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Meta and *para* metallation of EPh_4^+ (E = P, As) and $N(PPh_3)_2^+$ by the dinuclear acylanion $[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(C(Ph)O)]^-$. Formation of zwitterionic cluster complexes $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(x\text{-}C_6H_4EPh_3)$ (E = P, As; $x = m, p$) and $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(x\text{-}C_6H_4PPh_2NPPh_3)$

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Abstract

On treating the dirhenium salt $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(C(Ph)O)]$ (Li(**1**)) with EPh_4Cl (E = P, As) or $N(PPh_3)_2Cl$, respectively, in THF at room temperature, metathesis of the cations occurs to give the intermediates $EPh_4[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(C(Ph)O)]$ (EPh_4(**1**)) or $N(PPh_3)_2[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(C(Ph)O)]$ ($N(PPh_3)_2$(**1**)). PPh_4(**1**) was isolated and its X-ray structure was determined. Upon stirring these intermediates in THF solution at 20°C for 2 days, benzaldehyde (PhCHO) is eliminated and the *para* and *meta* metallated products $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(x\text{-}C_6H_4EPh_3)$ (E = P, $x = m$: **2a**, $x = p$: **2b**; As, $x = m$: **3a**, $x = p$: **3b**) and $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(x\text{-}C_6H_4PPh_2NPPh_3)$ ($x = m$: **4a**, $x = p$: **4b**) are formed by C–H oxidative addition. Heating to 45°C shortens the reaction time to 4 h. The products are zwitterionic, consisting of a negatively charged dirhenium unit and a positively charged phosphonium, arsonium or bistriphenylphosphine iminium ligand, respectively, bound to one of the rhenium atoms. In each case, the *m*- and *p*-isomers could be separated by PLC. Moreover, **2b** was crystallized from a benzene solution and its molecular structure was confirmed by X-ray analysis. The above sequence of reactions was repeated with d_{20}-PPh_4Br. It reacts completely analogous to give the deuterated products $Re_2(\mu\text{-}D)(\mu\text{-}PCy_2)(CO)_7(x\text{-}C_6D_4(d_{15}\text{-}EPh_3))$ (E = P, $x = m$: d_{20}-**2a**, $x = p$: d_{20}-**2b**). Hence, the μ-H and μ-D ligands, respectively, of the new compounds originate from the corresponding aromatic cation. The reaction of Li(**1**) with $SbPh_4Br$ proceeds completely different. PhCHO is eliminated again, but no metallated products were found. Only the decomposition product $Re_2(\mu\text{-}Br)(\mu\text{-}PCy_2)(CO)_7(eq\text{-}SbPh_3)$ (**5**) was isolated in 19% yield. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: *Para* metallation; *Meta* metallation; Zwitterionic cluster complex; Rhenium carbonyl complex

1. Introduction

Hydrido phosphido bridged cluster complexes are well known in organometallic chemistry. Especially compounds of the type $M_3(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_{10}$ (M = Ru, Os; R = organic residue) [1,2] and $M_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_8$ (M = Mn, Re) [3,4] have been intensively investigated. The latest studies on $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_8$ have been focused on its reactivity towards PhLi in THF solution at − 100°C. In this reaction, the salt $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(C(Ph)O)]$ (Li(**1**)) is formed selectively in nearly quantitative yield. It reacts with two equivalents of $XAuPPh_3$ (X = Cl, Br, I) under elimination of benzaldehyde (PhCHO) to give the metallatetrahedranes $Re_2(AuPPh_3)_2(\mu\text{-}PCy_2)(CO)_7X$ [5]. On treating Li(**1**) with carboxylic acids RCO_2H and heating to 60°C, PhCHO is eliminated again and the salts $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(\eta^1\text{-}OC(R)O)]$ are formed. The formyl proton of PhCHO originates predominantly from the hydrido bridge of Li(**1**) [6]. In order to find substrates other than $XAuPPh_3$ or RCO_2H, which could be added to the dirhenium unit

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after elimination of PhCHO, we decided to isolate the salts $EPh_4[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(C(Ph)O)]$ (E = P, As) or $N(PPh_3)_2[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(C(Ph)O)]$, respectively.

In this paper we wish to report the surprising reaction of Li(**1**) with EPh_4Cl and $N(PPh_3)_2Cl$, respectively, resulting in the formation of novel *meta* and *para* metallated, zwitterionic dirhenium cluster complexes under mild reaction conditions. Such *meta* and *para* metallation reactions are rare, only one example of *para* metallation by a transition metal is present in the literature. In that case, heating of the solid $(N\text{-}Mepy)_2PtCl_6$ (py = pyridine) to 180°C gave $(N\text{-}Mepy)[Cl_5Pt(C_5H_4NMe)]$ [7]. Additionally, our work provides information on the mechanism of the reaction, which was elucidated by the reaction of Li(**1**) with d_{20}-PPh_4Br and on the decomposition reaction of Li(**1**) with $SbPh_4Br$.

2. Results and discussion

2.1. Synthesis and reaction mechanism

On treating Li(**1**) (δ(μ-P): 63.4) with 1.5 equivalents PPh_4Cl in THF solution at room temperature a metathesis reaction occurs to give PPh_4(**1**) (δ(μ-P): 72.0, $\delta(PPh_4^+)$: 23.0) and LiCl (Scheme 1, step (i)). The ν(CO) IR and ^{31}P-NMR spectra of PPh_4(**1**) [5] in THF cannot be distinguished from spectra of a 1:1 mixture of Li(**1**) and PPh_4Cl in THF. Hence, the metathesis reaction proceeds quantitatively within a few minutes. PPh_4(**1**) was isolated in 86% yield and its molecular structure was determined by a single-crystal X-ray analysis (Fig. 1). However, when the above mentioned mixture is stirred at room temperature for 2 days the formation of benzaldehyde (PhCHO) is observed by IR measurements. This new reaction is followed easily by ^{31}P-NMR and IR measurements. Within 2 days, the resonances of PPh_4(**1**) disappeared completely. Instead signals of **2a** (δ(μ-P): 59.2, $\delta(P^+)$: 22.8) and **2b** (δ(μ-P): 58.2, $\delta(P^+)$: 23.6) appeared. In the same period of time the ν(CO) band of the acyl ligand (1545 cm^{-1}) of PPh_4(**1**) disappeared and a large ν(CO) band of PhCHO (1704 cm^{-1}) is formed. Compounds **2a** and **2b** (Scheme 1) were isolated by PLC as air-stable, amorphous, colorless solids in 44% (**2a**) and 8% (**2b**) yield, respectively. Heating to 45°C shortens the reaction time to 4 h. The isomer distribution as measured by ^{1}H-NMR was determined to be 85% **2a** and 15% **2b**. Compounds **2a** and **2b** were characterized by ν(CO) IR, ^{1}H-, ^{31}P-NMR spectra and elemental analysis. Also, the molecular structure of **2b** was determined by a single-crystal X-ray analysis (Fig. 2). The comparison of the spectroscopic data of **2a** and **2b** allows the identification of **2a**. Both compounds show a characteristical ν(CO) IR spectrum consisting of seven absorption bands. Compared with the ν(CO) IR spectrum of PPh_4(**1**), the bands of both products are almost unshifted. Therefore, it is reasonable to assume that a negative charge remains at the dirhenium core and consequently a positive charge at the phosphorous of the phosphonium ligand (zwitterionic structure). This hypothesis is also supported by the X-ray data of **2b** (cf. Section 3) and the ^{31}P-NMR data of **2a** and **2b**. The ^{31}P-NMR signals of the phosphonium ligands in $CDCl_3$ are at 22.8 ppm for **2a** and 23.6 ppm for **2b**. In comparison, the signal of PPh_4Cl in $CDCl_3$ is at 23.8 ppm. The ^{1}H spectra of

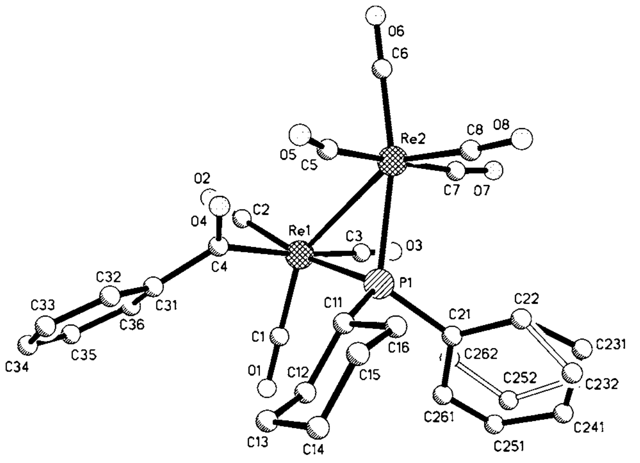
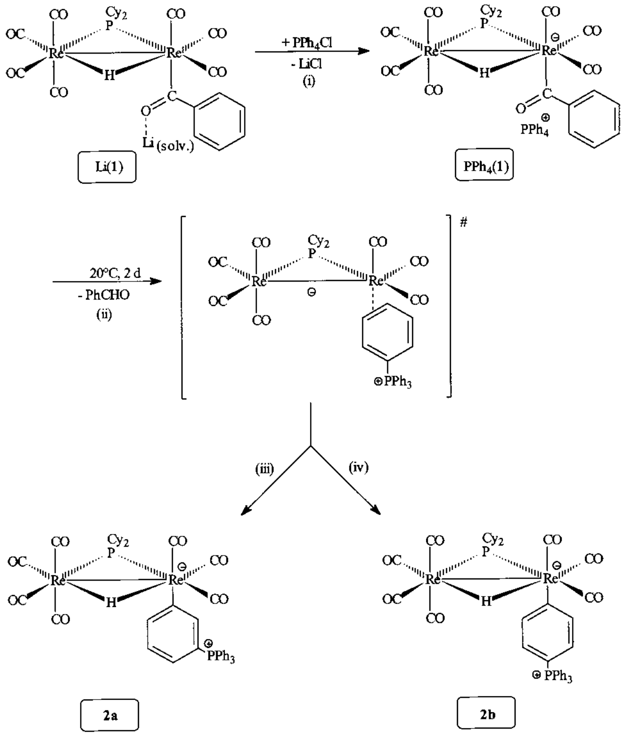


Fig. 1. Molecular structure of $(\mathbf{1})^-$. Hydrogen atoms omitted.



Scheme 1. Proposed reaction mechanism.

2a and **2b** exhibit doublets at -13.23 or -13.01, respectively, confirming the existence of a μ-bound H ligand. The main difference between both ^{1}H spectra is the substitution pattern of the phenyl ring bound to rhenium. In **2b**, two double doublets are present confirming *para* substitution. In **2a**, four groups of signals are found proving *meta* substitution.

In Scheme 1 the proposed mechanism of the formation of **2a** and **2b** is illustrated. First, the above mentioned metathesis reaction takes place (step (i)) resulting in the formation of PPh_4(**1**). This is decisive for the next step as Li(**1**) itself eliminates PhCHO only in small amounts on heating to 60°C. But now (step (ii)), PhCHO is eliminated easily, possibly due to formation of a contact ion pair. In the hypothetical transition state, the valence electron deficit of the dirhenium core is compensated by a η^2-bound phenyl ring of PPh_4^+. This bonding pattern is well known for organometallic compounds [8]. The transition state is electronically similar to the anionic cluster complexes $[M_2(\mu\text{-}PR_2)(CO)_8]^-$ (M = Mn, Re; R = organic residue) [9]. Finally, the *m*- (step (iii)) or *p*- (step (iv)) C–H bond, respectively, is cleaved affording a new μ-H ligand and an axial (with respect to the plain Re–(μ-P)–Re) phosphonium ligand.

The origin of the μ-H ligand was established by the reaction of Li(**1**) with d_{20}-PPh_4Br. The products of this reaction, d_{20}-**2a** and d_{20}-**2b**, showed ν(CO) IR and ^{31}P-NMR spectra almost identical to **2a** and **2b**. The ^{1}H-NMR spectra, however, showed no resonances in the aromatics region and no resonances at high field. Accordingly, the presence of a d_{19}-phosphonium ligand and a μ-D ligand is indicated. Hence, the μ-H ligand in **2a** and **2b** originates from a phenyl ring of PPh_4^+.

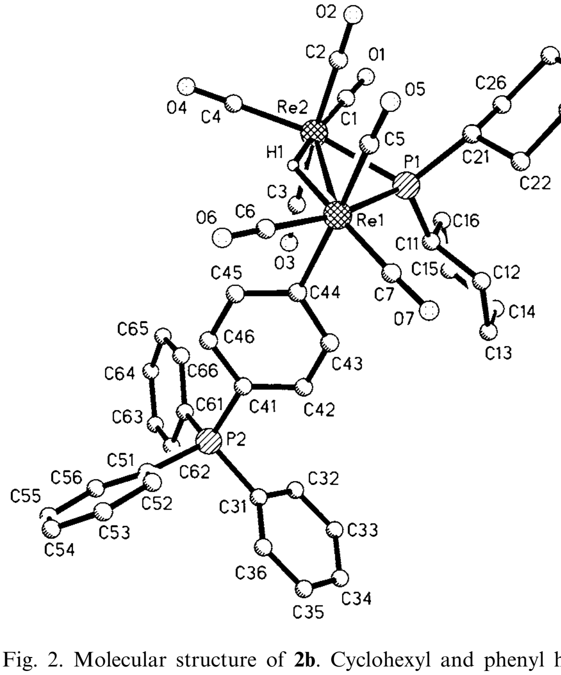


Fig. 2. Molecular structure of **2b**. Cyclohexyl and phenyl hydrogen atoms omitted.

In order to find out if this kind of reaction is transferable to other aromatic cations and to get a better understanding of the isomer distribution, the reaction was repeated using $AsPh_4Cl{\cdot}H_2O$, $SbPh_4Br$ and $N(PPh_3)_2Cl$, respectively. In the case of $AsPh_4Cl{\cdot}H_2O$ and $N(PPh_3)_2Cl$, the expected products $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(x\text{-}C_6H_4AsPh_3)$ ($x = m$: **3a**, $x = p$: **3b**; yield: 23% **3a**, 5% **3b**; isomer distribution: 82% **3a**/18% **3b**) and $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(x\text{-}C_6H_4PPh_2\text{-}NPPh_3)$ ($x = m$: **4a**, $x = p$: **4b**; yield: 20% **4a**, 17% **4b**; isomer distribution: 54% **4a**/46% **4b**) were found. The yields of these products when compared with **2a** and **2b** are distinctly lower. This cannot be attributed to side reactions. ^{31}P-NMR spectra of the reaction mixtures revealed almost complete formation of **2a**, **2b** and **3a**, **3b** and **4a**, **4b**, respectively. Hence, the isomers decompose during PLC separation. Interestingly, the isomer distribution is not affected by the above mentioned decomposition. The ν(CO) IR spectra of all new compounds show seven absorption bands due to the low symmetry of the molecules (point group C_1). The chemical shift of the μ-P ligand is almost unaffected by the different cationic ligands. It varies only slightly from 57.9 ppm for d_{20}-**2b** to 59.4 ppm for **3a**. The ^{31}P-NMR spectrum of **4a** and **4b**, respectively, shows three signals. The signal at low field belongs to the μ-P ligand. The other two resonances are doublets with a $^{2}J_{PP}$ coupling constant of 6 Hz. They must be assigned to the phosphorous atoms of the iminium ligand.

The reaction of Li(**1**) with $SbPh_4Br$ yielded none of the expected isomers. ^{31}P-NMR spectra of the reaction mixture showed no shift of the μ-P signal of Li(**1**) after addition of $SbPh_4Br$. Hence, no metathesis reaction takes place and there is no reaction at room temperature. On heating to 60°C PhCHO is formed again and the color of the solution turns brown. ^{31}P-NMR spectra of these solutions show at least ten different signals and indicate a decomposition reaction. The novel dirhenium complex $Re_2(\mu\text{-}Br)(\mu\text{-}PCy_2)(CO)_7(eq\text{-}SbPh_3)$ **5** was found to be the only isolable product (19% yield). Its molecular structure was determined by a single-crystal X-ray analysis [10]. These experimental results suggest that Li^+ in Li(**1**) is not exchanged for $SbPh_4^+$. Consequently, higher reaction temperatures are needed as PhCHO is now eliminated from Li(**1**). The cluster complex formed in this way is labile due to its valence electron deficit and decomposes under these conditions rapidly. The formation of **5** is a consequence of the reactivity of $SbPh_4^+$. The latter cation, in contrast to PPh_4^+ and $AsPh_4^+$, is known to be a phenylating agent [11]. Therefore, we suppose that it partially breaks down into ‘Ph^+’ and $SbPh_3$. Finally, **5** is formed by a dirhenium fragment of the above mentioned decomposition reaction, the bromide of $SbPh_4Br$ and $SbPh_3$.

2.2. Isomer distribution

The isomer distribution **2a**/**2b**, **3a**/**3b** and **4a**/**4b**, respectively, is constant during the entire reaction as proved by ^{31}P-NMR spectra recorded each 30 min at 45°C. As expected there is almost no change in the isomer distribution of **2a**/**2b** ($p/m = 1/5.5$) compared with **3a**/**3b** ($p/m = 1/4.6$). The m-isomer is always favored to the sterically less hindered p-isomer. But in case of the extremely bulky $N(PPh_3)_2^+$, the ratio is shifted to $p/m = 1/1.2$. These facts are best explained in terms of electronic and steric arguments. Starting from the transition state (Scheme 1) the electrophilic Re is binding faster to the m-C atom than to the p-C atom as the m-C atom has the lowest positive partial charge of the aromatic ring. In case of very bulky cations the rate of formation of the m-product decreases due to increasing sterical hindrance. The rate of formation of the p-product, however, is less affected by sterical hindrance.

2.3. Conclusion

The salt Li(**1**) has proven to be extremely reactive towards aromatic cations like PPh_4^+. The resulting zwitterionic cluster complexes are very unusual and deserve further investigations regarding their reactivity. Moreover, the reaction of $N(PPh_3)_2^+$ shows that Li(**1**) after release of PhCHO is able to metallate very different aromatic cations. Therefore, we are currently studying the reaction of Li(**1**) with other aromatic cations. First results of these reactions with pyridinium cations prove the transferability of the metallation reaction to heteroaromatic substrates.

3. Structural descriptions

PPh_4(**1**) belongs to a well known family of hydrido-phosphido-bridged dinuclear rhenium complexes $Re_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_8$ with a metal–metal bond [12]. In $(\mathbf{1})^-$ each Re atom has a distorted octahedral coordination sphere from both the bridging H and P atom and terminal four carbonyl groups at Re(2) and three CO and one PhCO group at Re(1), respectively. These terminal ligands show an almost eclipsed arrangement at the Re centers, the axially attached PhCO ligand has a Re–C(4) bond length of 2.21(2) Å. The Re–Re bond length of 3.166(1) Å compares well with those from the above mentioned unsubstituted octacarbonyl complexes, where the distances range from 3.132 to 3.165(1) Å. In these complexes both Re–P bond lengths are equal, whereas $(\mathbf{1})^-$ shows a different bonding pattern. Here, the Re(2)–P distance of 2.469(4) Å is significantly longer than the Re(1)–P bond of 2.444(4) Å, the latter Re atom bearing the PhCO ligand. The same bonding geometries are valid for the complex Li(**1**), which has been described earlier [5]. The position of the μ-H atom could not be determined, but the typical arrangement of the equatorial CO groups 2 and 6 with Re–Re–C opening angles of 120.0(6)° and 113.7(4)°, respectively, clearly indicate its presence [12a,c,d]. In the anion $[Re_2(\mu\text{-}PPh_2)(CO)_8]^-$ without this sterically demanding μ-H ligand, the corresponding angles Re–Re–C are only 100° [4b].

Table 1
Crystal data and refinement details

Compound	PPh_4(**1**)	**2b**·benzene
Formula	$C_{50}H_{48}O_8P_2Re_2$	$C_{43}H_{42}O_7P_2Re_2$, C_6H_6
M_w	1211.2	1183.2
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	11.389(2)	11.092(3)
b (Å)	14.051(2)	14.363(3)
c (Å)	30.664(5)	15.538(5)
α (°)		99.90(2)
β (°)	100.31(1)	96.36(2)
γ (°)		92.34(2)
V (Å^3)	4827.8(13)	2391.0(11)
Z	4	2
D_{calc} (g cm^{-3})	1.666	1.643
μ (mm^{-1})	5.127	5.173
F(000)	2368	1156
Diffractometer	Siemens R3m; graphite monochromator, Mo–K_α radiation	
Scan type	ω, $4 \leq 2\theta \leq 55°$	
R_1, wR_2 (all data)	7.98, 23.41	4.80, 10.85

2b: This structure is closely related to that of $(\mathbf{1})^-$. The main difference is the substitution of the PhCO group in $(\mathbf{1})^-$ versus a likewise axially coordinated phosphonium ligand, which is attached to the Re(1) atom through the *para*-C atom of one phenyl group. According to a search in the Cambridge data base [13] this is the first transition metal compound exhibiting this bonding pattern. The resulting Re–C(44) single bond length is 2.235(8) Å and, consistent with this substitution, both Re–P bond lengths show the same differences as for $(\mathbf{1})^-$ with Re(2)–P of 2.469(2) and Re(1)–P of 2.442(2) Å. The Re–Re bond length of 3.1637(8) Å, which is the same as that of $(\mathbf{1})^-$, is elongated by ca. 0.021 Å compared with that of the unsubstituted complex $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_8$ [12a]. The position of the μ-H atom was determined from difference Fourier map and refined (see Tables 1 and 2).

4. Experimental

4.1. General conditions

All reactions were performed with standard Schlenk techniques in solvents free of oxygen which were dried according to literature methods, distilled and stored under argon atmosphere. PLC was carried out on glass plates (20 × 20 cm^2) coated with a mixture of gypsum and silica gel (Merck 60 PF_{254}, 1 mm thick).

4.1.1. Instrumentation

The reaction products were characterized by ν(CO) FTIR spectroscopy (Nicolet P510, CaF_2 optics), ^{1}H- and ^{31}P-NMR spectroscopy (Bruker AMX 300).

4.1.2. Starting materials

PPh_4Cl, $AsPh_4Cl \cdot H_2O$ and PCl_3 were purchased from Fluka. $N(PPh_3)_2Cl$ and $SbPh_4Br$ were obtained from Aldrich. d_5-Bromobenzene (99.5% *d*) was purchased from Deutero GMBH. All reagents were laboratory grade and used as received. $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(C(Ph)O)]$ and $PPh_4[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(C(Ph)O)]$ [5] were prepared according to the literature procedure. d_{15}-PPh_3 was prepared from d_5-PhMgBr and PCl_3 in diethyl ether. It was subsequently phenylated with d_5-PhBr according to the method of Horner [14] to give d_{20}-PPh_4Br.

4.2. Preparation of $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(x\text{-}C_6H_4\text{-}EPh_3)$ (E = P, x = m: **2a**, x = p: **2b**; As, x = m: **3a**, x = p: **3b**) and $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(x\text{-}C_6H_4PPh_2\text{-}NPPh_3)$ (x = m: **4a**, x = p: **4b**)

To a yellow solution of 0.189 mmol $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(C(Ph)O)]$ in 10 ml THF 1.5 equivalents of PPh_4Cl (106 mg), d_{20}-PPh_4Br (112 mg), $AsPh_4Cl(H_2O$ (124 mg) or $N(PPh_3)_2Cl$ (163 mg), respectively, were added. The latter salts were not completely dissolved. The resulting suspension was heated to 45°C for 4 h. The formation of **2a**–**b**, d_{20}–**2a**–**b**, **3a**–**b**, **4a**–**b**, was controlled by ^{31}P-NMR and was found to be almost quantitative. Accompanying ν(CO) IR spectra confirmed the release of PhCHO. The resulting suspensions were concentrated in vacuo to 1 ml. Subsequently, the *m*- and *p*-isomers were separated by PLC using the following solvent mixtures: **2a**/**2b** and d_{20}-**2a**/d_{20}-**2b**, dichloromethane:*n*-hexane = 1:1.5; **3a**/**3b**, dichloromethane:*n*-hexane = 1:1.25; **4a**/**4b**, dichloromethane:*n*-hexane = 1:1. After evaporation the amorphous, colorless products were obtained in the following yields: **2a**, 44% (92 mg); **2b**, 8% (17 mg); d_{20}-**2a** 40% (85 mg); d_{20}-**2b**, 7% (15 mg); **3a**, 23% (50 mg); **3b**, 5% (10 mg); **4a**, 20% (49 mg); **4b**, 17% (42 mg).

Table 2
Selected bond lengths (Å) and angles (°)

For 1^-		For **2b**	
Bond lengths			
Re(1)–Re(2)	3.1667(9)		3.1637(8)
Re(1)–P(1)	2.444(4)		2.442(2)
Re(2)–P(1)	2.469(4)		2.469(2)
Re(1)–C(4)	2.21(2)	Re(1)–C(44)	2.235(8)
C(4)–O(4)	1.23(2)		
C(4)–C(31)	1.54(2)		
Bond angles			
Re(1)–P(1)–Re(2)	80.27(11)		80.22(7)
P(1)–Re(1)–Re(2)	50.21(9)		50.26(5)
P(1)–Re(2)–Re(1)	49.52(9)		49.52(5)
Re(1)–Re(2)–C(6)	113.7(4)	Re(1)–Re(2)–C(4)	116.0(2)
Re(2)–Re(1)–C(2)	120.0(6)	Re(2)–Re(1)–C(6)	117.5(2)

4.3. Reaction of $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(C(Ph)\text{-}O)]$ with $SbPh_4Br$

A yellow solution of 0.189 mmol $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7ax\text{-}(C(Ph)O)]$ in 10 ml THF was heated with 1.5 equivalents of $SbPh_4Br$ (145 mg) to 60°C for 5 h. Within the first hour, the color of the suspension turned brown. Accompanying ^{31}P-NMR spectra showed at least ten new signals. After cooling to room temperature the volatiles were removed in vacuo and the brown residue was separated by PLC with a dichloromethane:*n*-hexane (1:2) solvent mixture. This yielded in order of elution: PhCHO and **5** (19%, 44 mg).

4.4. Spectroscopic data

δ values ^{1}H-NMR spectra ($CDCl_3$, standard TMS): **2a**, − 13.2 (d, $^2J_{PH} = 7.6$ Hz, 1H, μ-H); 0.8–2.3 (m, 22H, Cy); 6.8 (dd, $^3J_{PH} = 13.2$ Hz, $^3J_{HH} = 7.6$ Hz, 1H, $Re(C_6H_4)\text{-}H^4$); 7.0 (dt, $^3J_{HH} = 7.4$ Hz, $^4J_{PH} = 4.6$ Hz, 1H, $Re(C_6H_4)\text{-}H^5$); 7.5–7.9 (m, 15H, Ph); 8.1 (d, $^3J_{PH} = 13.2$ Hz, 1H, H^2); 8.2 (d, $^3J_{HH} = 7.1$ Hz, 1H, $Re(C_6H_4)\text{-}H^6$). **2b**, − 13.0 (d, $^2J_{PH} = 7.6$ Hz, 1H, μ-H); 0.8–2.3 (m, 22H, Cy); 6.7 (dd, $^3J_{PH} = 13.2$ Hz, $^3J_{HH} = 7.6$ Hz, 2H, $Re(C_6H_4)\text{-}H^3$); 7.2–7.8 (m, 15H, Ph); 8.2 (dd, $^3J_{HH} = 7.6$ Hz, $^4J_{PH} = 5.1$ Hz, 2H, $Re(C_6H_4)\text{-}H^2$). d_{20}-**2a**, 0.8–2.34 (m, 22H, Cy). d_{20}-**2b**, 0.78–2.32 (m, 22H, Cy). **3a**, − 13.19 (d, $^2J_{PH} = 7.4$ Hz, 1H, μ-H); 0.82–2.26 (m, 22H, Cy); 6.76 (d, $^3J_{HH} = 7.8$ Hz, 1H, $Re(C_6H_4)\text{-}H^4$); 6.98 (t, $^3J_{HH} = 7.5$ Hz, 1H, $Re(C_6H_4)\text{-}H^5$); 7.55–7.91 (m, 15H, Ph); 8.04 (s, 1H, $Re(C_6H_4)\text{-}H^2$); 8.15 (d, $^3J_{HH} = 7.3$ Hz, 1H, $Re(C_6H_4)\text{-}H^6$). **3b**, − 13.0 (d, $^2J_{PH} = 7.7$ Hz, 1H, μ-H); 0.85–2.3 (m, 22H, Cy); 6.67 (d, $^3J_{HH} = 8.1$ Hz, 2H, $Re(C_6H_4)\text{-}H^3$); 7.5–7.8 (m, 15H, Ph); 8.22 (d, $^3J_{HH} = 7.9$ Hz, 2H, $Re(C_6H_4)\text{-}H^2$). **4a**, − 13.18 (d, $^2J_{PH} = 7.5$ Hz, 1H, μ-H); 0.9–2.4

(m, 22H, Cy); 6.63–6.68 (m, 2H, Re(C_6H_4)-H^4 and H^5); 7.35–7.9 (m, 25H, Ph); 7.92(d, $^3J_{HH} = 5.0$ Hz, 1H, Re(C_6H_4)-H^6); 8.0 (d, $^3J_{PH} = 14.1$ Hz, 1H, Re(C_6H_4)-H^2). **4b**, − 13.04 (d, $^2J_{PH} = 7.8$ Hz, 1H, μ-H); 0.9–2.3 (m, 22H, Cy); 6.42 (dd, $^3J_{PH} = 13.9$, $^3J_{HH} = 7.9$ Hz, 2H, Re(C_6H_4)$_3$-H^3); 7.3–7.7 (m, 25H, Ph); 7.85 (dd, $^3J_{HH} = 7.6$, $^4J_{PH} = 4.7$ Hz, 2H, Re(C_6H_4)-H^2). **5**, 0.8–2.3 (m, 22H, Cy), 7.1–7.4 (m, 15H, Ph).

δ values ^{31}P-NMR spectra ($CDCl_3$, standard 85% H_3PO_4): **2a**, 22.8 (s, 1P, P^+); 59.2 (s, 1P, μ-P). **2b**, 23.6 (s, 1P, P^+); 58.2 (s, 1P, μ-P). d_{20}-**2a**, 22.6 (s, 1P, P^+); 58.8 (s, 1P, μ-P). d_{20}-**2b**, 23.3 (s, 1P, P^+); 57.9 (s, 1P, μ-P). **3a**, 59.4 (s, 1P, μ-P). **3b**, 58.5 (s, 1P, μ-P). **4a**, 19.4 (d, $^2J_{PP} = 6$ Hz, 1P, PPh_2); 23.5 (d, $^2J_{PP} = 6$ Hz, 1P, PPh_3); 59.0 (s, 1P, μ-P). **4b**, 20.1 (d, $^2J_{PP} = 6$ Hz, 1P, PPh_2); 24.1 (d, $^2J_{PP} = 6$ Hz, 1P, PPh_3); 58.6 (s, 1P, μ-P). **5**, − 76.5 (s, 1P, μ-P).

ν(CO) IR data in THF (cm^{-1}): **2a**, 2076 m, 1987 vs, 1975 m, 1962 m, 1927 vs, 1889 vs, 1871 vs. **2b**, 2076 m, 1987 vs, 1975 m, 1962 m, 1927 vs, 1889 vs, 1871 vs. d_{20}-**2a**, 2075 s, 1986 s, 1975 sh, 1957 m, 1925 s, 1886 vs, 1871 vs. d_{20}-**2b**, 2075 m, 1986 s, 1975 sh, 1961 m, 1927 vs, 1890 vs, 1871 vs. **3a**, 2076 s, 1987 s, 1975 sh, 1962 m, 1927 vs, 1889 vs, 1871 vs. **3b**, 2076 s, 1987 s, 1975 sh, 1962 m, 1927 vs, 1891 vs, 1871 vs. **4a**, 2076 m, 1985 s, 1973 sh, 1964 m, 1925 vs, 1885 vs, 1869 vs. **4b**, 2074 m, 1987 m, 1975 sh, 1962 m, 1925 vs, 1887 vs, 1870 vs. **5**, 2094 m, 2067 w, 2038 w, 2017 sh, 1996 vs, 1936 vs, 1898 vs.

Elemental analysis: **2a**, $C_{43}H_{42}O_7P_2Re_2$ ($M_r = 1105.16$), C 46.80 (calc. 46.73); H 3.77 (3.83). **2b**, $C_{43}H_{42}O_7P_2Re_2$ ($M_r = 1105.16$), C 46.91 (46.73); H 3.71 (3.83). **3a**, $C_{43}H_{42}AsO_7PRe_2$ ($M_r = 1149.11$), C 45.10 (44.95); H 3.77 (3.68). **3b**, $C_{43}H_{42}AsO_7PRe_2$ ($M_r = 1149.11$), C 45.12 (44.95); H 3.75 (3.68). **4a**, $C_{55}H_{52}NO_7P_3Re_2$ ($M_r = 1304.36$), C 50.66 (50.64); H 4.19 (4.02); N 1.12 (1.07). **4b**, $C_{55}H_{52}NO_7P_3Re_2$ ($M_r = 1304.36$), C 50.61 (50.64); H 4.08 (4.02); N 1.01 (1.07). **5**, $C_{37}H_{37}BrO_7PSbRe_2$ (M_r 1198.74), C 36.98 (37.29); H 3.02 (3.11).

4.5. X-ray data collection, structure solution and refinement

PPH$_4$. An orange-yellow crystal, size 0.60 × 0.35 × 0.16 mm^3, was used for data collection at $T = 293$ K. Lattice parameters were refined from 34 reflections $15 \leq 2\theta \leq 40°$. A total of 11 152 intensities were collected $-14 \leq h \leq 14$, $0 \leq k \leq 18$, $0 \leq l \leq 39$; three standard reflections were recorded every 400. LP correction, absorption correction via ψ-scans, min/max transmission 0.44/0.99, after merging ($R_{int} = 0.043$) 10 959 unique intensities. The structure was solved by direct and conventional Fourier methods, full-matrix least-squares refinement based on F^2 and 549 parameters; all but H-atoms and disordered cyclohexyl-C-atoms were refined anisotropically; cyclohexyl group C21–C26 was found disordered over two sites and refined with a split model with half occupation of C23–C26 each and full occupation for C21 and C22; hydrogen atoms were refined at idealized positions with riding model, the μ-H position was not determined.

2b. A colorless crystal, size 0.36 × 0.31 × 0.09 mm^3, was used for data collection as before. Lattice parameters were refined from 25 reflections $14 \leq 2\theta \leq 25°$. 10 697 intensities collected $-14 \leq h \leq 14$, $-18 \leq k \leq 18$, $0 \leq l \leq 19$; standards and corrections as before, min/max transmission 0.39/0.70, after merging ($R_{int} = 0.033$) 10 293 unique intensities. Structure solution and refinement as before, 530 parameters, hydrogen atoms as before, the μ-H position was determined from ΔF-map and refined. Two independent half benzene solvent molecules per asymmetric unit.

For both structures SHELXTL V5 [15] was used for structure solution and refinement.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC-104497 for PPh_4(**1**) and CCDC-104498 for **2b**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-366-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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