Thermolysis of Re$_2$(CO)$_{10-n}$(P(C$_6$H$_5$)$_3$)$_n$ (*n* = 1, 2)

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Heating Re$_2$(CO)$_8$(ax-L)$_2$ (1) [L = P(C$_6$H$_5$)$_3$] in xylene solution in a sealed glass tube at 180–230 °C gives six products of two types: first, Re$_2$(CO)$_{8-n}$L$_n$(μ-H)(μ-P(C$_6$H$_5$)$_2$) (*n* = 1, eq-L, 2; *n* = 2, eq-L, 3); second, (C$_6$H$_5$)$_2$PC$_6$H$_3$(C=O)Re(CO)$_{4-m}$L$_m$Re-(CO)$_{4-n}$L$_n$ (*m* = 1, ax-L, *n* = 0, 4; *m* = *n* = 1, ax-L, 5; *m* = 1, eq-L, *n* = 1, ax-L, 6; *m* = 0, *n* = 2, ax-L, 7). At 160 °C only 2 and 3 are observed. The complex Re$_2$(CO)$_8$(μ-H)(μ-P(C$_6$H$_5$)$_2$) (8) is obtained by thermolysis of Re$_2$(CO)$_9$(ax-L) (9) in xylene solution at 180 °C. Thermolysis of 2 in decalin solution at 240 °C leads to Re$_3$(CO)$_9$(μ-P(C$_6$H$_5$)$_2$)$_3$ (10). ^{1}H and ^{31}P NMR data have been measured for the newly synthesized compounds. The molecular structures of 2, 4, and 10 have been determined from X-ray data collected on an automated diffractometer with monochromatized Mo Kα radiation. Compounds 2 and 4 crystallize in the monoclinic space group P2$_1$/n (No. 14), and 10 crystallizes in P2$_1$/a (No. 14), with Z = 4: 2, *a* = 13.431 (9) Å, *b* = 11.804 (5) Å, *c* = 23.072 (12) Å, β = 102.78 (6)°; 4, *a* = 16.800 (2) Å, *b* = 12.077 (3) Å, *c* = 23.048 (3) Å, β = 92.82 (1)°; 10, *a* = 11.670 (3) Å, *b* = 23.151 (14) Å, *c* = 16.327 (3) Å, β = 90.08 (3)°. The molecular structure of the diamagnetic compound 2 contains two octahedrally coordinated rhenium atoms with a hydrido- and diphenylphosphido-bridged Re–Re bond (Re–Re = 3.152 (1) Å). The μ-H position could not be evaluated from a Fourier map. Therefore, the presence of the monohydride compound was shown by the results of ^{1}H high-field NMR measurements. The eq-L ligand in 2 is trans-positioned to the μ-P(C$_6$H$_5$)$_2$ group. The molecular structure of the secondary metalation product 4 possesses two rhenium atoms, each with an essentially octahedral arrangement of the ligands. One rhenium atom is coordinated by four carbonyl groups while the other is coordinated by three carbonyl groups and a triphenylphosphine. The two rhenium atoms are bridged by a quadridentate ligand that is bidentate to each metal atom. The molecule has an extended planar tricyclic ring system that includes the bridging ligand and both metal atoms. A comparison of its bond parameters with those of related rhenium and manganese compounds is given. The molecular structure of 10 shows as a central fragment a three-membered ring of rhenium atoms [average Re–Re = 2.914 (4) Å] edged-bridged by diphenylphosphido groups. Each rhenium coordination sphere contains, besides the two trans-positioned μ-P ligand atoms, three additional CO groups having a meridional ligand arrangement.

Introduction

This study follows earlier work on the high-temperature reduction of Re$_2$(CO)$_{10}$ or Re$_2$(CO)$_8$L$_2$ (L = PPh$_3$) with indium[1,2] or indium(I) halides.[3] We undertook the present examination to determine what types of products may be obtained from a triphenylphosphine-substituted dirhenium decacarbonyl in the absence of these indium compounds. Indeed, we observe carbon–phosphorus cleavage and/or ortho-metalation products, as might be expected.[4–8] These types of reactions are of importance in metal cluster compounds if they are suitable for a catalytic reaction process.[9–11] Furthermore, complexes with metallacycles are of general interest with regard to a direct synthesis,[12,13] extended π-delocalization effects in their fused-ring system, and preparation of materials with pseudo-one-dimensional electronic properties.[14] Finally, the hydrido- and phosphido-bridged dirhenium clusters will be used for a neutron diffraction study because the present structural knowledge about μ-H bonds in organometallic dirhenium compounds is hitherto based on X-ray data.[12,15]

Experimental Section

The reactions were performed in deoxygenated solvents dried by standard methods. The thermolysis reactions of Re$_2$(CO)$_8$(P(C$_6$H$_5$)$_3$)$_2$ were carried out in sealed glass tubes (inner diameter 10 mm and length 180 mm) that were dried by heating under vacuum conditions and stored at room temperature under an argon atmosphere before use.

Materials. *trans*-Re$_2$(CO)$_8$(P(C$_6$H$_5$)$_3$)$_2$ was prepared according to the

Table I. ^{31}P{^{1}H} NMR Data for 2–7 and 10

complex	^{31}P{^{1}H} resonance, δ^a
2	54.84 (d, ^2J(PP) = 69.4 Hz; 1 P, μ-PPh$_2$)
	9.1 (d, ^2J(PP) = 69.3 Hz; 1 P, PPh$_3$)
3	51.34 (t, ^2J(PP) = 70.7 Hz; 1 P, μ-PPh$_2$)
	9.69 (d, ^2J(PP) = 70.6 Hz; 2 P, PPh$_3$)
4	28.42 (s; 1 P, PPh$_2$)
	20.85 (s; 1 P, PPh$_3$)
5	30.95 (d, ^2J(PP) = 24.9 Hz; 1 P, PPh$_2$)
	19.38 (s; 1 P, ax-PPh$_3$)
	3.82 (d, ^2J(PP) = 24.8 Hz; 1 P, ax-PPh$_3$)
6	32.94 (d, ^2J(PP) = 118.75 Hz; 1 P, PPh$_2$)
	19.55 (s; 1 P, PPh$_3$)
	14.99 (d, ^2J(PP) = 119.10 Hz; 1 P, eq-PPh$_3$)
7	27.72 (s; 1 P, PPh$_2$)
	26.61 (s; 2 P, PPh$_3$)
10	56.53 (s, 1 P, μ-PPh$_2$)

^{a} Bruker FT-NMR WP 250; CDCl$_3$ solution at 25 °C; H$_3$PO$_4$ (85%) as standard.

literature method.[16] Re$_2$(CO)$_{10}$ was purchased from Strem Chemicals.

Thermolysis Products. A 0.37-g (0.33-mmol) sample of Re$_2$(CO)$_8$-(ax-L)$_2$ (1) [L = P(C$_6$H$_5$)$_3$] in xylene solution (2 mL) was heated for 14 days at 230 °C. The color of the solution changed from colorless to orange. To separate the reaction products, the contents of the glass tube were washed out with xylene and the solvent was vacuum-stripped to leave an orange air-stable solid. The components of this residue were obtained by use of the TLC separation procedure (PSC plate, silica 60, Fa. Merck) with CHCl$_3$/*n*-hexane (3:1) as eluant. The chromatogram obtained was divided into four yellow regions, from each of which one or two components were dissolved in CHCl$_3$, crystallized by the vapor diffusion method (CHCl$_3$/*n*-hexane), and identified as the following products, listed in order of decreasing R_f values: colorless Re$_2$(CO)$_7$L-(μ-H)(μ-P(C$_6$H$_5$)$_2$) (2) (150 mg, 40.5% based on 1); yellow (C$_6$H$_5$)$_2$PC$_6$H$_3$(C=O)Re(CO)$_3$(ax-L)Re(CO)$_4$ (4) (120 mg; 32.4%); yellow (C$_6$H$_5$)$_2$PC$_6$H$_3$(C=O)Re(CO)$_3$(ax-L)[Re(CO)$_3$(ax-L)] (5) (20 mg; 5.4%) and the isomeric orthometalated compound 6 ($\leq$10 mg; $\leq$2.7%); orange (C$_6$H$_5$)$_2$PC$_6$H$_3$(C=O)Re(CO)$_4$[Re(CO)$_2$(ax-L)$_2$] (7) (5 mg; 1.4%) and Re$_2$(CO)$_6$(ax-L)$_2$(μ-H)(μ-P(C$_6$H$_5$)$_2$) (3) (25 mg, 6.8%). Product pairs were separated by fractional crystallization from the CHCl$_3$/hexane solvent mixture.

Analytical and Spectral Data. ^{31}P NMR (Bruker WP 250) absorbance resonance signals of the products 2–8 are given in Table I.

2. Mp: 220 °C. Anal. Calcd for 2: C, 43.40; H, 2.5. Found: C, 43.52; H, 2.80. IR frequencies (cm^{-1}) (Perkin-Elmer, 577): ν(C=O)

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Table II. Crystal Data for **2**, **4**, and **10**

	2	**4**	**10**
formula	$C_{37}H_{26}O_7P_2Re_2$	$C_{44}H_{28}O_8P_2Re_2$	$C_{45}H_{30}O_9P_3Re_3$
mol wt	1015.9	1119.1	1366.3
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)
a, Å	13.431 (9)	16.800 (2)	11.670 (3)
b, Å	11.804 (5)	12.077 (3)	23.151 (14)
c, Å	23.072 (12)	23.048 (3)	16.327 (3)
β, deg	102.78 (6)	92.82 (1)	90.08 (3)
V, Å^3	3567	4670.6	4411.1
Z	4	4	4
D_{calcd}, g cm^{-3}	1.891	1.591	2.056
radiation	Mo Kα	Mo Kα	Mo Kα
μ, cm^{-1}	66.1	50.8	80.1
$F(000)$	1932	2144	2568
cryst dimens, mm	0.15 × 0.35 × 0.45	0.10 × 0.20 × 0.35	0.20 × 0.20 × 0.05
no. of reflcns	2818	8863	5984
2θ range, deg	2–36	2–50	1–45
min/max h,k,l	−11/11,0/10,0/19	−20/20,0/14,0/27	0/12,−23/23,0/17
stds/repeated every reflcn	2/300	2/280	3/500
no. of unique rflcns, $F > 4\sigma(F)$	2206	5604	2847
R_{int}	0.044	0.015	0.053
no. of refined params	154	186	200
max Δ/σ in final cycle	0.002	0.008	0.01
max height in final ΔF, e/Å^3	0.8	1.0 (near Re position)	1.2 (near Re position)
R	0.057	0.065	0.087
programs used and other resources[d]	SHELX 76,[a] PLUTO[b]	SHELX 76, PLUTO	SHELXTL PLUS[c]

[a] Sheldrick, G. M. "SHELX 76"; University of Göttingen: Göttingen, FRG, 1976. Sheldrick, G. M. "SHELXTL PLUS"; University of Göttingen: Göttingen, FRG, 1985. (Programs for crystal structure determination.) [b] Motherwell, S. "PLUTO"; University of Cambridge: Cambridge, England, 1978. [c] Nicolet Instrument Corp., 1987. [d] Scattering factors corrected for anomalous dispersion from: *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(CHCl$_3$) 2087 w, 2040 w, 1998 vs, 1950 s, 1919 m. ^{1}H NMR data (δ) (CDCl$_3$ solution): 7.30 (m, 25 H, Ph), −13.87 (dd, ^2J(PH) = 4.15 and 15.5 Hz, 1 H, ReH).

3. Dec pt: 238 °C. Anal. Calcd for **3**: C, 51.82; H, 3.33. Found: C, 51.47; H, 3.61. IR frequencies (cm^{-1}): ν(C=O) (CHCl$_3$) 2050 vw, 2025 w, 1970 vs, 1915 sh, 1908 m. ^{1}H NMR data (δ) (CDCl$_3$): 7.30 (m, 40 H, Ph), −13.34 (dt, ^2J(PH) = 3.5 and 12.4 Hz, 1 H, ReH).

4. Mp: 219 °C. Anal. Calcd for **4**: C, 47.25; H, 2.50. Found: C, 47.28; H, 2.59. IR frequencies (cm^{-1}): ν(C=O) (CHCl$_3$) 2090 m, 2010 vs, 1995 s, 1972 m, 1935 m, 1885 m; ν(C=O) (KBr) 1453 m.

5. Mp: 224 °C. IR frequencies (cm^{-1}): ν(C=O) (CHCl$_3$) 2090 w, 2030 m, 2008 vs, 1958 m, 1922 s, 1885 m, 1822 w, 1800 w; ν(C=O) (KBr) 1451 m.

7. Mp: 205 °C. IR frequencies (cm^{-1}): ν(C=O) (CHCl$_3$) 2090 m, 2000 sh, 1995 vs, 1967 s, 1917 s, 1895 sh, 1835 s; ν(C=O) (KBr) 1454.

Effect of Other Selected Reaction Conditions on the Thermolysis Reaction of 1 Obtained by Separate Experiments. Following the aforementioned procedure for this reaction, we found that a shortening of the reaction time from 14 to 7 days and an addition of indium or gallium metal (0.7 g; 10 mmol) failed to affect the nature and yield of the products **2–7**. However, they were affected by decreasing the reaction temperature from 230 via 200 to 160 °C. At 200 °C the reaction showed first a loss of the products **5** and **7**, second an improved yield of about 6% of **2**, and third a lower yield of **4** (100 mg; 27%). Finally, at 160 °C after 7 days the reaction gave the dirhenium clusters **2** (220 mg; 60.0%) and **3** (45 mg; 12.2%) without the orthometalated compounds.

Thermolysis of 2. The starting material **2** (0.08 g; 0.08 mmol) was heated in decalin solution (2 mL) at 240 °C for 3 days. The colorless solution became red. The product was chromatographically (Al$_2$O$_3$ column, 20-mm i.d., 200 mm) separated with CHCl$_3$/n-hexane 3:1 as eluant. From the eluted solution was obtained 0.02 g (56%) of red Re$_3$(CO)$_9$(μ-P(C$_6$H$_5$)$_2$)$_3$ (**10**) as the only product of crystallization (vapor diffusion method).

Thermolysis of Re$_2$(CO)$_9$(PPh$_3$) (9). In a glass tube, 4 mL of a xylene solution of **9**[16] (0.11 g; 0.12 mmol) was heated for 3 days at 180 °C. Separation of the reaction mixture was done by TLC, and 0.08 g (73%) of colorless Re$_2$(CO)$_8$(μ-H)(μ-PPh$_2$) was isolated. Anal. Calcd for Re$_2$(CO)$_8$(μ-H)(μ-PPh$_2$): C, 30.67; H, 1.41. Found: C, 30.44; H, 1.67. IR frequencies (cm^{-1}): ν(C=O) (CHCl$_3$) 2105 m, 2080 m, 2008 s, 1995 m, 1955 s. ^{1}H NMR data (δ) (CDCl$_3$): 7.35 (m, 10 H, Ph), −15.02 (d, ^2J(PH) = 4.5 Hz, ^{1}H, ReH). Mass spectroscopic measurements (Varian MAT 311A) were carried out at 70 eV with vaporization at 140 °C: m/e 784.4 [M$^+$(^{185}Re)].

X-ray Analysis of 2. Lattice parameters were refined from 23 reflections for $2 \le 2\theta \le 12°$. The space group was determined from Buerger precesion photographs. Reflections were collected on a Syntex
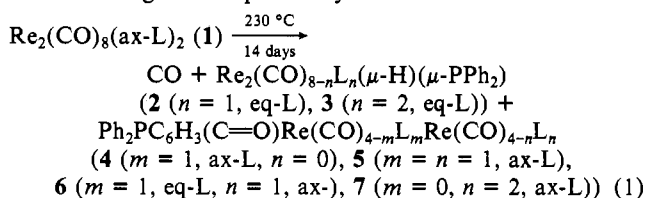
P3 diffractometer by using the ω–2θ scan technique. Lp and absorption (via ψ scans) corrections were applied. The structure was solved by interpretation of the Patterson map (Re atoms); the remaining atoms could be located from subsequent ΔF syntheses; hydrogen atoms were located from geometrical considerations. Re and P atoms were refined anisotropically. Phenyl groups were treated as rigid bodies (C–C = 1.395 Å, C–H = 0.96 Å). Further information is given in Table II. The localization of the bridging H atom could only be estimated by calculations based on the known position of the bridging H atom in the analogous dimanganese compound Mn$_2$(CO)$_8$(μ-H)(μ-P(C$_6$H$_5$)$_2$).[17]

X-ray Analysis of 4. Lattice parameters were refined from 25 reflections for $5 \le 2\theta \le 13°$. The space group was determined from Weissenberg photographs. Reflections were collected on a Syntex P3 diffractometer, with a ω–2θ scan and Lp and absorption corrections (ψ scans) applied. Structure solving and refinement are as described for **2**.

X-ray Analysis of 10. Lattice parameters were refined from 22 reflections for $4 \le 2\theta \le 16°$. The space group was determined from Buerger precesion photographs. Reflections were collected on a Nicolet R 3m/V diffractometer, with a ω–2θ scan and Lp and absorption corrections (ψ scans) applied. Structure solving and refinement were as described above.

Results and Discussion

The thermolysis reaction of Re$_2$(CO)$_8$(ax-L)$_2$ (**1**) (L = PPh$_3$) in xylene solution, in the presence or absence of molten indium metal, leads to the organometallic dirhenium compounds **2–7** with the formulas given in eq 1. They have been characterized with

$$Re_2(CO)_8(ax\text{-}L)_2 \ (1) \xrightarrow[14\ days]{230\ °C}$$
$$CO + Re_2(CO)_{8-n}L_n(\mu\text{-}H)(\mu\text{-}PPh_2)$$
$$(2 \ (n = 1, \ eq\text{-}L), \ 3 \ (n = 2, \ eq\text{-}L)) +$$
$$Ph_2PC_6H_3(C=O)Re(CO)_{4-m}L_mRe(CO)_{4-n}L_n$$
$$(4 \ (m = 1, \ ax\text{-}L, \ n = 0), \ 5 \ (m = n = 1, \ ax\text{-}L),$$
$$6 \ (m = 1, \ eq\text{-}L, \ n = 1, \ ax\text{-}), \ 7 \ (m = 0, \ n = 2, \ ax\text{-}L)) \quad (1)$$

the exception of **6** by the results of X-ray single-crystal analyses, because no distinction on the basis of their ^{1}H and ^{31}P NMR and IR spectral data could be made between the possible isomers of each substance. Afterward, the structure proposed for the remaining product **6**, a stereoisomer of **5**, was derived from a comparison of the ^{31}P NMR data for both compounds. These

(17) Doedens, R. J.; Robinson, W. T.; Ibers, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 4323.

compounds can be divided into the following two types: first, the triphenylphosphine substitution products of $(\mu$-hydrido$)(\mu$-diphenylphosphido)bis(tetracarbonylrhenium) **2** and **3**; second, heptacarbonyl$(\mu$-2-formyl-3-(diphenylphosphino)phenylido-*O*,-*P*,C^α,C^1)(triphenylphosphine)dirhenium (**4**) and its triphenylphosphine derivatives **5–7**. The compounds of both types are obtained in a total yield of 90% [41% **2**, 7% **3**, 32% **4**, 5% **5**, 3% **6**, and 1% **7**, each with respect to **1** (100%)]. All identified thermolysis products were previously unknown, but a related compound of the second type, the secondary metalated substance Ph$_2$PC$_6$H$_3$(C=O)Re(CO)$_4$Re(CO)$_4$, has been formerly prepared by another synthetic route.[18]
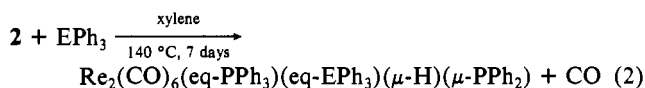
As has been shown by the results of separate experiments, the type and yield of the substances obtained are not changed by shortening of the reaction time from 14 to 7 days, a change of the inner volume of the tube from 8 to 16 mL, addition of PPh$_3$ (0.03 mmol), or addition of In or Ga. In contrast, a decided alteration in the observed products of both types takes place if the reaction temperature is lowered from 230 via 200 to 160 °C. Above all, this stepwise temperature decrease creates a reduced product yield and a loss of the secondary metalated compounds, whereas the yields of the hydrido-bridged compounds **2** and **3** are always simultaneously improved from 48 via 54 to 72%. Compounds **2** and **4** are also present as thermolysis products of **1** at 180 °C in toluene-d_8 solution. The compound separated from this deuteriated solvent shows, furthermore, by the result of ^{1}H NMR measurements, that the μ-H atom of **2** has its origin from a PPh$_3$ ligand. Because the origin of μ-H atom is controversial,[19] it has been ascertained in separate experiments that traces of water are not involved in the observed thermolysis reaction.

Mechanistic pathways for both product types at least have one essential difference in that the P–C bond cleavage is necessary for the first but not for the second type of compound isolated. Such P–C bond fission is not inhibited if one of the PPh$_3$ ligands is replaced by a CO group, since the monosubstituted compound Re$_2$(CO)$_9$(PPh$_3$) (**9**) has been reacted at 180 °C to give the pyrolysis product Re$_2$(CO)$_8(\mu$-H$)(\mu$-PPh$_2$) (**8**) without the occurrence of a secondary metalation product. This result shows, therefore, that the formation of such a metalation product needs two PPh$_3$ ligands as in **1**. The observed formation of both monohydrides is possibly connected with the key reaction step of an oxidative-addition reaction between the P–C bond of PPh$_3$ and a valence-electron-deficient transition-metal atom[10] resulting from a CO ligand rupture in dirhenium compounds of the type used.[20,21] A reasonable subsequent intermediate may be a triple-bridged dirhenium octacarbonyl compound with bridging hydrido, diphenylphosphido, and σ^2-C$_6$H$_4$ groups, which is analogous to described thermolysis products of Os$_3$(CO)$_{10-n}$(PPh$_3$)$_n$ in refluxing *n*-octane solution.[5,22] This intermediate then decomposes, because of the CO(g) pressure in the sealed tube, to the obtained monohydrides.

The indicated pathway from **1** to **2** with a relatively low activation energy barrier is accompanied at higher reaction temperatures in the range of 180 to 230 °C by the competitive formation of **4**. The formation of the secondary metalation compound has a higher activation energy barrier for Ph–H rupture than for the P–C bond scission. This reaction pathway seems to be associated with a simultaneous Re–Re bond fission in **1**, forming the unobserved but known compounds of PPh$_2$C$_6$H$_4$Re(CO)$_4$[23,24] and HRe(CO)$_4$PPh$_3$. Such intermediates have possibly the capability of undergoing a secondary metalation reaction as PPh$_2$C$_6$H$_4$Re(CO)$_4$ and CH$_3$Re(CO)$_5$ to PPh$_2$C$_6$H$_4$(C=O)Re-

(CO)$_4$Re(CO)$_4$.[18] A PPh$_3$ derivative of the last-named secondary metalated compound is **4**, which is favored over the corresponding unsubstituted compound under CO pressure. Perhaps there is no kinetic pathway for the exchange of the CO and PPh$_3$ ligands. Regarding the PPh$_3$ disubstituted product **7**, it can also be concluded that the Re atom in the oxygen-containing chelate ring is more reactive toward a CO vs PPh$_3$ ligand substitution reaction than the Re atom in the other ring. The facile CO ligand substitution at Re is a feature in common with the corresponding manganese secondary metalation product,[24] but the PPh$_3$-disubstituted stereoisomers isolated for each transition metal are different (Table VII).

Furthermore, the PPh$_3$ disubstitution of **3** results, because of steric reasons, in an unusual cis arrangement at the different Re atoms.[24] This ligand substitution product of **2** suggests that even other EPh$_3$ ligands (E = As, Sb) with a lower π-acceptor capability relative to CO may undergo an equivalent, stereochemically controlled replacement. The correctness of this assumption is shown by structural studies on the products shown in eq 2.

$$\textbf{2} + \text{EPh}_3 \xrightarrow[\text{140 °C, 7 days}]{\text{xylene}}$$
$$\text{Re}_2(\text{CO})_6(\text{eq-PPh}_3)(\text{eq-EPh}_3)(\mu\text{-H})(\mu\text{-PPh}_2) + \text{CO} \quad (2)$$

According to their Guinier powder patterns, they are isostructural with the derivative **7**.[25] The specific mode of ligand substitution can be explained by a thermodynamic trans influence exercised along the $(\mu$-P$)$–Re–CO bond axis (see below).

An attempt to obtain Re clusters of a higher nuclearity with phosphorus atoms has been carried out by pyrolyzing **2** in decalin at 240 °C. This successful reaction leads to Re$_3$(CO)$_9(\mu$-PPh$_2$)$_3$ (**10**), which has been characterized by an X-ray crystal analysis. The comparable thermolysis reaction of the PPh$_3$-unsubstituted compound **8** has recently yielded a first sample of a 44-chemical-valence-electron (44-CVE) cluster of Re$_3$(CO)$_6(\mu_3$-H$)_2(\mu$-PPh$_2$)$_3$[26] instead of the expected **10** with 48 CVE.

Scheme I summarizes the transformations observed in this work.

Spectroscopic Measurements. The results of ^{31}P NMR measurements of the substances are summarized in Table I. The following ^{31}P assignments are made for the secondary metalation compounds. The substance **4** shows two singlets for the ^{31}P chemical shift: one of 20.85 ppm for the triphenylphosphine ligand [P(1), Figure 2] and the second of 28.47 ppm for the ring member PPh$_2$ [P(2)]. The value for the corresponding P ring atom of **6** is 27.72 ppm and indicates little change. The singlet of the trans-positioned triphenylphosphine ligands at the other Re atom in **7** has the δ value of 26.61, and the integral ratio is 1:2. Also, **5** has three P ligand atoms: the P ring atom and PPh$_3$ are cis-positioned at one Re atom, and the PPh$_3$ ligand at the other Re atom has a coordination geometry the nature of which is known from compound **4**. The δ value of 19.38 for the last-named P ligand atom corresponds to that of **4** (20.85 ppm), and the doublets of the cis P atoms were observed at 3.82 ppm [^2J(PP) = 24.95 Hz] and 30.95 ppm [^2J(PP) = 24.88 Hz]. These measured ^{31}P NMR data for the metalated compounds allow the determination of the PPh$_3$ ligand arrangement in compound **6**. It is a diastereoisomer of substance **5** and has five ^{31}P resonance signals: two doublets at 32.94 and at 14.99 ppm [J(PP) = 119 Hz] and a singlet at 19.55 ppm. Whereas the δ values found for the P ring atom in **5** and **6** (32.90 and 32.94 ppm) and the singlet for one PPh$_3$ ligand in **5** and **6** (14.89 and 14.99 ppm) are in good agreement, the doublet of the remaining PPh$_3$ ligand has shifted from 3.82 ppm in **5** to 14.99 ppm in **6** and is accompanied by a ^2J(PP) change from 29.95 to 119 Hz. This means that the cis geometry of the P ligand atoms in **5** is replaced at the corresponding Re atom in **6** by a trans arrangement; the observed ^2J(PP) values of such trans P ligand atoms are comparable to those in similar coordination compounds. The present ^{31}P NMR data from this series of ortho-metalation compounds may be helpful

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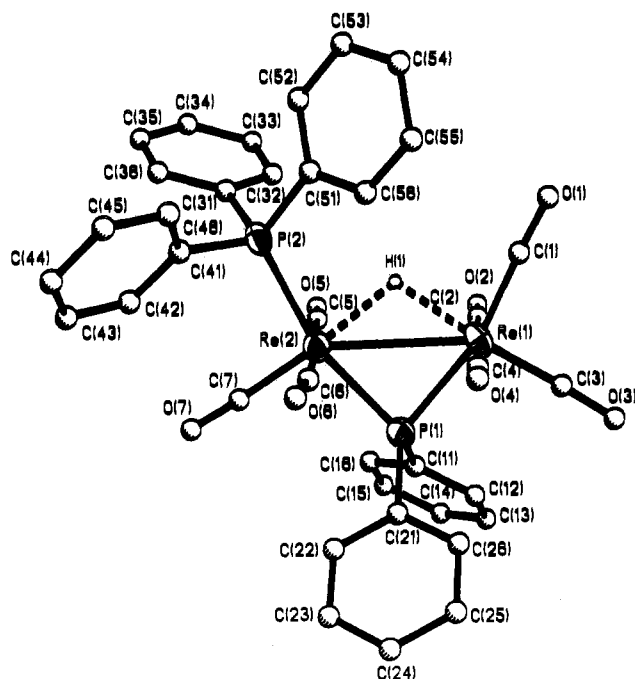(26) Haupt, H. J.; Balsaa, P. *Angew. Chem.*, in press.

Figure 1. Molecular structure of **2** showing the atom-numbering scheme.

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for the Re Atoms and Selected Ligand Atoms in **4** with Esd's in Parentheses

	x	y	z	$U(eq)^a$
Re(1)	1829 (4)	1608 (5)	8995 (3)	38 (3)
Re(2)	1009 (4)	−101 (6)	1285 (3)	44 (4)
P(1)	1275 (24)	3444 (34)	8719 (17)	40 (21)
P(2)	−708 (26)	−484 (34)	7737 (19)	42 (23)
C(1)	2262 (98)	212 (145)	9182 (73)	49 (41)
O(1)	2564 (86)	−653 (127)	9315 (65)	82 (43)
C(2)	2010 (105)	2050 (151)	9780 (81)	56 (45)
O(2)	2109 (86)	2241 (125)	10279 (67)	82 (42)
C(3)	2817 (103)	2042 (143)	769 (75)	51 (42)
O(3)	3437 (96)	2311 (135)	8589 (69)	91 (47)
C(4)	−613 (92)	−1351 (132)	8983 (68)	43 (37)
O(4)	−353 (92)	−2206 (136)	9135 (70)	90 (47)
C(5)	−1350 (113)	1582 (175)	8468 (84)	64 (49)
O(5)	−1553 (94)	2434 (141)	8318 (71)	91 (47)
C(6)	−1003 (116)	591 (165)	9513 (89)	64 (51)
O(6)	−943 (96)	882 (139)	9992 (75)	95 (49)
C(7)	−2112 (129)	−374 (178)	8668 (92)	72 (57)
O(7)	−2781 (107)	−644 (148)	8598 (77)	104 (54)
C(8)	218 (90)	616 (126)	8688 (66)	40 (36)
O(8)	623 (61)	1038 (86)	9104 (46)	44 (25)
C(11)	1861 (63)	4667 (77)	8930 (49)	43 (37)
C(21)	312 (51)	3798 (85)	9019 (41)	39 (35)
C(31)	1129 (61)	3598 (93)	7943 (34)	41 (36)
C(41)	−670 (69)	−1968 (73)	7628 (52)	49 (41)
C(51)	−1273 (64)	5 (98)	7102 (43)	43 (36)
C(61)	275 (82)	72 (125)	7645 (62)	38 (33)
C(65)	1424 (88)	1006 (125)	8152 (65)	39 (35)
C(66)	651 (78)	546 (111)	8147 (58)	30 (30)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

for the further structural determination of octahedrally coordinated transition-metal complexes.

^{1}H resonance absorption signals of the monohydrides **2** and **3** are in the case of the μ-H atom and the phenyl protons in the expected range.[27,28] The coupling constants for Re–H are in good agreement with those of comparable hydrido-bridged rhenium compounds.[28]

Structural Description. Compounds **2**, **4**, and **10** crystallize in a monoclinic unit cell (Table II). Their molecular structures are

(27) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.
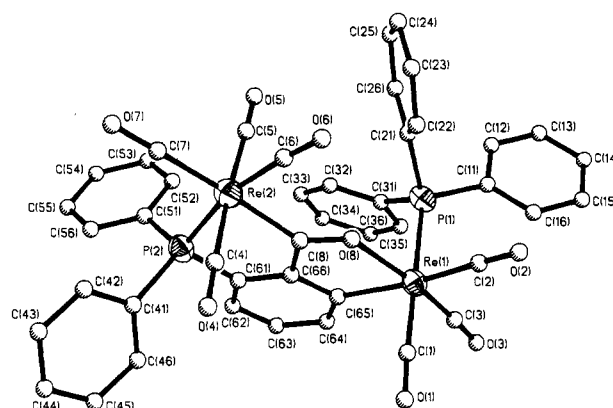(28) Gard, D. R.; Brown, T. L. *Organometallics* **1982**, *1*, 1143.

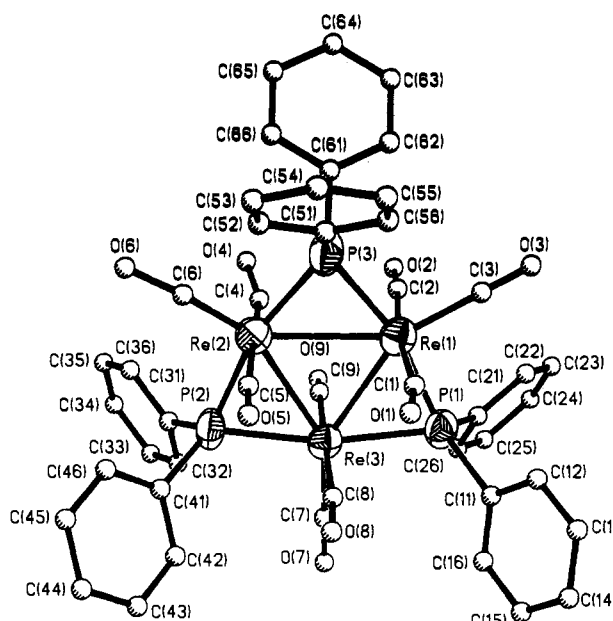**Figure 2.** Molecular structure of **4** showing the atom-numbering scheme.

Figure 3. Molecular structure of **10** showing the atom-numbering scheme.

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for the Re Atoms and Selected Ligand Atoms in **2** with Esd's in Parentheses

	x	y	z	$U(eq)^a$
Re(1)	2169 (1)	2493 (1)	3072 (1)	54 (1)
Re(2)	730 (1)	1494 (1)	3855 (1)	36 (1)
P(1)	2174 (3)	2725 (3)	4119 (2)	41 (3)
P(2)	−717 (3)	440 (4)	3273 (2)	39 (3)
C(1)	1889 (16)	2063 (19)	2265 (10)	80 (6)
O(1)	1731 (13)	1818 (15)	1743 (8)	114 (5)
C(2)	3120 (18)	1150 (20)	3304 (10)	82 (6)
O(2)	3624 (13)	429 (15)	3423 (8)	109 (5)
C(3)	3245 (20)	3433 (20)	3016 (11)	100 (8)
O(3)	3948 (14)	4072 (17)	3006 (8)	129 (6)
C(4)	1234 (15)	3821 (18)	2867 (9)	64 (6)
O(4)	689 (12)	4507 (13)	2719 (7)	93 (5)
C(5)	1544 (15)	122 (18)	4067 (9)	67 (6)
O(5)	2024 (11)	−644 (13)	4215 (6)	88 (4)
C(6)	−123 (13)	2828 (15)	3700 (7)	47 (5)
O(6)	−720 (10)	3559 (10)	3616 (6)	69 (4)
C(7)	423 (12)	1379 (13)	4623 (8)	44 (5)
O(7)	194 (10)	1311 (11)	5072 (7)	80 (4)
C(11)	3365 (8)	2331 (10)	4630 (5)	53 (5)
C(21)	1962 (8)	4127 (7)	4411 (5)	38 (4)
C(31)	−654 (8)	−1088 (7)	3365 (5)	40 (4)
C(41)	−1947 (6)	834 (9)	3441 (4)	33 (4)
C(51)	−973 (9)	579 (10)	2466 (4)	49 (5)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for the Re Atoms and Selected Ligand Atoms in **10** with Esd's in Parentheses

	x	y	z	$U(eq)^a$
Re(1)	−716 (2)	−2412 (1)	8241 (2)	56 (2)
Re(2)	715 (2)	−2410 (1)	6765 (2)	52 (2)
Re(3)	−5 (2)	−3495 (1)	7501 (2)	48 (2)
P(1)	−1136 (12)	−3383 (9)	8748 (12)	58 (14)
P(2)	1140 (12)	−3353 (9)	6289 (10)	47 (13)
P(3)	−32 (16)	−1572 (9)	7469 (13)	63 (13)
C(1)	−2206 (73)	−2355 (48)	7669 (64)	57 (14)
O(1)	−2954 (45)	−2393 (30)	7156 (41)	66 (16)
C(2)	712 (37)	−2418 (23)	8959 (32)	31 (9)
O(2)	1475 (35)	−2418 (22)	9326 (30)	71 (11)
C(3)	−1611 (41)	−1974 (30)	9086 (41)	46 (13)
O(3)	−1938 (28)	−1730 (21)	9584 (27)	52 (9)
C(4)	2009 (35)	−2466 (22)	7459 (29)	24 (10)
O(4)	2997 (34)	−2341 (23)	7692 (32)	75 (11)
C(5)	−708 (64)	−2437 (40)	6041 (54)	88 (20)
O(5)	−1437 (40)	−2368 (25)	5608 (36)	93 (14)
C(6)	1005 (48)	−1913 (31)	5885 (45)	57 (14)
O(6)	1843 (40)	−1793 (26)	5526 (36)	95 (14)
C(7)	−20 (63)	−4271 (41)	7501 (54)	85 (21)
O(7)	10 (36)	−4765 (24)	7569 (33)	75 (12)
C(8)	−1516 (43)	−3521 (27)	6870 (37)	46 (12)
O(8)	−2266 (34)	−3541 (22)	6427 (30)	72 (11)
C(9)	1461 (99)	−3469 (62)	8113 (87)	63 (13)
O(9)	2104 (45)	−3590 (29)	8443 (39)	84 (17)
C(11)	−2585 (22)	−3726 (20)	8785 (34)	65 (16)
C(21)	−572 (36)	−3620 (18)	9732 (22)	59 (14)
C(31)	2625 (25)	−3634 (21)	6316 (23)	48 (13)
C(41)	532 (27)	−3580 (17)	5296 (21)	41 (11)
C(51)	−973 (40)	−1069 (19)	6905 (35)	80 (18)
C(61)	959 (31)	−1100 (19)	8023 (26)	50 (13)

^{a}Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Selected Bond Lengths (Å) and Bond Angles of **2** and **10** with Esd's in Parentheses

Compound 2			
Re(1)–Re(2)	3.152 (1)	P(1)–Re(1)–Re(2)	48.7 (1)
Re(1)–P(1)	2.430 (4)	P(1)–Re(2)–Re(1)	49.7 (1)
Re(1)–C(1)	1.886 (22)	Re(1)–P(1)–Re(2)	81.6 (1)
Re(1)–C(2)	2.032 (23)	P(1)–Re(1)–C(1)	165.5 (6)
Re(1)–C(3)	1.849 (22)	P(1)–Re(1)–C(3)	99.9 (8)
Re(1)–C(4)	1.998 (19)	P(1)–Re(1)–C(4)	90.6 (6)
Re(2)–P(1)	2.392 (4)	C(1)–Re(1)–C(2)	91.6 (9)
Re(2)–P(2)	2.444 (4)	P(2)–Re(2)–Re(1)	112.9 (1)
Re(2)–C(5)	1.955 (20)	P(2)–Re(2)–P(1)	161.9 (1)
Re(2)–C(6)	1.934 (16)	P(2)–Re(2)–C(7)	99.5 (4)
Re(2)–C(7)	1.911 (17)		
P–C(av)	1.828 (10)		
C–O(av)	1.147 (25)		

Compound 10^a			
Re–Re	2.914 (4)	Re–Re–Re	60.0 (1)
Re–P$_{ring}$	2.425 (31)	P–Re–Re	53.0 (1)
Re–C	1.96 (6)	Re–P–Re	74.0 (1)
P–C	1.85 (6)	P–Re–P	165.9 (1)
C–O	1.13 (7)		

^{a} Average values.

Re(2), 48.7 (1)°; P(1), 81.6 (1)°. **3**: Re, 48.3 (1)°; P(1), 83.4 (1)°.

It was acertained by ^{1}H NMR data for **2** in CDCl$_3$ solution at room temperature that the dirhenium compound has a symmetrically bridging H atom, although the position of the μ-H atom could not be derived from the difference Fourier map for the single crystal. To make a proposal for the position of the μ-H atom in the solid structure, a possible extrapolation of the corresponding structural features from the X-ray-determined dirhenium cluster $(\mu\text{-}H)Re_2(CO)_7(\mu\text{-}NC_5H_4)(CH_3NO)$ is also unsuitable because its μ-H atom position is unrefined.[29] At the moment, the proposal must therefore be based on the H–Mn–Mn = 43.9 (2)° and the Mn–H–Mn = 104.1 (5)° bond angles of the homologous derivative $Mn_2(CO)_8(\mu\text{-}H)(\mu\text{-}P(C_6H_5)_2)$ (C_{2v}), which has a planar(μ-H)-Mn$_2$P ring.[17] Using these structural parameters and the Re–Re bond length of **3**, a vector computation delivers the proposed μ-H position in Figure 1. In order to obtain the exact μ-H bond parameters in the dirhenium compounds **3** and **2**, a neutron diffraction crystal analysis is in progress.
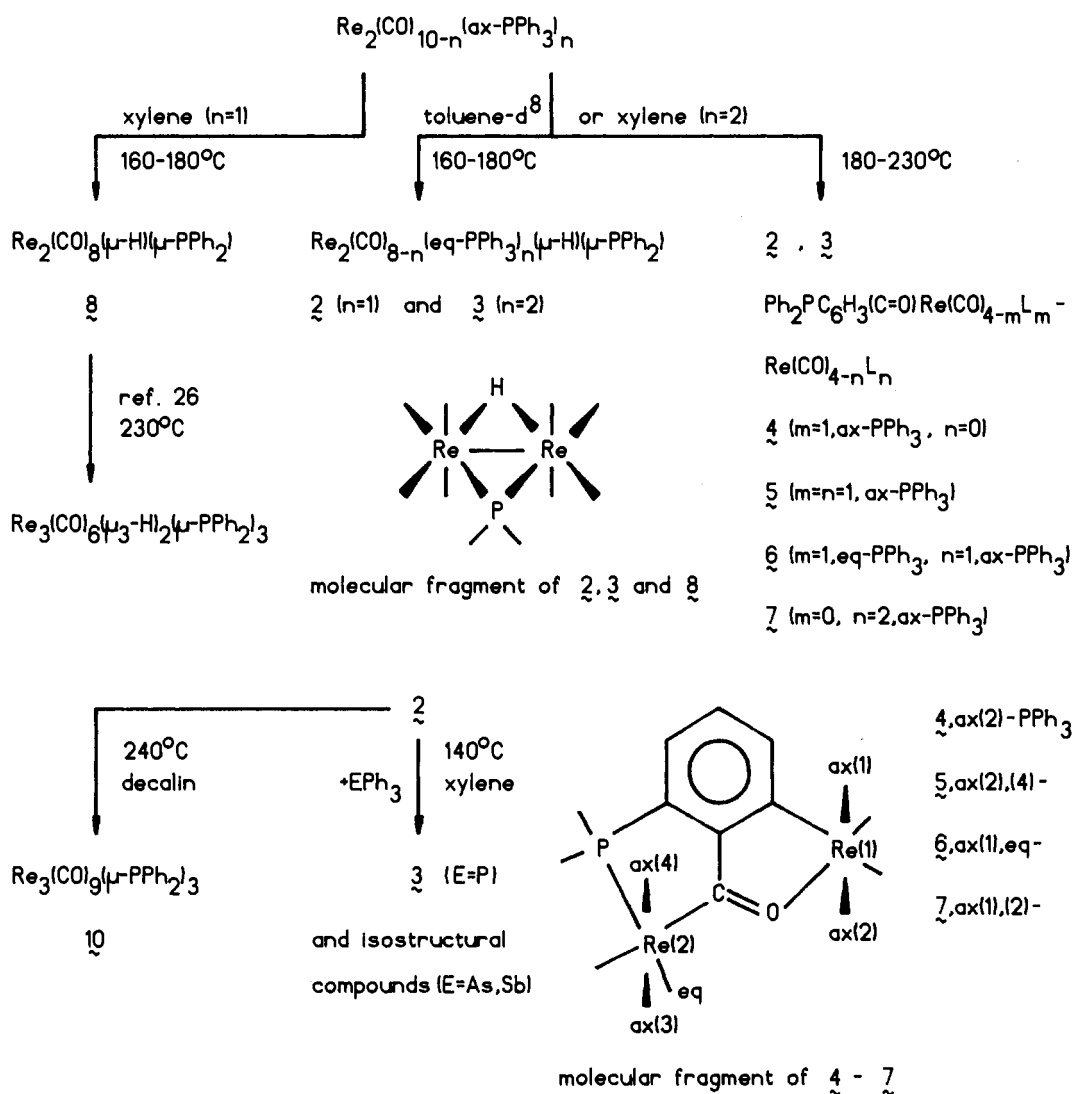
The central molecular framework of **2** is of the type M(μ-H)(μ-P)M (M = transition metal atoms). For this kind of bridge, a MO description has been published[30] and requires a covalent Re–Re single bond. The optimal C_{2v} symmetry of the molecular framework is lost in the series **3**[25] to **2**. This can also be seen from the values of the bond lengths [**3**: Re(1)–P(1), 2.400 (5) Å; Re(2)–P–(1), 2.399 (5) Å. **2**: Re(1)–P(1), 2.430 Å; Re(2)–P(1), 2.392 (4) Å] and of the bond angles subtended at the Re atoms [**3**: 48.3 (1)°. **2**: Re(1), 48.7 (1)°; Re(2), 49.7 (1)°]. Considering the P(1)–Re(1) bond axis the reason for the bond lengthening from **2** to **3** is recognizable as an effect depending on the trans ligands (**3**, PPh$_3$; **2**, CO) with different π-acceptor capabilities. The better π-acceptor ligand CO lengthens the Re(1)–P(1) bond via a synergic interaction, as seen from the simultaneous shortening of the Re–C bond; its value of 1.886 (22) Å and that of the Re(1)–C(3) bond, which nearly is in the same plane, are shorter than the other measured Re–CO bond lengths in **2** and **3**.[25] The thermodynamic trans influence must be responsible for the unusual cis arrangement of both PPh$_3$ ligands in **3** and prevents the possible formation of stereoisomers (see also eq 2).

4. The molecular structure of the secondary metalation compound contains two Re atoms with a distorted-octahedral ligand arrangement (Figure 2). The Re(1) atom is attached to three carbonyl groups and an axially coordinated PPh$_3$, while the Re(2) atom is coordinatively bonded to four carbonyl groups. Compound

presented in Figures 1–3, and the positional parameters of the atoms and selected bond angles and bond lengths are given in Table III–VII.

2. The geometry of the independent Re atoms in the diamagnetic compound **2** is octahedrally distorted due to the unlocated μ-H atom, and the molecular structure results from the sharing of an edge of the two coordination octahedrons at the pseudo-2-fold axis of the Re$_2$(μ-P) ring (Figure 1). Both metal–metal-bonded Re atoms are doubly bridged by a μ-H atom and a μ-PPh$_2$ group, and additionally, Re(1) is coordinatively bonded to four carbonyl ligands and the other Re atom to three carbonyl ligands and a PPh$_3$ group. When viewed down the Re–Re bond, the trans-positioned terminal ligands are approximately eclipsed. To illustrate this geometrical situation in the case of ligand atoms Y [P(2), C(1), C(3), C(7)] near the ring plane, the dihedral angles between the Re(μ-P)Re plane and each Re$_2$Y plane are given. Y, angle: P(2), 6.0°; C(1), 0.8°; C(3), 4.2°; C(7), 1.8°. The eclipsed geometry found, which contrasts with the staggered D_{4d} geometry of Re$_2$(CO)$_{10}$, indicates no significant influence due to a nonbonded intramolecular interaction with the neighboring ligands and needs this orientation for a good overlap of both Re atoms.

The Re–Re bond length of 3.152 (1) Å is consistent with the values reported for other hydrido-bridged Re–Re single bonds. This bond is lengthened by 0.042 (1) Å if the ligand substitution of PPh$_3$ for CO takes place with the formation of Re$_2$(CO)$_6$(eq-PPh$_3$)$_2$(μ-H)(μ-PPh$_2$).[25] The bond elongation in **7**, in which the PPh$_3$ ligands adapt the sterically less favorable cis arrangement at the two Re atoms, is accompanied by an increase of the bond angles P(2)–Re–Re = 112.9 (1)° and C(1)–Re–Re = 116.9 (1)° in **2** to the corresponding angles P(2)–Re–Re = 118.0 (1)° and P–Re–Re = 123.9 (1)° in **3**. The main factor influencing the lengthening of the Re–Re bond and the specified increase in angles is doubtless a repulsive nonbonding interaction between the bulky cis PPh$_3$ ligands. Its effect is also revealed in the expected decrease of the Re$_2$P bond angles subtended at the Re atoms and an increase of the analogous angles at the P atoms. **2**: Re(1), 49.7 (1)°;

(29) Nubel, P. O.; Wilson, S. R.; Brown, T. L. *Organometalllics* **1983**, *2*, 515.

(30) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *J. Organomet. Chem.* **1974**, *30*, 413.

Scheme I

7 can be derived from **4** through a replacement of the CO(6) ligand by PPh$_3$ at the Re(1) atom. The other derivative **5**, which is a diastereoisomer of **7**, results from a CO(4) vs. PPh$_3$ ligand exchange at the Re(2) atom in **4**. All three compounds show a bridging of both Re atoms with a quadridentate ligand that is bidentate to each Re atom.

The central molecular fragment of this chelate ligand exhibits an extended tricyclic ring system containing one 1,2,3-trisubstituted benzene ring fused with the rings containing Re(1) and Re(2). The first structural description of such a ring system with two manganese atoms and a combination of manganese and rhenium atoms was given by Kaesz et al.[18,24] Their ring parameters and those of the rhenium compounds in this work are summarized in Table VII. A least-squares plane treatment of the ring atoms in the two compounds has been undertaken to characterize the planarity of each tricyclic system. The computation shows for PPh$_2$C$_6$H$_3$COMn(CO)$_3$(ax-PPh$_3$)Mn(CO)$_5$ and **3** the largest deviations of 0.31 (1) and 0.34 (1) Å for each O$_{acyl}$ atom from a best-fitted plane of the ring atoms. The other ring atoms have in general deviations that are smaller than 0.1 (1) Å.

The possibility of π delocalization in such planar tricyclic ring systems of secondary metalated products is suggested for the dimanganese compounds by a careful comparison of C–O, acyl C–O, Mn–P, Mn–C, and P–C bond lengths of these and related derivatives.[24] To examine the influence of homologous transition metals in these metallacyclic rings, the bond lengths and angles of their five-membered chelate rings analogous to those of the compounds Ph$_2$PC$_6$H$_3$CO(M(1))(CO)$_3$(ax-PPh$_3$)(M(2))(CO)$_4$ (M = Mn, Re) are given in Table VII. The comparison of the

corresponding bond angles in the M(1) and M(2) rings provides good agreement with the exception of the bond angles subtended at the M(1) and M(2) atoms. Going from the Mn to the Re compound, one sees that the value has changed by 4.3 (4)° in the M(1) rings and by 3.4 (4)° in the M(2) rings. The observation can be best expressed in terms of a rigid extended non-metal atom ring system with a certain flexibility with regard to the ring bond angles subtended at the various M atoms.

For the manganese and rhenium secondary metalated products the acyl C–O bond length is significantly longer than that found for a normal double bond in acetophenone [1.216 (2) Å].[31] The interpretation of the acyl C–O bond lengthening can be based on a contribution of four canonical structures postulated by other authors.[18] Their contribution demands furthermore a shortening of the acyl C–C(Ph), Re–P, and P–C bonds in the dirhenium compounds compared to the same bonds with a predominant σ property. The following consideration of these bond lengths shows that the demand is fulfilled.

First, the acyl C–C(Ph) bond lengths of the compounds are shorter than that of the similar acetophenone C–C(Ph) bond [1.494 (22) Å]. Second, the measured Re–P bonds are shortened significantly compared to the Re–P bond distance for each terminal PPh$_3$ group. Third, the chelate P–C distance in each rhenium metalated compound is slightly less than the average of the other P–C distances in the respective structures. Fourth, the sequence of rhenium–carbon bond distances found is as follows: Re–CO

(31) Tanimoto, Y.; Kobayaski, H.; Nagakura, S.; Saito, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1822.

Table VII. Selected Structural Parameters of Ortho-Metalated Compounds with Esd's in Parentheses

	M(1)–O–C$_{acyl}$–C–C, deg		M(2)–P–C–C–C$_{acyl}$, deg		ring bond lengths, Å M(1)		M(2)		ref
Ph$_2$PC$_6$H$_3$COMn(CO)$_4$Mn(CO)$_3$(eq-PPh$_3$)	O–Mn–C	79.8 (2)	P–Mn–C	82.4 (2)	Mn–O 2.053 (5)	Mn–P	2.276 (2)	18
	Mn–O–C	118.5 (4)	Mn–P–C	104.7 (2)	O–C 1.257 (8)	P–C	1.812 (8)	
	O–C–C	113.7 (6)	P–C–C	112.9 (5)	C–C 1.474 (9)	C–C	1.403 (7)	
	C–C–C	117.3 (6)	C–C–C	118.9 (6)	C–C 1.410 (9)	C–C	1.474 (9)	
	C–C–Mn	110.7 (5)	C–C–Mn	121.1 (5)	C–Mn 2.045 (7)	C–Mn	2.040 (7)	
Ph$_2$PC$_6$H$_3$COMn(CO)$_3$(ax-PPh$_3$)Mn(CO)$_4$	O–Mn–C	79.4 (4)	P–Mn–C	82.7 (4)	Mn–O 2.094 (3)	Mn–P	2.274 (8)	24
	Mn–O–C	118.9 (8)	Mn–P–C	103.1 (4)	O–C 1.270 (13)	P–C	1.82 (2)	
	O–C–C	112.9 (10)	P–C–C	114.2 (10)	C–C 1.47 (2)	C–C	1.37 (2)	
	C–C–C	117.3 (10)	C–C–C	118.8 (11)	C–C 1.40 (2)	C–C	1.47 (2)	
	C–C–Mn	111.4 (9)	C–C–Mn	120.9 (8)	C–Mn 2.00 (2)	C–Mn	2.06 (2)	
Ph$_2$PC$_6$H$_3$COMn(CO)$_3$(ax-PPh$_3$)Mn(CO)$_3$(eq-PPh$_3$)	O–Mn–C	79.5 (7)	P–Mn–C	82.7 (7)	Mn–O 2.094 (13)	Mn–P	2.274 (8)	24
	Mn–O–C	115.3 (14)	Mn–P–C	103.3 (8)	O–C 1.264 (21)	P–C	1.823 (21)	
	O–C–C	114.7 (19)	P–C–C	114.0 (18)	C–C 1.473 (25)	C–C	1.366 (64)	
	C–C–C	116.0 (19)	C–C–C	119.3 (19)	C–C 1.397 (24)	C–C	1.473 (25)	
	C–C–Mn	112.9 (16)	C–C–Mn	119.8 (16)	C–Mn 2.001 (21)	C–Mn	2.058 (21)	
Ph$_2$PC$_6$H$_3$COMn(CO)$_4$Re(CO)$_4$ (M(1) = Mn)	O–Mn–C	79.3 (3)	P–Mn–C	79.0 (3)	Mn–O 2.07 (1)	Mn–P	2.438 (3)	18
	Mn–O–C	116.5 (6)	Mn–P–C	103.7 (4)	O–C 1.27 (1)	P–C	1.82 (1)	
	O–C–C	115.6 (8)	P–C–C	127.2 (9)	C–C 1.48 (1)	C–C	1.39 (1)	
	C–C–C	115.4 (9)	C–C–C	120.3 (9)	C–C 1.39 (1)	C–C	1.48 (1)	
	C–C–Mn	112.8 (7)	C–C–Mn	120.7 (7)	C–Mn 2.05 (1)	C–Mn	2.180 (8)	
Ph$_2$PC$_6$H$_3$CORe(CO)$_3$(ax-PPh$_3$)Re(CO)$_4$ (4)	O–Re–C	75.1 (4)	P–Re–C	79.3 (4)	Re–O 2.166 (11)	Re–P	2.437 (6)	this work
	Re–O–C	120.9 (12)	Re–P–C	103.5 (5)	O–C 1.257 (18)	P–C	1.807 (16)	
	O–C–C	113.4 (13)	P–C–C	115.4 (11)	C–C 1.477 (20)	C–C	1.412 (20)	
	C–C–C	117.5 (13)	C–C–C	119.7 (13)	C–C 1.411 (20)	C–C	1.477 (20)	
	C–C–Re	113.0 (10)	C–C–Re	121.3 (11)	C–Re 2.151 (16)	C–Re	2.158 (11)	
Ph$_2$PC$_6$H$_3$CORe(CO)(ax-PPh$_3$)Re(CO)$_3$(ax-PPh$_3$) (5)	O–Re–C	75.1 (4)	P–Re–C	78.8 (6)	Re–O 2.165 (12)	Re–P	2.443 (5)	a
	Re–O–C	120.9 (14)	Re–P–C	102.4 (4)	O–C 1.242 (22)	P–C	1.841 (18)	
	O–C–C	113.7 (15)	P–C–C	115.5 (15)	C–C 1.465 (23)	C–C	1.362 (23)	
	C–C–C	115.9 (15)	C–C–C	120.0 (15)	C–C 1.435 (24)	C–C	1.465 (23)	
	C–C–Re	114.2 (13)	C–C–Re	122.7 (12)	C–Re 2.094 (19)	C–Re	2.142 (18)	

*a*U. Flörke and H.-J. Haupt. The complete set of single-crystal X-ray data of **4** and **5** can be obtained by request.

(CO trans to ligand atom with lower π-acceptor capability) < Re–CO (trans to another CO) < Re–C(Ph) < Re–C(acyl). This means that a rhenium–carbon bond shortening through a π-delocalization effect in the metallacycles is a reasonable proposition.

The bond alterations in the fused five-membered rings of **4** and **5** discussed above have parallels with those of the related manganese compounds. A comparison of corresponding alterations with regard to the non-metal atoms of this kind of chelate ring shows that the extent is somewhat more distinct for the tricyclic manganese than for the rhenium compounds but in general is similar for both transition metals.

10. The central molecular framework of this diamagnetic substance contains a triangular arrangement of Re atoms that is edge-bridged by the diphenylphosphido groups (Figure 3). The metal–metal bonds in the Re$_3$ ring are necessary to enable each Re atom with two PPh$_2$ and three CO ligands to satisfy the EAN rule. The local geometry of the five non-metal ligand atoms (2 P and 3 C) is idealized C_{2v} symmetry, and the total coordination geometry of the Re atoms is distorted pentagonal bipyramidal. The Re$_3$P$_3$ molecular fragment has almost D_{3h} symmetry, in accordance with the result of the least-squares treatment, with the P(1) atom showing the largest deviation of 0.07 (1) Å from the best-fitted plane defined by the following equation: $-0.8226x + 0.0011y - 0.5686z + 6.9697 = 0$.

The extended-Hückel MO description of a three-membered transition-metal ring without bridging groups produces 24 CV–MO and 6 HLAB–MO.[32] The first-named bonding set is completely occupied in compound **10** with 48 chemical valence electrons (CVE: 3 Re, 21; 9 CO, 18; 3 PPh$_2$, 9), and this fact agrees with its Re–Re-bonded Re$_3$P$_3$ molecular fragment. The Re–Re bond found in **10** (average 2.914 (4) Å) is significantly shorter than that in Re$_5$(CO)$_{15}$(μ_4-PMe)(μ-PMe$_2$)(μ_3-P)Re(CO)$_5$ (average 2.986 (2) Å),[33] Re$_2$(CO)$_{10}$ (3.104 (1) Å),[34] Re$_6$-

(CO$_{18}$)(μ_4-PMe)$_3$ (average 3.113 (1) Å), or **2** (3.152 (1) Å). The relative Re–Re bond lengths for the substances Re$_2$(CO)$_{10}$ and **2** as compared to that for **10** represent in the first case the infrequent decrease in length of a covalent metal–metal single bond on going from an unbridged to a bridged bond. In the second case there is a considerable shortening of 0.238 (4) Å even though the same bridging group is present. The decreased bond length in the latter case is accompanied by a change in the ligand coordination sphere from **2** (Figure 1) to **10** (Figure 3) that favors energetically a stabilization of the centrally directed metal–metal-bonding and edge-bonding orbitals in **10**. The average Re–P distance of 2.425 (31) Å in **10** is similar to the average Re–(μ-P) distance of 2.430 (4) Å in **2**, both being shorter than the terminal Re–PPh$_3$ bond length of 2.481 (4) a in (2-benzoylphenyl)tricarbonyl(triphenylphosphine)rhenium,[35] suggesting a stronger rhenium–phosphorus bond.

The average ring bond angles at the μ-P atoms and at the Re atoms of the Re$_2$P rings are 74.0 (1) and 53.0 (1)°. A decrease in the Re$_2$P ring bond angle Re–P–Re from 81.6 (1)° in **2** to 74.0 (1)° in **10** accompanies the Re–Re bond shortening.

Intermolecular distances in **2**, **4**, and **10** do not indicate interactions greater than van der Waals forces.

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