiphenylphosphine. Crystal and molecular structures of *eq*-Re₂(CO)₉(PPh₂H) and *cis*-ReCl(CO)₄(PPh₂H)

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Abstract

Oxidation of [Re(CO)₅][−] by a molar equivalent of PPh₂Cl at *ca.* −70°C yielded three dinuclear complexes, Re₂(μ-Cl)(μ-PPh₂)(CO)₈ (1), Re₂(CO)₉(PPh₂H) (2) and Re₂(μ-H)(μ-PPh₂)(CO)₈ (3), as major products. When PPh₂Cl was present in two-fold excess, only 2 and ReCl(CO)₄(PPh₂H) (4) were isolated. All the complexes were characterized by IR and NMR (¹H and ³¹P) spectroscopy. The crystal structures of 2 and 4 were determined by single-crystal X-ray diffraction analyses. Crystal data: ReCl(CO)₄(PPh₂H), space group *P*2₁/*c*, *a* = 11.358(1), *b* = 10.365(1), *c* = 14.765(3) Å, β = 96.07(1)°, final *R* = 0.022 for 1891 observations; Re₂(CO)₉(PPh₂H), space group *P*2₁/*a*, *a* = 12.709(1), *b* = 12.072(2), *c* = 15.462(2) Å, β = 92.14(1)°, final *R* = 0.029 for 2093 observations. Complex 2 is the first structurally characterized Re₂(CO)₉(PR₃) complex with the phosphine substituent at the equatorial site. The complex Re₂(μ-PPh₂)₂(CO)₈ was not detected and there is no evidence of direct nucleophilic attack of the rhenate on chlorodiphenylphosphine.

1. Introduction

Nucleophilic attack on halophosphines by metallates represents one of the popular synthetic routes to phosphido complexes [2]. In the case of halo complexes, metal–metal bond formation [3] usually results, although the mechanism may involve an initial electron transfer [4] rather than direct nucleophilic substitution. Continuing our interest in the phosphine substituted rhenium carbonyl complexes [5], we examine the reactivity of [Re(CO)₅][−] towards PPh₂Cl in an attempt to establish the substitution and redox behaviour of the latter towards the carbonyl anion. The analogous reac-

tion with [Mn(CO)₅][−] was reported to give Mn₂(μ-PPh₂)₂(CO)₈ under stringent conditions in toluene reflux [6]. Studies of this type of oxidative attack on the *d*⁸-carbonyl metallates are significant in view of the roles played by many electrophiles and carbonyl anions in various catalytic reactions. For example, a proposed key step in the rhodium-catalyzed carbonylation of methanol requires the oxidative addition of CH₃I to [Rh^II₂(CO)₂][−] to give [Rh^{III}(CH₃)I₃(CO)₂][−] [7]. Reported here is the isolation of two phosphido-bridged dirhenium(I) and two unexpected diphenylphosphine substituted Re^I and Re⁰ complexes from the reaction of [Re(CO)₅][−] with PPh₂Cl. Neutral diphenylphosphine complexes (M–PPh₂H) are uncommon and rarely characterized crystallographically [8]. Due to its high acidity, the P–H bond readily cleaves to give phosphido and hydrido complexes.

* For Part XIX, see ref. 1.

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2. Results and discussion

PPh_2Cl reacts rapidly with an equimolar quantity of $[\text{Re}(\text{CO})_5]^-$ at -70°C to give three dinuclear complexes which are formulated as $\text{Re}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{CO})_8$ (1), $\text{Re}_2(\text{CO})_9(\text{PPh}_2\text{H})$ (2) and $\text{Re}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_8$ (3) in 5.5, 3.4 and 2.1% yield respectively. Complex 1 was recently obtained in 2% yield upon heating $\text{Re}_2(\mu\text{-PPh}_2)_2(\text{CO})_8$ with InCl_3 at 220°C but no detailed spectroscopic data were reported [9]. No M–M bond is envisaged when the two hetero-bridging ligands serve as 4-electron donors in their anionic state. The observed high field shift ($\delta(^{31}\text{P}) = -73.23$ ppm) is indicative of a bridging phosphido group without the support of an M–M bond [10]. Complex 2, like the parent $\text{Re}_2(\text{CO})_{10}$, requires an M–M bond for stabilization, whereas the metal centres in 3 are linked by the hetero-ligands and a Re–Re bond. The strong M–M interaction is reflected in the low field shift ($\delta(^{31}\text{P}) = 42.39$ ppm) in the NMR spectrum. All the complexes were characterized spectroscopically and the structure of 2 was also elucidated by X-ray crystallography. Complex 3 has been previously obtained via the thermolysis of $\alpha\text{-Re}_2(\text{CO})_9(\text{PPh}_3)$ in xylene [11]. Strong $(\text{Ph}_2)\text{P}\text{--}\text{H}$ coupling of 362 Hz, typical for diphenylphosphine complexes [12], is observed in both the ^1H and ^{31}P spectra of 2, while a weak two-bond coupling constant (4.56 Hz) for the high-field hydride resonance ($\delta = -15.00$ ppm) of 3 is characteristic of a hydrido- and phosphido-cobridged system.

The molecular structure of 2 is shown in Fig. 1. Crystallographic data of 2 are given in Table 1, and atomic positional and thermal parameters in Table 2. Some pertinent molecular data are listed in Table 3.

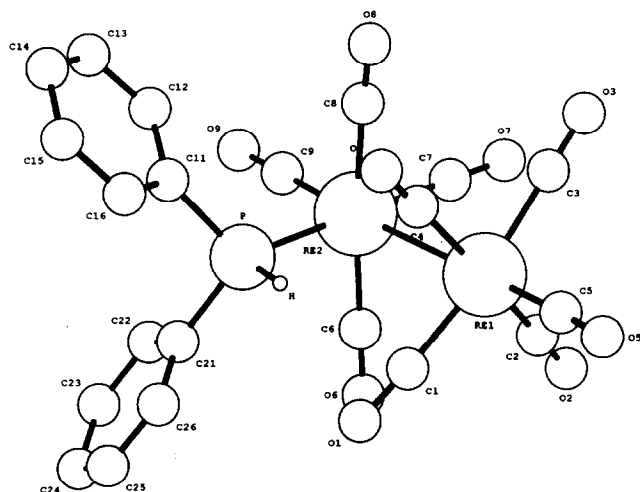


Fig. 1. PLUTO plot of $\text{Re}_2(\text{CO})_9(\text{PPh}_2\text{H})$ (hydrogen atoms are omitted for clarity).

TABLE 1. Crystallographic data and refinement details for $\text{Re}_2(\text{CO})_9(\text{PPh}_2\text{H})$ and $\text{ReCl}(\text{CO})_4(\text{PPh}_2\text{H})$

	$\text{Re}_2(\text{CO})_9(\text{PPh}_2\text{H})$	$\text{ReCl}(\text{CO})_4(\text{PPh}_2\text{H})$
Space group	monoclinic, $P2_1/a$	Monoclinic, $P2_1/c$
a (Å)	12.709(1)	11.358(1)
b (Å)	12.072(2)	10.365(1)
c (Å)	15.462(2)	14.765(3)
β (°)	92.14(1)	96.07(1)
V (Å ³)	2370.6(4)	1728.4(4)
Empirical formula	$\text{C}_{21}\text{H}_{11}\text{O}_9\text{PRe}_2$	$\text{C}_{16}\text{H}_{11}\text{ClO}_4\text{PRe}$
Crystal dimensions (mm)	$0.26 \times 0.19 \times 0.19$	$0.32 \times 0.19 \times 0.31$
FW	810.70	519.89
Z	4	4
$F(000)$	1495.52	983.74
D_{calc} (g cm ⁻³)	2.272	1.998
μ (mm ⁻¹)	10.46	7.39
λ (Å)	0.70930	0.70930
2θ (max)	44.9	44.8
Diffractometer	Nonius CAD4	Nonius CAD4
Scan mode	$\theta-2\theta$	$\theta-2\theta$
Data ranges	$-13 < h < 13$ $0 < k < 12$ $0 < l < 16$	$-12 < h < 12$ $0 < k < 11$ $0 < l < 15$
Unique reflections	3088	2247
Observations $I > 2\sigma(I)$	2093	1891
Absorption corrections	Yes	
<i>trans</i> factors	0.728–1.000	0.649–1.000
Total atoms	44	34
Parameters	302	212
Weights	Counting-statistics	Counting-statistics
Weight modifier	0.000100	0.000100
R_F	0.029	0.022
R_w	0.033	0.025
Goodness of fit	1.61	1.35
Max shift/ σ	0.775	0.020
Peaks in D-map, (e Å ⁻³)		
High	0.580	0.400
Low	–0.980	–0.660

Complex 2 is isostructural to its manganese analogue [13] with PPh_2H occupying an equatorial position, which is unusual for phosphines in monosubstituted dirhenium(0) carbonyls. Such an isostructural relationship between $\text{M}_2(\text{CO})_9(\text{PR}_3)$ complexes of Mn and Re does not always hold, however, as exemplified by $\alpha\text{-Mn}_2(\text{CO})_9(\text{PMe}_2\text{Ph})$ [14] and $eq\text{-Re}_2(\text{CO})_9(\text{PMe}_2\text{Ph})$ [15]. The present structure, to our knowledge, represents the only structurally characterized equatorial form of $\text{Re}_2(\text{CO})_9(\text{PR}_3)$ complexes, although spectroscopic evidence has been reported elsewhere for PMe_3 [16], PMe_2Ph [17] and PF_3 [18]; PF_3 shows coexistence of both isomeric forms. The slightly higher π -acidity and lower σ -donating ability of PPh_2H compared to PPh_3 and many tertiary phosphines should discourage its occupation of the equatorial site. Its site preference indicates a delicate balance of electronic and steric effects. With a cone angle of 128° [19], the steric

demand of PPh_2H is substantially lower than those of the phosphines found in many *ax*- $\text{Re}_2(\text{CO})_9(\text{PR}_3)$ complexes and comparable with that in *eq*- $\text{Re}_2(\text{CO})_9(\text{PMe}_2\text{Ph})$ (122°). Statistical distribution may also favour the more abundant equatorial sites. The Re–Re bond in **2** ($3.0526(7)$ Å) is not significantly longer than that in the parent decacarbonyl [20]. The two Re spheres are approximately staggered ($\phi = 40.4(5)^\circ$). The presence of the phosphine on the equatorial position possibly precludes an ideal staggered form. The “sweeping in”

TABLE 2. Final fractional coordinates for $\text{Re}_2(\text{CO})_9(\text{PPh}_2\text{H})$; e.s.d.s in parentheses refer to the last digit printed

Atom	x	y	z	B_{iso} (Å) ^a
Re1	0.22210(4)	0.57079(5)	0.28865(3)	3.06(3)
Re2	−0.00346(4)	0.56875(5)	0.21356(3)	2.43(2)
P	−0.0325(3)	0.3811(3)	0.2667(2)	2.62(14)
O1	0.2203(8)	0.3266(8)	0.2219(6)	4.6(5)
O2	0.2926(9)	0.6472(9)	0.1100(8)	6.1(6)
O3	0.1753(9)	0.8191(9)	0.3382(8)	6.5(7)
O4	0.1158(8)	0.4909(9)	0.4566(6)	5.1(6)
O5	0.4452(9)	0.5537(12)	0.3752(9)	9.2(8)
O6	0.0995(8)	0.4646(9)	0.0521(6)	5.2(5)
O7	0.0438(9)	0.8057(8)	0.1522(7)	5.7(6)
O8	−0.0641(8)	0.6681(9)	0.3920(6)	5.4(5)
O9	−0.2242(8)	0.5851(9)	0.1309(7)	5.6(6)
C1	0.2237(10)	0.4170(12)	0.2448(8)	3.2(6)
C2	0.2694(12)	0.6185(13)	0.1767(10)	4.6(7)
C3	0.1931(11)	0.7288(15)	0.3226(10)	4.3(8)
C4	0.1527(11)	0.5191(12)	0.3987(10)	3.7(7)
C5	0.3631(13)	0.5633(14)	0.3436(11)	5.6(9)
C6	0.0611(10)	0.5029(12)	0.1113(9)	3.4(6)
C7	0.0273(11)	0.7187(11)	0.1755(8)	3.5(7)
C8	−0.0448(11)	0.6317(11)	0.3294(9)	3.4(7)
C9	−0.1413(10)	0.5783(12)	0.1637(8)	3.6(6)
C11	−0.1374(10)	0.3544(10)	0.3418(7)	2.7(5)
C12	−0.2280(10)	0.4211(12)	0.3422(8)	3.5(6)
C13	−0.3089(11)	0.3933(15)	0.3959(9)	4.6(8)
C14	−0.3027(14)	0.3068(15)	0.4483(9)	4.8(8)
C15	−0.2149(16)	0.2376(14)	0.4489(9)	5.5(9)
C16	−0.1316(11)	0.2639(11)	0.3964(8)	3.9(7)
C21	−0.0508(10)	0.2733(10)	0.1856(7)	2.7(6)
C22	−0.1171(12)	0.2889(12)	0.1162(9)	4.3(7)
C23	−0.1329(13)	0.2076(14)	0.0550(9)	5.0(8)
C24	−0.0799(17)	0.1085(15)	0.0643(12)	6.7(10)
C25	−0.0140(17)	0.0936(14)	0.1374(13)	7.1(12)
C26	0.0020(12)	0.1759(12)	0.1952(9)	4.5(8)
H	0.050(9)	0.351(10)	0.317(7)	7.7(32)
H12	−0.2337	0.4884	0.3037	4.2
H13	−0.3754	0.4414	0.3985	4.5
H14	−0.3613	0.2835	0.4843	4.6
H15	−0.2107	0.1712	0.4900	5.0
H16	−0.0653	0.2160	0.3992	4.4
H22	−0.1548	0.3634	0.1093	4.5
H23	−0.1855	0.2226	0.0035	4.7
H24	−0.0916	0.0519	0.0181	5.3
H25	0.0208	0.0201	0.1411	5.4
H26	0.0532	0.1632	0.2464	4.6

^a B_{iso} is the mean of the principal axes of the thermal ellipsoids.

TABLE 3. Selected bond distances (Å) and angles ($^\circ$) for $\text{Re}_2(\text{CO})_9(\text{PPh}_2\text{H})$

Re(1)–Re(2)	3.0526(7)	P–C(11)	1.829(12)
Re(1)–C(1)	1.977(15)	P–C(21)	1.816(12)
Re(1)–C(2)	1.941(15)	P–H	1.33(12)
Re(1)–C(3)	2.016(18)	O(1)–C(1)	1.147(18)
Re(1)–C(4)	2.043(16)	O(2)–C(2)	1.137(19)
Re(1)–C(5)	1.957(16)	O(3)–C(3)	1.141(21)
Re(2)–P	2.443(3)	O(4)–C(4)	1.082(19)
Re(2)–C(6)	1.976(14)	O(5)–C(5)	1.140(20)
Re(2)–C(7)	1.947(14)	O(6)–C(6)	1.150(17)
Re(2)–C(8)	2.032(15)	O(7)–C(7)	1.133(17)
Re(2)–C(9)	1.891(13)	O(8)–C(8)	1.098(18)
		O(9)–C(9)	1.155(16)
Re(2)–Re(1)–C(1)	83.3(4)	P–Re(2)–C(9)	92.6(4)
Re(2)–Re(1)–C(2)	88.9(5)	C(6)–Re(2)–C(7)	92.2(5)
Re(2)–Re(1)–C(3)	85.9(4)	C(6)–Re(2)–C(8)	169.9(5)
Re(2)–Re(1)–C(4)	83.5(4)	C(6)–Re(2)–C(9)	96.0(6)
Re(2)–Re(1)–C(5)	175.4(5)	C(7)–Re(2)–C(8)	88.9(5)
C(1)–Re(1)–C(2)	88.0(6)	C(7)–Re(2)–C(9)	90.8(6)
C(1)–Re(1)–C(3)	169.2(5)	C(8)–Re(2)–C(9)	94.0(6)
C(1)–Re(1)–C(4)	90.5(5)	Re(2)–P–C(11)	120.0(4)
C(1)–Re(1)–C(5)	94.9(6)	Re(2)–P–C(21)	116.7(4)
C(2)–Re(1)–C(3)	91.0(6)	Re(2)–P–H	108(5)
C(2)–Re(1)–C(4)	172.3(6)	C(11)–P–C(21)	103.5(5)
C(2)–Re(1)–C(5)	95.3(7)	C(11)–P–H	99(5)
C(3)–Re(1)–C(4)	89.0(6)	C(21)–P–H	106(5)
C(3)–Re(1)–C(5)	95.9(6)	Re(1)–C(1)–O(1)	176.5(11)
C(4)–Re(1)–C(5)	92.3(6)	Re(1)–C(2)–O(2)	177.0(14)
Re(1)–Re(2)–P	91.77(8)	Re(1)–C(3)–O(3)	177.0(13)
Re(1)–Re(2)–C(6)	84.0(4)	Re(1)–C(4)–O(4)	179.3(13)
Re(1)–Re(2)–C(7)	84.9(4)	Re(1)–C(5)–O(5)	176.7(15)
Re(1)–Re(2)–C(8)	86.1(4)	Re(2)–C(6)–O(6)	179.5(11)
Re(1)–Re(2)–C(9)	175.7(4)	Re(2)–C(7)–O(7)	178.8(13)
P–Re(2)–C(6)	88.2(4)	Re(2)–C(8)–O(8)	177.5(12)
P–Re(2)–C(7)	176.6(4)	Re(2)–C(9)–O(9)	177.9(12)
P–Re(2)–C(8)	90.2(4)	P–C(11)–C(12)	121.3(9)
		P–C(11)–C(16)	120.2(10)

displacement of the equatorial ligands towards the Re–Re bond has been described elsewhere [21]. Although the degree of bending on either side of the Re–Re bond is rather insensitive to the substituent effect (average $\text{CO}_{\text{ax}}\text{--Re(1)--CO}_{\text{eq}} = 94.6(6)^\circ$ vs. $\text{CO}_{\text{ax}}\text{--Re(2)--CO}_{\text{eq}} = 93.6(6)^\circ$), the phosphine substitution induces a more uneven degree of such bending on the Re sphere to which it is attached ($\text{CO}_{\text{ax}}\text{--Re(1)--CO}_{\text{eq}}$ ranging from $90.8(6)^\circ$ to $96.0(6)^\circ$). The steric effect of the substituent plays little effect on its distortion from the equatorial plane ($92.6(4)^\circ$ for $\text{CO}_{\text{ax}}\text{--Re(2)--P}$ in **2**, $92.1(6)^\circ$ for $\text{CO}_{\text{ax}}\text{--Re--CN}$ in *eq*- $\text{Re}_2(\text{CO})_9(\text{CN}^t\text{Bu})$ [22]).

When the reaction was carried out in a two-fold excess of PPh_2Cl , a new product, $\text{ReCl}(\text{CO})_4(\text{PPh}_2\text{H})$ (**4**), was formed together with **2** in 14.3 and 10.3% yield, respectively whereas negligible amounts of complexes **1** and **3** were formed. Like **2**, a strong P–H coupling (380 Hz) is observed in both the ^1H and ^{31}P

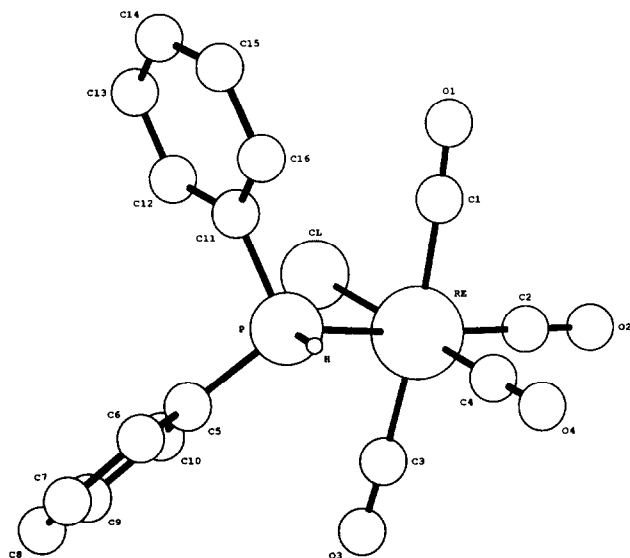


Fig. 2. PLUTO plot of $\text{ReCl}(\text{CO})_4(\text{PPh}_2\text{H})$ (hydrogen atoms are omitted for clarity).

TABLE 4. Final fractional coordinates for $\text{ReCl}(\text{CO})_4(\text{PPh}_2\text{H})$; e.s.d.s in parentheses refer to the last digit printed

Atom	x	y	z	$B_{\text{iso}} (\text{\AA})^a$
Re	0.54807(2)	0.76310(2)	0.14694(2)	2.70(2)
Cl	0.66704(15)	0.65884(15)	0.27854(10)	4.04(7)
P	0.71842(14)	0.74874(14)	0.05720(11)	2.91(7)
O1	0.6584(5)	1.0249(4)	0.2195(4)	5.5(3)
O2	0.3343(5)	0.8056(5)	0.2573(4)	6.4(3)
O3	0.4659(4)	0.4811(5)	0.0971(3)	4.5(2)
O4	0.4016(5)	0.8886(5)	-0.0152(4)	7.1(3)
C1	0.6164(6)	0.9327(6)	0.1922(4)	3.7(3)
C2	0.4141(6)	0.7881(6)	0.2185(5)	4.2(3)
C3	0.4939(5)	0.5844(7)	0.1118(4)	3.1(3)
C4	0.4590(6)	0.8405(6)	0.0455(5)	4.3(3)
C5	0.7731(5)	0.5928(6)	0.0229(4)	3.1(3)
C6	0.8226(6)	0.5820(6)	-0.0586(4)	3.9(3)
C7	0.8605(7)	0.4627(8)	-0.0866(5)	5.1(4)
C8	0.8497(7)	0.3574(7)	-0.0338(5)	5.3(4)
C9	0.8020(6)	0.3670(6)	0.0485(5)	4.6(3)
C10	0.7635(6)	0.4853(6)	0.0755(4)	3.6(3)
C11	0.8497(5)	0.8338(5)	0.1067(4)	3.0(3)
C12	0.9247(6)	0.7783(7)	0.1747(5)	4.5(3)
C13	1.0234(7)	0.8413(9)	0.2122(6)	6.1(4)
C14	1.0483(7)	0.9614(10)	0.1843(7)	6.7(5)
C15	0.9784(9)	1.0187(8)	0.1202(8)	7.5(6)
C16	0.8738(7)	0.9567(7)	0.0772(6)	6.1(5)
H	0.697(4)	0.812(5)	-0.022(3)	3.3(12)
H6	0.830	0.658	-0.096	4.7
H7	0.896	0.455	-0.144	6.0
H8	0.876	0.274	-0.054	6.1
H9	0.796	0.291	0.087	5.3
H10	0.729	0.493	0.133	4.4
H12	0.907	0.691	0.197	5.4
H13	1.078	0.799	0.259	6.9
H14	1.119	1.007	0.213	7.4
H15	0.998	1.105	0.100	8.5
H16	0.821	1.000	0.032	6.9

^a B_{iso} is the mean of the principal axes of the thermal ellipsoids.

spectra of **4**. The four carbonyl absorption bands found in the IR spectrum of **4** are consistent with the C_s symmetry expected for the *cis*-disposition of the phosphine and chloro ligands in a mononuclear octahedral geometry. This proposition was confirmed by an X-ray diffraction study carried out on **4**. The structure is illustrated in Fig. 2, crystallographic data are given in Table 1, atomic positional and thermal parameters in Table 4, and some pertinent molecular data in Table 5. The strongest Re–CO linkage occurs in the carbonyl group *trans* to the π -donating chloro ligand. The phosphorus-bonded hydrogen atom is located and refined to give a P–H length of 1.34(5) Å, compared to 1.33(12) Å found in **2**. Complex **4** has been reported as a hydrolytic product from *cis*- $\text{ReX}(\text{CO})_4(\text{Ph}_2\text{PSiMe}_3)$ [23] and a thermal product of $\text{ReX}(\text{CO})_4(\text{SePPh}_2\text{H})$ [24]. Its manganese analogue, however, is more conveniently synthesized by phosphine substitution of $\text{MnX}(\text{CO})_5$ [25].

The exact mechanism of the reaction is complex and presently uncertain. Formation of **1–4** and significantly the absence of the seemingly obvious $\text{Re}_2(\mu\text{-PPh}_2)_2(\text{CO})_8$ [26] do not support a direct nucleophilic attack of the rhenate on PPh_2Cl , or any coupling reaction which would yield a powerful oxidative addition substrate Ph_2PPPh_2 [27]. A parallel observation has recently been noted in the reactions between $[\text{Fe}(\text{CO})_4]^{2-}$ and some PR_2Cl complexes of nickel [28]. Complex **4** is possibly a primary product arising from the oxidative addition of the phosphine on the d^8

TABLE 5. Selected bond lengths (Å) and angles (°) for $\text{ReCl}(\text{CO})_4(\text{PPh}_2\text{H})$; e.s.d.s in parentheses refer to the last digit printed

Re–Cl	2.4926(16)	P–C(5)	1.822(6)
Re–P	2.4624(16)	P–C(11)	1.818(6)
Re–C(1)	2.008(7)	P–H	1.34(5)
Re–C(2)	1.959(7)	O(1)–C(1)	1.123(9)
Re–C(3)	2.003(7)	O(2)–C(2)	1.137(9)
Re–C(4)	1.895(7)	O(3)–C(3)	1.131(8)
		O(4)–C(4)	1.163(9)
Cl–Re–P	90.07(5)	C(2)–Re–C(4)	89.4(3)
Cl–Re–C(1)	87.79(18)	C(3)–Re–C(4)	93.6(3)
Cl–Re–C(2)	91.42(21)	Re–P–C(5)	120.91(20)
Cl–Re–C(3)	85.84(17)	Re–P–C(11)	114.35(19)
Cl–Re–C(4)	178.99(22)	Re–P–H	111.1(21)
P–Re–C(1)	86.20(18)	C(5)–P–C(11)	104.6(3)
P–Re–C(2)	175.86(18)	C(5)–P–H	103.1(21)
P–Re–C(3)	92.41(16)	C(11)–P–H	100.2(22)
P–Re–C(4)	89.11(21)	Re–C(1)–O(1)	177.2(6)
C(1)–Re–C(2)	90.0(3)	Re–C(2)–O(2)	177.2(6)
C(1)–Re–C(3)	173.48(25)	Re–C(3)–O(3)	175.8(5)
C(1)–Re–C(4)	92.7(3)	Re–C(4)–O(4)	178.0(6)
C(2)–Re–C(3)	91.55(24)	P–C(5)–C(6)	119.7(5)
		P–C(5)–C(10)	120.9(4)

carbonyl rhenate, which is accompanied by decarbonylation to give an anion $[\text{Re}(\text{CO})_4(\text{Cl})(\text{PPh}_2)]^-$ as an intermediate [29]. Abstraction of a proton from the reaction medium would generate complex **4** which would rapidly react with the strongly nucleophilic $[\text{Re}(\text{CO})_5]^-$ to give **2** as a secondary product. Evidence for the latter reaction is obtained from our independent synthesis of **2** from **4** and $[\text{Re}(\text{CO})_5]^-$, and the fact that **4** is observed only when the phosphine is present in excess; under these conditions the rhenate is rapidly consumed and thus unavailable for its consumption of **4**.

3. Conclusion

Most reactions using free PPh_2H as a substrate would give oxidative rather than substitution products. The present use of an oxidizing phosphine as an entry into PPh_2H complexes merits further investigations. The reactivity of the two novel PPh_2H complexes, especially at the P–H site, is also a subject of our interest.

4. Experimental details

4.1. General

All reactions were performed under pure dry argon using standard Schlenk techniques. All the solvents used for reactions and purifications were freshly distilled and dried by published methods. Chlorodiphenylphosphine was purchased from Aldrich Co, vacuum-distilled at 0.4 mbar and collected at 108°C, and stored under dry argon. $[\text{Re}(\text{CO})_5]^-$ was generated *in situ* from the reduction of $\text{Re}_2(\text{CO})_{10}$ by sodium amalgam (3%) in THF [30]. Proton NMR spectra were recorded in CDCl_3 on a JEOL FX 90Q or Bruker A.C.F. 300 MHz spectrometer at 89.56 and 300.13 MHz, respectively, using TMS as internal standard. Phosphorus-31 NMR spectra were recorded on the same two instruments at 36.25 and 121.50 MHz, respectively. Chemical shifts are reported in ppm to a high frequency of external H_3PO_4 (85%). Infrared spectra were recorded in CH_2Cl_2 solutions on a Shimadzu IR-470 or FT-IR Perkin–Elmer 1725 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of this Department in the National University of Singapore. Precoated silica plates of layer thickness 0.25 and 0.50 mm were obtained from Merck and Baker.

4.2. Reaction of $[\text{Re}(\text{CO})_5]^-$ with PPh_2Cl

$\text{Na}^+[\text{Re}(\text{CO})_5]^-$ generated *in situ* from $\text{Re}_2(\text{CO})_{10}$ (0.400 g, 0.61 mmol) and Na/Hg (*ca.* 2 g) in THF (20 cm^3) was filtered via a teflon transfer tube into a 150 cm^3 Schlenk flask precooled to *ca.* -70°C in an ace-

tone/dry ice bath. A mixture of PPh_2Cl (0.22 cm^3 , *ca.* 0.27 g, 1.22 mmol) in THF (3 cm^3) was carefully deoxygenated and added dropwise via a pressure-equalizing dropping funnel to the stirred solution of $[\text{Re}(\text{CO})_5]^-$ kept at *ca.* -70°C . The resultant orange-yellow solution was stirred for *ca.* 10 min in the low-temperature bath before being slowly warmed up to room temperature (24°C); stirring was continued for 1.5 h to give a light-yellow solution with a white deposit of NaCl. After vacuum evaporation of the solvent, the residue was extracted with a minimum amount of CH_2Cl_2 and chromatographed on silica TLC plates in air. Four main bands were eluted with a mixture of CH_2Cl_2 /hexane (1:4 v/v). The first band was identified as unreacted $\text{Re}_2(\text{CO})_{10}$ (*ca.* 0.08 g). The other bands (on decreasing R_f values) were extracted by CH_2Cl_2 and recrystallized from CH_2Cl_2 /hexane mixture to give $\text{Re}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_8$ (**3**), $\text{Re}_2(\text{CO})_9(\text{PPh}_2\text{H})$ (**2**) and $\text{Re}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\text{CO})_8$ (**1**), respectively. Complex **3** (0.008 g, 2.10%): Anal. Found; C, 30.93; H, 1.39; P, 4.48. $\text{C}_{20}\text{H}_{11}\text{O}_8\text{PRe}_2$ calc.: C, 30.69; H, 1.41; P, 3.96%. $\nu(\text{CO})$ 2108w, 2084m, 2013vs, 1960s cm^{-1} . $\delta(\text{H})$ 7.87–7.80 (m, 4H, Ph); 7.35–7.30 (m, 6H, Ph); -15.00 (d, 1H, Re–H, $^2J(\text{P-H}) = 4.56$ Hz) ppm. $\delta(\text{P})$ 42.39 (s) ppm. Complex **2** (0.015 g, 3.85%): Anal. Found C, 31.57; H, 1.37; P, 4.02. $\text{C}_{21}\text{H}_{11}\text{O}_9\text{PRe}_2$ calc.: C, 31.11; H, 1.37; P, 3.82%. $\nu(\text{CO})$ 2103m, 2041s, 1993vs, 1966(sh)w, 1928s cm^{-1} . $\delta(\text{H})$ 7.71–7.38 (m, 10H, Ph); 6.84 (d, 1H, P–H, $J(\text{P-H}) = 361.6$ Hz) ppm. $\delta(\text{P})$ -12.25 (s) ppm. Complex **1** (0.022 g, 5.50%): Anal. Found C, 35.60; H, 2.41; P, 3.95; Cl, 2.88. $\text{C}_{26}\text{H}_{24}\text{ClO}_8\text{PRe}_2$ calc.: C, 34.57; H, 2.67; P, 3.43; Cl 3.92%. $\nu(\text{CO})$ 2099m, 2037m, 2020s, 1945m cm^{-1} . $\delta(\text{H})$ 7.68–7.41 (m, 10H, Ph) ppm. $\delta(\text{P})$ -73.23 (s) ppm.

Repeat of the above procedure by reversing the addition of $[\text{Re}(\text{CO})_5]^-$ into the PPh_2Cl solution in THF gave essentially the same results except that the yield of **1** is decreased to 2.25% (0.009 g) whilst those of **2** and **3** are increased to 12.05% (0.047 g) and 4.74% (0.018 g), respectively.

When the preparation was carried out in a 2:1 molar ratio of PPh_2Cl (0.44 cm^3 , *ca.* 0.56 g, 2.45 mmol) to $[\text{Re}(\text{CO})_5]^-$ under similar conditions, three main bands were eluted from the TLC plates. The top band was identified as unreacted $\text{Re}_2(\text{CO})_{10}$ (0.08 g). The second and third bands were analyzed respectively as complex **2** (0.040 g, 10.25%) and *cis*- $\text{ReCl}(\text{CO})_4(\text{PPh}_2\text{H})$ (**4**) (0.073 g, 14.31%). Anal Found C, 34.63; H, 1.92; P, 6.44; Cl, 6.99. $\text{C}_{16}\text{H}_{11}\text{ClO}_4\text{PRe}$ calc.: C, 36.96; H, 2.13; P, 5.96; Cl, 6.82%. $\nu(\text{CO})$ 2112m, 2045(sh)w, 2014vs, 1945s cm^{-1} . $\delta(\text{H})$ 7.70–7.43 (m, 10H, Ph); 6.81 (d, 1H, P–H, $J(\text{P-H}) = 379.63$ Hz) ppm. $\delta(\text{P})$ -9.29 (s) ppm. When this preparation was carried out with the addition of the rhenate solution to the

phosphine, the yields of products **2** and **4** were reduced to 0.018 g (4.62%) and 0.043 g (8.43%), respectively.

4.3. Crystallographic analyses

Colourless crystals of complexes **2** and **4** were grown from solutions of CH_2Cl_2 /hexane mixtures. Single crystals suitable for X-ray diffraction were mounted on top of a glass fibre with epoxy glue for preliminary characterization and intensity data collection. The crystallographic data and refinement details of **2** and **4** are listed in Table 1. The structures were solved by Patterson methods. All hydrogen atoms were found at anisotropic convergence and were fixed as isotropic ellipsoids in the final cycles of least-squares refinement with the exception of phosphine hydrogen atoms which were refined and resulted in consistent P–H lengths. Attempts to refine the phenyl hydrogens were unsatisfactory. The non-hydrogen atoms were varied anisotropically. The atomic scattering curves of Re, Cl, P, O, C and H were taken from the *International Tables for X-Ray Crystallography*, Volume IV. Computations were carried out on a MicroVAX 3600 with the NRCC package [31]. The molecules of **2** and **4** are shown in Figs. 1 and 2, respectively. Final atomic fractional coordinates and selected bond distances and angles for **2** are listed in Tables 2 and 3 and those for **4** in Tables 4 and 5, respectively.

5. Supplementary materials

Lists of thermal parameters and final structure factors for $Re_2(CO)_9(PPh_2H)$ and $ReCl(CO)_4(PPh_2H)$ are available from the authors, and have been deposited with the Cambridge Crystallographic Data Centre.

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