Dinuclear Homo- and Heterometallic Rhodium Complexes Containing PMe_2 and PPh_2 Groups as Bridging Ligands. The Crystal and Molecular Structure of $[(C_5Me_5Rh)_2(\mu\text{-}PMe_2)(\mu\text{-}PPh_2)]$[1]

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Received August 17, 1987

The reaction of $[C_5Me_5Rh(PMe_2H)Cl_2]$ (**4**), which is prepared from $[C_5Me_5RhCl_2]_2$ (**2**) and PMe_2H, with excess diethylamine, produces a mixture of $[C_5Me_5(Cl)Rh(\mu\text{-}PMe_2)]_2$ (**6**), $[C_5Me_5Rh(PMe_2NEt_2)Cl_2]$ (**7**), and $[C_5Me_5Rh(\mu\text{-}PMe_2)]_2$ (**9**). **7** reacts with HF (in pyridine) and with HCl (in benzene) to form the complexes $[C_5Me_5Rh(PMe_2F)Cl_2]$ (**8**) and $[C_5Me_5Rh(PMe_2Cl)Cl_2]$ (**10**), respectively, the latter of which is reduced with sodium amalgam to give **9**. Compound **9** is also obtained by reduction of **6** with Na–Hg. Treatment of $[C_5Me_5Rh(PPh_2H)Cl_2]$ (**11**) with excess NEt_2H leads to the formation of $[C_5Me_5Rh(\mu\text{-}PPh_2)]_2$ (**13**) and $[(C_5Me_5Rh)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$ (**14**). The structurally related complexes $[(C_5Me_5Rh)_2(\mu\text{-}PMe_2)(\mu\text{-}PPh_2)]$ (**15**) and $[(C_5Me_5Rh)_2(\mu\text{-}PPh_2)(\mu\text{-}SMe)]$ (**16**) have been prepared from **14** by bridge-ligand exchange. The crystal and molecular structure of **15** have been determined. For $C_{34}H_{46}P_2Rh_2$ (**15**): triclinic, $P\bar{1}$; a = 10.053 (3), b = 11.271 (4), c = 16.761 (4) Å; α = 93.32 (2)°, β = 85.78 (2)°, γ = 116.45 (2)°; V = 1694.8 (6) Å^3; Z = 4; for 4938 observed reflections, R_F = 3.39%. **15** contains a folded "butterfly" Rh_2P_2 core with a 111.5 (2)° core dihedral angle and a Rh–Rh bond of 2.7952 (4) Å. The synthesis of the dinuclear homo- and heterometallic complexes $[C_5Me_5Rh(\mu\text{-}PMe_2)_2MC_5H_5]$ (**17**, M = Rh; **18**, M = Co) and $[C_5Me_5Rh(\mu\text{-}PMe_2)_2RuC_6H_6]$ (**19**) has been achieved starting from $[C_5Me_5Rh(PMe_2H)_2]$, CH_3Li, and $[C_5H_5M(CO)I_2]$ or $[C_6H_6RuCl_2]_2$, respectively.

Introduction

During the last decade, the chemistry of dinuclear transition-metal complexes in which the two metal atoms are near to each other and thus may behave cooperatively has received widespread interest. We became involved in this subject after we observed that the feature of metal basicity well-known for various half-sandwich type cyclopentadienyl cobalt and rhodium compounds[2] is not limited to species having only one metal center. The complex $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (**1**), which is prepared from $Co(C_5H_5)_2$ and PMe_2H in almost quantitative yield, reacts with various electrophilic substrates by oxidative addition and cleavage of the metal–metal bond.[3,4] With Brønsted acids, the cation $[(C_5H_5Co)_2(\mu\text{-}PMe_2)_2(\mu\text{-}H)]^+$ is formed,[3] which further reacts with Lewis bases L by hydride bridge opening and formation of $[C_5H_5(L)Co(\mu\text{-}PMe_2)_2Co(H)C_5H_5]^+$. For L = CNMe, the terminal hydride ligand can be transferred to the isocyanide to afford an *intramolecular* reduction and produce a μ-aminocarbyne and finally a formimidoyl group.[5]

In continuing this work we intended to broaden this field and in addition to **1** and $[C_5H_5Co(\mu\text{-}PPh_2)]_2$[3,6] also to prepare the corresponding phosphido-bridged dirhodium derivatives. According to the general trend,[7] they should be even better nucleophiles than the dicobalt analogues. After first attempts to obtain the cyclopentadienyl rhodium compound $[C_5H_5Rh(\mu\text{-}PMe_2)]_2$ failed, which was mainly due to unexpected side reactions accompanied by breaking of the C_5H_5–Rh bond,[8] we chose the analogous pentamethylcyclopentadienyl complexes as our next target. This paper reports on the synthesis of $[C_5Me_5Rh(\mu\text{-}PMe_2)]_2$ and some related dirhodium derivatives and also points to the application of one of the preparative routes to obtain *heterometallic* dimethylphosphido-bridged compounds. A short communication describing some preliminary results of this work has already appeared.[9]

Results

Preparation of $[C_5Me_5Rh(\mu\text{-}PMe_2)]_2$. As the synthetic route leading to **1** could not be applied to the corresponding pentamethylcyclopentadienyl rhodium complex $[C_5Me_5Rh(\mu\text{-}PMe_2)]_2$ because sandwiches such as $Rh(C_5Me_5)_2$ or $(C_5Me_5)Rh(C_5H_5)$ are unknown, we first attempted to use the compounds $[C_5Me_5(CO)Rh]_2(\mu\text{-}P_2Me_4)$[10] and $[C_5Me_5Rh(CO)(PMe_2H)]$[11] both containing a C_5Me_5Rh unit as starting materials. The experiments to convert these compounds on heating or on photolysis into $[C_5Me_5Rh(\mu\text{-}PMe_2)]_2$, remained, however, more or less unsuccessful. There was only some evidence that in the reaction of $[C_5Me_5(CO)Rh]_2(\mu\text{-}P_2Me_4)$ with Me_3NO a new compound was formed which according to the ^1H NMR spectrum probably had the expected composition.

The successful method to prepare $[C_5Me_5Rh(\mu\text{-}PMe_2)]_2$ (**9**) is outlined in Scheme I. The first step involving the cleavage of the halide bridges in the well-known dimers $[C_5Me_5RhX_2]_2$ (**2**, **3**) by dimethylphosphine to give the

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Scheme I

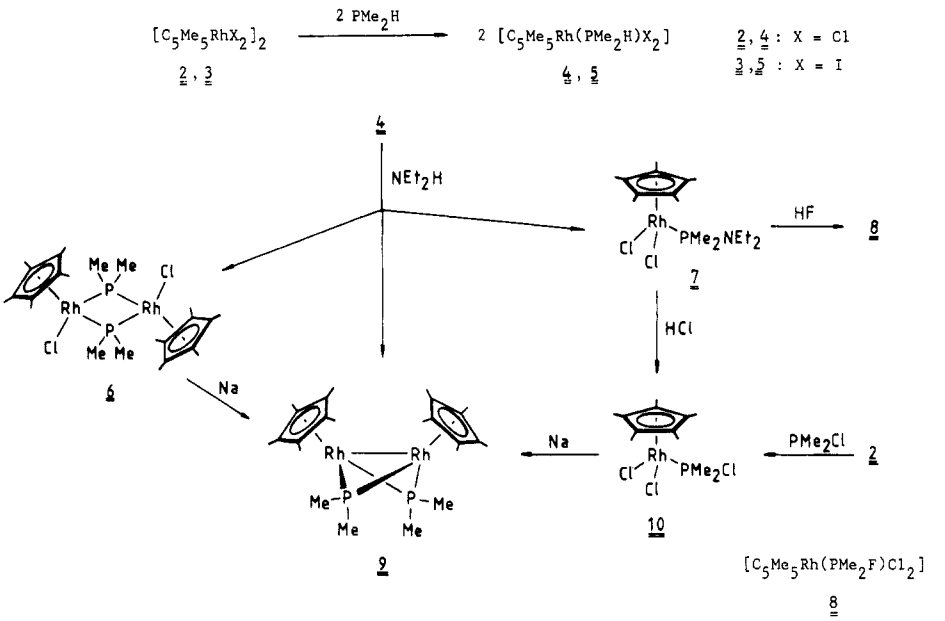

Table I. ^{1}H NMR and ^{31}P NMR Data of 4, 5, 7, 8, and 10–12[a]

	$\delta(C_5Me_5)$	[J(PH)]	$\delta(PR_2X)$	[J(PH); J(RhH)]	$\delta(PR_2X)$	[J(RhP)]
4	1.75 (d)	[4.0]	1.65 (ddd)	[12.6; 0.8][b]	−15.48 (d)	[142.9]
5	2.05 (d)	[4.0]	1.85 (ddd)	[11.7; 0.9][b]	−28.02 (d)	[139.9]
7	1.46 (d)	[3.7]	1.75 (dd)[c]	[10.6; 0.5]	79.35 (d)	[150.3]
8	1.50 (d)	[4.3]	1.93 (ddd)	[10.0; 0.4][d]	186.90 (dd)	[165.2][e]
10	1.70 (dd)	[4.9][f]	2.15 (dd)	[9.0; 0.5]	111.84 (d)	[163.8]
11	1.55 (d)	[3.9]	7.60 (m)[g]		13.46 (d)	[141.4]
12	1.90 (d)	[3.9]	7.60 (m)[g]		4.94 (d)	[142.9]

[a] Spectra of 7 and 8 in C_6D_6, otherwise in $CDCl_3$. ^{1}H: δ in ppm, Me_4Si internal standard. ^{31}P: δ in ppm, 85% H_3PO_4 external standard. J in Hz. Abbreviations used: d, doublet; t, triplet; q, quartet; m, multiplet. [b] J(HH) = 5.9 Hz; signal of PH proton not exactly located. [c] $\delta(NCH_2CH_3)$ 2.95 (dq) [J(PH) = 10.0 Hz, J(HH) = 7.0 Hz]; $\delta(NCH_2CH_3)$ 1.00 (t) [J(HH) = 7.0 Hz]. [d] J(FH) = 13.5 Hz. [e] J(PF) = 912.6 Hz. [f] J(RhH) = 0.3 Hz. [g] Signal of PH proton not exactly located.

mononuclear compounds $[C_5Me_5Rh(PMe_2H)X_2]$ (**4**, **5**) occurs almost quantitatively. **4** and **5** are red to violet crystalline solids which are air-stable and readily dissolve in chlorinated organic solvents without decomposition.

The second step follows earlier work by Yasufuku and Yamazaki who prepared dinuclear diphenylphosphido-bridged nickel and iron complexes on a similar route.[12] In the reaction of **4** with excess diethylamine, after 3 h in THF at room temperature a mixture of products is obtained of which **9** is extracted with pentane. The residue of the extraction contains the rhodium(III) compounds $[C_5Me_5(Cl)Rh(\mu\text{-}PMe_2)]_2$ (**6**) and $[C_5Me_5Rh(PMe_2NEt_2)Cl_2]$ (**7**) which are separated by chromatographic techniques. They are orange to red air-stable solids which have been characterized by elemental analysis and mass spectra. We assume that the (diethylamino)dimethylphosphine complex is formed by nucleophilic attack of the amine to the coordinated PMe_2H; NMR spectroscopic data reveal that the phosphine ligand is bound to rhodium via phosphorus (and not via nitrogen).

Compounds **6** and **7** have also been used as precursors to **9**. Whereas the reduction of **6** with Na/Hg occurs directly to produce **9** in 60% yield, the conversion of **7** to **9** proceeds via the chlorodimethylphosphine complex $[C_5Me_5Rh(PMe_2Cl)Cl_2]$ (**10**). As shown in Scheme I, **7** reacts both with HF (in pyridine) and with HCl (in benzene) by breaking the P–N bond to form **8** and **10**, respectively. A similar reaction with HF has recently been described by Brunner et al. who converted the cyclopentadienyl iron compound $[C_5H_5Fe(CO)(PPh_2N(Me)CHMePh)I]$ to the corresponding PPh_2F derivative.[13] Complex **10** is also obtained from **2** and PMe_2Cl, i.e., on the same route used for the preparation of **4**. The reduction of **10** to give **9** occurs under the same conditions which we applied for the conversion of **6** to the dimethylphosphido-bridged rhodium(II) compound.

The structure of the new C_5Me_5Rh complexes has been elucidated by NMR spectroscopy (Tables I and II). The ^{1}H NMR spectrum of **9** shows two signals of equal intensity for the methyl protons of the bridging PMe_2 groups, indicating that a nonplanar four-membered Rh_2P_2 ring is present. As the complex is diamagnetic, we assume that in analogy to **1** a Rh–Rh bond exists. The ^{31}P NMR spectrum of **9** confirms this proposal and shows a triplet at δ 70.75. There is broad support from literature data[14] that the signals of μ-PR_2 ligands in dinuclear complexes *containing* a metal–metal bond are usually observed at δ 50–300 whereas in compounds *without* such a bond these signals appear at higher fields. In agreement with this, the expected triplet in the ^{31}P NMR spectrum of **6** is found at δ −95.70. As the ^{1}H NMR of this complex (which contains Rh^{III}) also shows only *one* signal for the PMe_2 protons, we conclude that the structure of **6** proposed in

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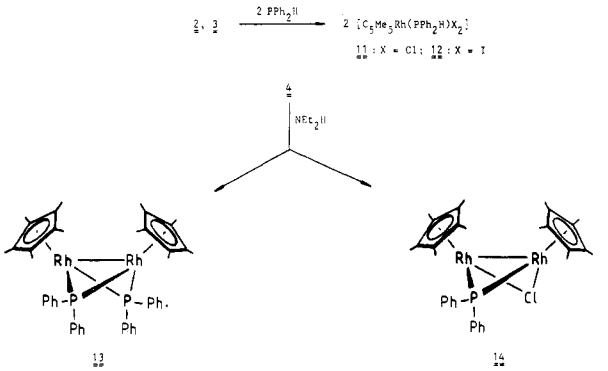
Table II. ^{1}H NMR and ^{31}P NMR Data of 6, 9, and 13–19[a]

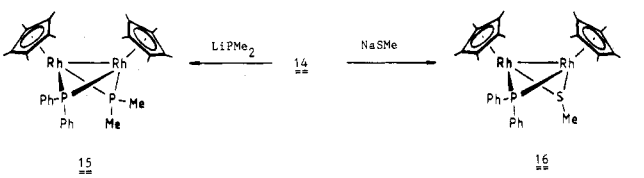
	$\delta(C_5Me_5)$	$[J(PH)]$	$\delta(PR_2)$	$[J(PH)/J; J(RhH)]$	$\delta(PR_2)$	$[J(RhP); J(PP)]$
6	1.67 (t)	[2.8]	1.97 (tvt)	[12.5; 0.7]	−95.70 (t)	[95.3]
9	2.10 (tvt)	[1.7][b]	1.45 (tvt)	[10.8; 1.0]	70.75 (t)	[142.9]
			1.65 (vt)	[11.6]		
13	1.75 (tvt)	[1.7][b]	7.00 (m)		111.02 (t)	[142.9]
14	1.75 (dd)	[1.7][c]	7.20 (m)		115.56 (t)	[166.7]
15	1.93 (tvt)	[1.7][b]	0.65 (d)[d]	[11.5]	80.23 (dt)[e]	[139.9; 116.1]
			1.50 (d)[d]	[10.4]	101.83 (dt)[f]	[144.4; 116.1]
			7.40 (m)[g]			
16[h]	1.80 (d)	[1.8]	7.40 (m)		114.33 (t)	[157.8]
17[i]	2.10 (dt)	[1.8][j]	1.55 (tvt)	[11.2; 1.0]	88.59 (dd)[k]	
			1.75 (vt)	[11.8]		
18[l]	2.10 (dt)	[1.7][j]	1.43 (dvt)	[12.1; 1.1]	81.56 (d)[m]	[138.4]
			1.76 (vt)	[12.2]		
19[n]	2.15 (dt)	[1.5][j]	1.56 (dvt)	[10.4; 1.0]	70.20 (d)	[141.4]
			1.62 (vt)	[11.0]		

[a] Spectrum of **13** in $CDCl_3$, otherwise in C_6D_6. ^{1}H: δ in ppm, Me_2Si internal standard. ^{31}P: δ in ppm, 85% H_3PO_4 external standard. J and N in Hz. Abbreviations used: d, doublet; t, triplet; q, quartet; m, multiplet; vt, virtual triplet; dvt, doublet of virtual triplets; tvt, triplet of virtual triplets. [b] N = 0.6 Hz. [c] J(RhH) = 0.2 Hz. [d] Intensity 3 H (one methyl group). [e] PMe_2 phosphorus. [f] PPh_2 phosphorus. [g] Intensity 10 H (two phenyl groups). [h] δ(SMe) 2.10 [dd, J(PH) = J(RhH) = 1.4 Hz]. [i] $\delta(C_5H_5)$ 5.30 (m). [j] J(RhH) = 0.6 Hz. [k] J(RhP) = 141.6 and 143.8 Hz. [l] $\delta(C_5H_5)$ 4.70 [t, J(PH) = 0.7 Hz]. [m] In toluene-d_8 at −60 °C. [n] $\delta(C_6H_6)$ 5.03 [t, J(PH) = 0.8 Hz].

Scheme II



Scheme III



Scheme I with a planar Rh_2P_2 ring and a trans position of the C_5Me_5 and Cl ligands is correct.

Preparation of $[C_5Me_5Rh(\mu\text{-}PPh_2)]_2$ and $[(C_5Me_5Rh)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$. The synthetic strategy that was used to obtain **9** can also be applied to the preparation of the corresponding *diphenylphosphido-bridged* complex $[C_5Me_5Rh(\mu\text{-}PPh_2)]_2$ (**13**) (Scheme II). The reactions of **2** and **3** with PPh_2H take place under the same conditions described for the synthesis of **4** and **5** and give the compounds $[C_5Me_5Rh(PPh_2H)X_2]$ (**11**, **12**) in almost quantitative yield. Subsequent treatment of **11** with excess diethylamine in acetone leads to the formation of two products, **13** and $[(C_5Me_5Rh)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$ (**14**), which can be separated by column chromatography. There is no evidence that in the reaction of **11** with NEt_2H monomeric or dimeric rhodium(III) compounds similar to **6** and **7** (Scheme I) are formed.

The composition of the air-stable, deeply colored (**13**, red; **14**, black) dinuclear complexes has been confirmed by elemental analysis and mass spectroscopy. Owing to the NMR spectroscopic data (Table II), there is no doubt that the structure is analogous to that of the dimethylphosphido-bridged analogue **9**. In accord with the above-mentioned rule, the ^{31}P NMR spectra of **13** and **14** show the triplet resonance at comparatively low field, the difference of ca. 40 ppm between **9** and **13** probably being due to the deshielding effect of the phenyl groups.

Bridge-Ligand Exchange Reactions of 14. Earlier work by Chatt et al. has shown that chloride-bridging ligands in dinuclear platinum complexes of general composition $[L(R)Pt(\mu\text{-}Cl)]_2$ are readily displaced by phosphido and thiolato anions to give the corresponding μ-PR_2 and μ-SR derivatives.[15] We originally attempted to prepare **6** by ligand exchange from **2** and $LiPMe_2$ but obtained only small amounts of the chloride-free product **9**.

A clean reaction takes place, however, between **14** and excess $LiPMe_2$ in THF to produce the "mixed" $Rh_2(\mu\text{-}PMe_2)(\mu\text{-}PPh_2)$ complex **15** in 67% yield (Scheme III). **15** representing the link between the "pure" $Rh_2(\mu\text{-}PMe_2)_2$ and $Rh_2(\mu\text{-}PPh_2)_2$ analogues, **9** and **13**, forms red air-stable crystals that are soluble in nearly all organic solvents. Even on standing in solution for several days, no comproportionation of **15** to give **9** and **13** occurs.

The linking position of **15** between **9** and **13** is also illustrated by the NMR spectroscopic data of the compound. In the ^{31}P NMR, the signal of the PMe_2 phosphorus is shifted downfield approximately to the same extend (compared to **9**) as the PPh_2 signal is shifted upfield (compared to **13**). A similar relation exists for the chemical shift values of the C_5Me_5 protons in the ^{1}H NMR spectra (Table II).

Exchange of the chloride bridge in **14** also occurs on treatment with NaSMe. After 15 h in acetone at 50 °C, the dark blue "mixed" μ-diphenylphosphido/μ-methylthiolato complex $[(C_5Me_5Rh)_2(\mu\text{-}PPh_2)(\mu\text{-}SMe)]$ (**16**) is obtained which probably has a similar structure as **15** and the related bis(μ-methylthiolato) compound $[C_5H_5Rh(\mu\text{-}SMe)]_2$.[16] In all cases, presumably a nonplanar Rh_2EE' framework (where E and E' are P and/or S) exists in which the rhodium atoms are linked by a metal–metal bond. Attempts to displace the chloride bridge in **14** by a carbonylate anion such as $[C_5H_5Fe(CO)_2]^-$ failed.

Unsymmetrical Dimethylphosphido-Bridged Homo- and Heterometallic Complexes. Besides the three pathways to prepare **9** which are outlined in Scheme I, the synthesis of this dinuclear complex is also possible by a somewhat different route. Recently, Finke et al. reported

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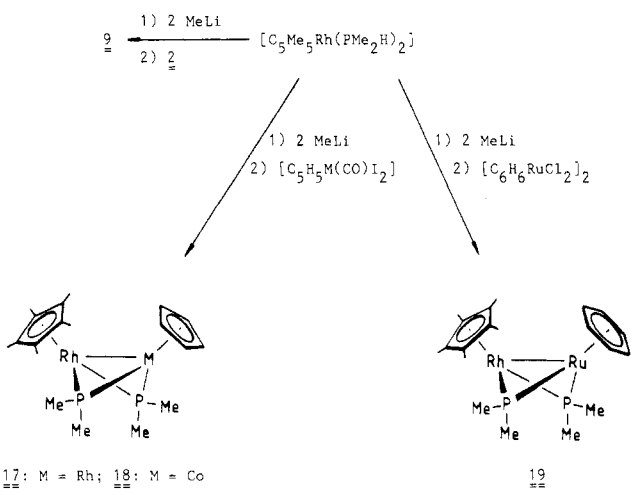
(16) Connelly, N. G.; Johnson, G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1375.

Scheme IV



17: M = Rh; 18: M = Co

19

that the heterometallic compound $[C_5Me_5Rh(\mu\text{-}PMe_2)Mo(CO)_4]$ is accessible from **2** and *cis*-$[Mo(CO)_4(PMe_2H)_2]$.[17] The dinuclear complexes $[(C_5H_5)_2M(\mu\text{-}PHPh)_2Mo(CO)_4]$ (M = Ti, Zr) and $[H(CO)(PPh_3)Ir(\mu\text{-}PPh_2)_2W(CO)_4]$ in which the two phosphido groups also bridge two different 14-electron species have similarly been prepared.[14a,18] In all these reactions, the phosphine ligands are first deprotonated by methyl- or butyllithium to form the corresponding lithiated derivative which is treated in situ with the chloro metal complex to give the phosphido-bridged dinuclear product.

This procedure can also be applied to obtain **9** as well as the novel homo- and heterometallic compounds $[C_5Me_5Rh(\mu\text{-}PMe_2)_2MC_5H_5]$ (**17**, M = Rh; **18**, M = Co) and $[C_5Me_5Rh(\mu\text{-}PMe_2)_2RuC_6H_6]$ (**19**) (Scheme IV). LiMe is used to transform the bis(dimethylphosphine) complex $C_5Me_5Rh(PMe_2H)_2$[19] into the lithiated intermediate which in ether reacts with **2**, $[C_5H_5M(CO)I_2]$, or $[C_6H_6RuCl_2]_2$ to produce **9** and **17–19**. The bis(diphenylphosphido)-bridged bis(cyclopentadienyl) analogue of **18**, $[C_5H_5Rh(\mu\text{-}PPh_2)_2CoC_5H_5]$, has previously been prepared by Yasufuku and Yamazaki on treatment of a mixture of $[C_5H_5Rh(PPh_2H)_2I]I$ and $[C_5H_5Co(CO)I_2]$ with excess Grignard reagent.[20] The yield of **17–19** is rather low which might be due to the lability of the primary intermediate. Using NMe_3 or NEt_3 instead of MeLi did not improve this result.

The ^1H and ^{31}P NMR data of **17–19** are summarized in Table II. Owing to the chemical shift values and the coupling constants, there is no doubt that the structure of the new homo- and heterometallic complexes **17–19** is completely similar to that of the bis(pentamethylcyclopentadienyl) dirhodium analogues. It should be mentioned that we failed to prepare the mixed-metal complex $[C_5Me_5Rh(\mu\text{-}PMe_2)_2IrC_5Me_5]$ using the same route which led to **17** and **18** although suitable precursors such as $[C_5Me_5Ir(CO)I_2]$[21] and $[C_5Me_5Ir(PMe_2H)Cl_2]$ (**20**) are known.

$$^1/_2[C_5Me_5IrCl_2]_2 \xrightarrow{PMe_2H} [C_5Me_5Ir(PMe_2H)Cl_2]$$
20

Crystal and Molecular Structure of 15. Despite the large number of dinuclear, bis(diorganophosphido) complexes that are known, we can find no previous report of any structures of $[(C_5R_5)Rh(\mu\text{-}R'_2P)]_2$ complexes. $[(C_5Me_5Rh)_2(\mu\text{-}PMe_2)(\mu\text{-}PPh_2)]$ (**15**) crystallizes as discrete molecules containing a folded ("butterfly") central Rh_2P_2 core (Figure 1); the "butterfly" dihedral is 111.5 (2)°. The Rh–Rh distance, 2.7952 (4) Å, is somewhat longer than in related C_5Me_5 complexes, e.g., $[C_5Me_5(CO)Rh]_2(\mu\text{-}CO)$, 2.743 (1) Å, and $[C_5Me_5(CO)Rh]_2(\mu\text{-}CH_2)$, 2.672 (1) Å.[22] The Rh–Rh bonds in two bis(μ-R_2P) dirhodium complexes, $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$, 2.7609 (9) Å,[23] and $[(COD)Rh(\mu\text{-}Ph_2P)_2Rh(PEt_3)_2]$, 2.752 (1) Å,[24] are also slightly shorter. The C–P–C angle is expectedly larger at PPh_2, 102.6 (2)°, as compared to the angle at PMe_2, 98.8 (3)°. The Rh–P distances in **15** do not differ significantly as a function of phosphido substitution (average 2.230 (2) Å), but a wide range of Rh–phosphido distances are found among other $Rh_2(\mu\text{-}PR_2)_2$-containing compounds: $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$, average Rh–P = 2.458 (2) Å;[23] $[(COD)Rh(\mu\text{-}PPh_2)_2Rh(PEt_3)_2]$, average (COD)Rh–P = 2.379 Å[24] and average $(PEt_3)_2Rh$–P = 2.199 Å; and $[(dppe)Rh(\mu\text{-}PPh_2)_2Rh(dppe)]$, which has no Rh–Rh bond, average Rh–PR_2 = 2.359 (2) Å.[25] Except for the phenyl ring twist angles, **15** possesses pseudo-mirror symmetry defined by the plane containing the P atoms and the midpoint of the Rh–Rh vector. In agreement is the small centroid–Rh–Rh–centroid torsion angle (2.5°). Attempts to determine the structure of the symmetrical $(\mu\text{-}PMe_2)_2$ complex **9** failed; of 13 specimens screened, all revealed unresolvable twinning problems.

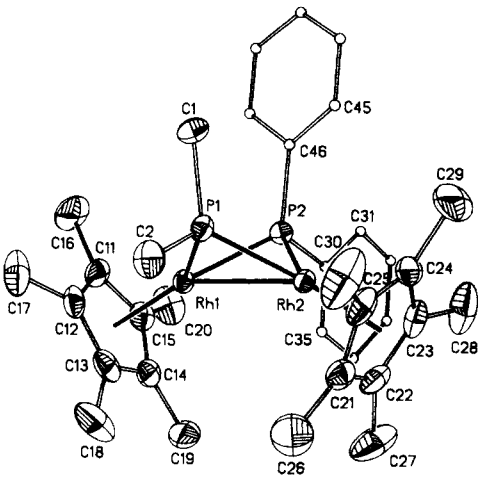


Figure 1. Molecular structure and labeling scheme for $[(C_5Me_5Rh)_2(\mu\text{-}PMe_2)(\mu\text{-}PPh_2)]$ (**15**) with 50% thermal ellipsoids. Hydrogen atoms have been omitted, and phenyl rings are shown with arbitrary size carbon atoms for clarity.

Experimental Section

NMR spectra were recorded on a Varian XL 100 (^1H), and a Bruker WH 90 FT (^{31}P) and mass spectra on a Varian MAT CH 7 instrument (70 eV). The starting materials $[C_5Me_5RhX_2]_2$ (**2**, **3**),[26] PMe_2H,[27] PPh_2H,[28] $LiPMe_2$,[29] $[C_5Me_5Rh(PMe_2H)_2]$,[19] $[C_5H_5M(CO)I_2]$ (M = Co, Rh),[30] $[C_6H_6RuCl_2]_2$,[31] and

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$[C_5Me_5IrCl_2]_2$[26] were prepared by published methods.

Preparation of $[C_5Me_5Rh(PMe_2H)X_2]$ (4, 5). A solution of 1.0 mmol of **2** or **3** in 15 mL of acetone was treated with 2.0 mmol of PMe_2H and stirred for 2 h at room temperature. After removal of the solvent in vacuo, the residue was recrystallized from CH_2Cl_2–pentane; yield 90–95%.

4: red crystals, mp 185 °C dec; MS, *m/e* (I_r) 370 (16, M^+), 334 (26, $M^+ - HCl$), 308 (20, $M^+ - PMe_2H$), 273 (100, $C_5Me_5RhCl^+$), 237 (89, $C_5Me_4CH_2Rh^+$). Anal. Calcd for $C_{12}H_{22}Cl_2PRh$: C, 38.84; H, 5.98; Rh, 27.73. Found: C, 38.42; H, 5.93; Rh, 27.33.

5: violet crystals; mp 274 °C dec. Anal. Calcd for $C_{12}H_{22}I_2PRh$: C, 26.02; H, 4.00; Rh, 18.58. Found: C, 26.08; H, 3.87; Rh, 18.04.

Preparation of $[C_5Me_5(Cl)Rh(\mu\text{-}PMe_2)]_2$ (6), $[C_5Me_5Rh(PMe_2NEt_2)Cl_2]$ (7), and $[C_5Me_5Rh(\mu\text{-}PMe_2)]_2$ (9). A solution of 1.484 g (4.0 mmol) of **4** in 30 mL of THF was treated with 2.07 mL (20.0 mmol) of NEt_2H and stirred for 3 h at room temperature. After removal of the solvent and excess amine in vacuo, the residue was extracted repeatedly with pentane (5 × 10 mL), and the pentane solution was filtered. The solution was concentrated to ca. 5 mL and chromatographed on Al_2O_3 (Woelm, neutral, activity grade V) with pentane. The eluate was concentrated to ca. 3 mL in vacuo and stored at −78 °C. Red crystals of **9** were formed that were filtered off and dried in vacuo; yield 360 mg (30%). The residue that was insoluble in pentane was dissolved in 10 mL of acetone, and the solution was chromatographed on Al_2O_3 (see above). With acetone a dark red fraction was obtained which was concentrated in vacuo until the first crystals appeared. The crystallization was completed by careful addition of ether and pentane. Red air-stable needles of **7** were obtained that were filtered off and dried in vacuo; yield 265 mg (15%). After the eluation of **7** was finished, chromatography was continued with methanol as the solvent. A dark red fraction was first obtained (which contained besides small amounts of **6** and $[NEt_2H_2]Cl$ some unidentified byproducts) followed by an orange fraction that was eluated with CH_2Cl_2. The solvent was removed in vacuo, and the residue was recrystallized from CH_2Cl_2–pentane. Orange air-stable crystals of **6** were formed; yield 135 mg (10%).

6: mp 240 °C dec; MS, *m/e* (I_r) 668 (2, M^+), 598 (100, $M^+ - 2\ Cl$), 572 (59, $M^+ - PMe_2Cl$), 533 (11, $M^+ - C_5Me_5$), 373 (7, $Rh(C_5Me_5)_2^+$), 273 (5, $C_5Me_5RhCl^+$), 237 (13, $C_5Me_4CH_2Rh^+$). Anal. Calcd for $C_{24}H_{42}Cl_2P_2Rh_2$: C, 43.07; H, 6.33; Rh, 30.75. Found: C, 43.26; H, 6.24; Rh, 30.31.

7: mp 190 °C dec; MS, *m/e* (I_r) 441 (19, M^+), 406 (2, $M^+ - Cl$), 308 (35, $M^+ - PMe_2NEt_2$), 273 (67, $C_5Me_5RhCl^+$), 237 (100, $C_5Me_4CH_2Rh^+$). Anal. Calcd for $C_{16}H_{31}Cl_2NPRh$: C, 43.46; H, 7.07; N, 3.17; Rh, 23.27. Found: C, 43.33; H, 7.15; N, 2.84; Rh, 22.98.

9: mp 150 °C dec; MS, *m/e* (I_r) 598 (100, M^+), 583 (71, $M^+ - CH_3$), 416 (11, $C_5Me_5Rh(PMe_2)CH_2Rh^+$), 373 (3, $Rh(C_5Me_5)_2^+$). Anal. Calcd for $C_{24}H_{42}P_2Rh_2$: C, 48.18; H, 7.08; Rh, 34.40. Found: C, 47.89; H, 6.82; Rh, 34.02.

Preparation of 9 from 2 and $[C_5Me_5Rh(PMe_2H)_2]$. A solution of 362 mg (1.0 mmol) of $[C_5Me_5Rh(PMe_2H)_2]$ in 20 mL of ether was treated at −78 °C dropwise with a solution of 2.0 mmol of methyllithium in 6 mL of ether. The solution was slowly warmed to room temperature where gas evolution occurred. After being stirred for 30 min, the solution was again cooled to −78 °C and treated with 309 mg (0.50 mmol) of **2**. The reaction mixture was then brought to 25 °C, stirred for 3 h, and worked up as described above; yield 105 mg (35%).

Preparation of 9 from 6. A suspension of sodium amalgam, prepared from 46 mg (2.0 mmol) of Na and 2 mL (136.0 mmol) of Hg, in 20 mL of ether was treated with 535 mg (0.8 mmol) of **6**. The reaction mixture was stirred for 3 h at room temperature, the solution was filtered, and the filtrate was brought to dryness in vacuo. The residue was dissolved in 20 mL of pentane, and the solution was chromatographed on Al_2O_3 (see above). After removal of the solvent, **9** was isolated in pure form; yield 287 mg (60%).

Preparation of $[C_5Me_5Rh(PMe_2F)Cl_2]$ (8). **7** (640 mg, 1.4 mmol) was added to 3 mL of a 70% solution of HF in pyridine, and the reaction mixture was stirred for 30 min at room temperature. After removal of the solvent the residue was extracted for 5 h with ether under reflux. The ether solution was cooled to 25 °C, then filtered, and brought to dryness in vacuo. The residue was recrystallized from CH_2Cl_2–ether–pentane (1:5:5) to give red air-stable crystals: yield 397 mg (71%); mp 182 °C dec; MS, *m/e* (I_r) 388 (16, M^+), 353 (28, $M^+ - Cl$), 308 (22, $M^+ - PMe_2F$), 273 (76, $C_5Me_5RhCl^+$), 237 (100, $C_5Me_4CH_2Rh^+$); ^{19}F NMR (CH_2Cl_2, $CFCl_3$ internal standard) δ 150.27 (s). Anal. Calcd for $C_{12}H_{21}Cl_2FPRh$: C, 37.04; H, 5.44; Rh, 26.45. Found: C, 37.06; H, 5.58; Rh, 26.68.

Preparation of $[C_5Me_5Rh(PMe_2Cl)Cl_2]$ (10). A slow stream of HCl was bubbled for 3 h through a solution of 221 mg (0.5 mmol) of **7** in 10 mL of benzene at room temperature. The solvent was removed, and the dark red residue was worked up as described for **8**. Red air-stable crystals were formed: yield 182 mg (90%); mp 182 °C dec; MS, *m/e* (I_r) 404 (9, M^+), 369 (9, $M^+ - Cl$), 308 (25, $M^+ - PMe_2Cl$), 273 (84, $C_5Me_5RhCl^+$), 237 (100, $C_5Me_4CH_2Rh^+$). Anal. Calcd for $C_{12}H_{21}Cl_3PRh$: C, 35.54; H, 5.22; Rh, 25.37. Found: C, 35.59; H, 5.28; Rh, 25.09.

Preparation of 10 from 2. A solution of 309 mg (0.5 mmol) of **2** in 10 mL of acetone was treated with 145 mg (1.5 mmol) of PMe_2Cl and stirred for 2 h at room temperature. The solution was filtered, the solvent was removed, and the residue was recrystallized from CH_2Cl_2–ether–pentane; yield 364 mg (90%).

Preparation of 9 from 10. The procedure was completely similar to that described for the preparation of **9** from **6**. Using the same quantity of sodium amalgam and 243 mg (0.6 mmol) of **10**, 45 mg of **9** was obtained; yield 25%.

Preparation of $[C_5Me_5Rh(PPh_2H)X_2]$ (11, 12). These compounds were prepared analogously as described for **4**, **5**, starting with 1.0 mmol of **2** or **3** and 2.0 mmol of PPh_2H; yield 90–95%.

11: red crystals; mp 250 °C dec. Anal. Calcd for $C_{22}H_{26}Cl_2PRh$: C, 53.36; H, 5.29; Rh, 20.78. Found: C, 53.47; H, 5.61; Rh, 21.06.

12: violet crystals; mp 233 °C dec. Anal. Calcd for $C_{22}H_{26}I_2PRh$: C, 38.97; H, 3.86; Rh, 15.17. Found: C, 39.04; H, 4.09; Rh, 15.05.

Preparation of $[C_5Me_5Rh(\mu\text{-}PPh_2)]_2$ (13) and $[(C_5Me_5Rh]_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$ (14). A solution of 495 mg (1.0 mmol) of **11** in 20 mL of acetone was treated with 0.52 mL (5.0 mmol) of NEt_2H and stirred for 3 h at room temperature. After removal of the solvent and excess amine in vacuo, the residue was dissolved in 20 mL of pentane, and the solution was chromatographed on Al_2O_3 (see above). With pentane an orange-red fraction was obtained from which red air-stable crystals of **13** were isolated; yield 64 mg (15%). Further eluation with pentane–ether (10:1) gave a red-brown solution which was concentrated in vacuo to ca. 2 mL. After the solution was stored at −78 °C, black crystals of **14** were formed; yield 105 mg (30%).

13: mp 200 °C dec; MS, *m/e* (I_r) 846 (100, M^+), 711 (5, $M^+ - C_5Me_5$), 479 (17, $(C_5Me_5)_2Rh_2H_3^+$), 423 (18, $C_5Me_5RhPPh_2^+$), 237 (1, $C_5Me_4CH_2Rh^+$). Anal. Calcd for $C_{44}H_{50}P_2Rh_2$: C, 62.42; H, 5.95; Rh, 24.31. Found: C, 62.08; H, 5.96; Rh, 24.02.

14: mp 225 °C dec; MS, *m/e* (I_r) 696 (100, M^+), 660 (4, $M^+ - HCl$), 423 (33, $C_5Me_5RhPPh_2^+$), 237 (31, $C_5Me_4CH_2Rh^+$). Anal. Calcd for $C_{32}H_{40}ClPRh$: C, 55.15; H, 5.79; Rh, 29.53. Found: C, 55.01; H, 5.70; Rh, 29.25.

Preparation of $[(C_5Me_5Rh)_2(\mu\text{-}PPh_2)(\mu\text{-}PMe_2)]$ (15). A solution of 100 mg (0.14 mmol) of **14** in 10 mL of THF was treated with 95 mg (1.4 mmol) of PMe_2Li and stirred for 2 h at room temperature. After removal of the solvent, the residue was extracted with pentane (2 × 10 mL), and the solution was filtered. The filtrate was brought to dryness in vacuo, the residue was dissolved in 10 mL pentane, and the solution was chromatographed on Al_2O_3 (see above) with pentane. An orange-red fraction was obtained that was concentrated in vacuo to ca. 2 mL and then stored at −78 °C. After standing for 24 h, red crystals were isolated; yield 68 mg (67%); mp 190 °C dec; MS, *m/e* (I_r) 722 (100, M^+), 707 (17, $M^+ - CH_3$), 479 (16, $(C_5Me_5)_2 - Rh_2H_3^+$), 237 (32, $C_5Me_4CH_2Rh^+$). Anal. Calcd for $C_{34}H_{46}P_2Rh_2$: C, 56.52; H, 6.42; Rh, 28.49. Found: C, 56.16; H, 6.50; Rh, 28.25.

Preparation of $[(C_5Me_5Rh)_2(\mu\text{-}PPh_2)(\mu\text{-}SMe)]$ (16). A solution of 200 mg (0.28 mmol) of **14** in 10 mL of acetone was treated with 70 mg (1.0 mmol) of NaSMe and stirred for 15 h at 50 °C. After removal of the solvent, the residue was dissolved in 10 mL of pentane, and the solution was chromatographed on Al_2O_3 (see above) with pentane–ether (10:1). A dark violet fraction was obtained that was brought to dryness in vacuo. The residue was

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Table III. Crystallographic Data for 15

(a) Crystal Parameters

formula	$C_{34}H_{46}P_2Rh_2$	V, Å^3	1694.8 (6)
cryst system	triclinic $P\bar{1}$	Z	2
a, Å	10.053 (2)	color	deep red
b, Å	11.271 (4)	size, mm	0.21 × 0.33 × 0.33
c, Å	16.761 (4)	μ(Mo Kα), cm^{-1}	10.53
α, deg	93.32 (2)	temp, K	293
β, deg	85.78 (2)	T_{max}/T_{min}	0.89/0.82
γ, deg	116.45 (2)	D(calcd), g cm^{-3}	1.416

(b) Data Collection

diffractometer	Nicolet R3m/μ	scan speed, deg min^{-1}	var 4–10
radiation	Mo Kα	rflns collctd	5864
wavelength, Å	0.71073	indpdnt rflns	5659
monochromator	graphite	obs rflns [$3\sigma(F_o)$]	4938
scan limits, deg	$4 \le 2\theta \le 50$	R(int), %	1.70
octants collcted	$\pm h, \pm k, +l$	std rflns	3 std/197 rflns
scan method	$\theta/2\theta$	var. of stds	<1%

(c) Refinement

$R(F)$, %	3.39	Δ/σ(final)	0.09
$R(wF)$, %	3.69	$\Delta(\rho)$, e Å^{-3}	0.55
GOF	1.468	N_o/N_v	14.4

recrystallized from pentane to give blue-violet crystals: yield 74 mg (36%); mp 260 °C dec; MS, m/e (I_r) 708 (41, M^+), 693 (100, $M^+ - CH_3$), 508 (12, $(C_5Me_5)_2Rh_2S^+$), 373 (5, $Rh(C_5Me_5)_2^+$), 237 (7, $C_5Me_4CH_2Rh^+$). Anal. Calcd for $C_{33}H_{43}PRh_2S$: C, 55.94; H, 6.12; Rh, 29.05. Found: C, 56.04; H, 6.33; Rh, 29.10.

Preparation of $[C_5Me_5Rh(\mu\text{-}PMe_2)_2MC_5H_2]$ (17, 18). A solution of 362 mg (1.0 mmol) of $[C_5Me_5Rh(PMe_2H)_2]$ in 20 mL of ether was treated at −78 °C dropwise with a solution of 2.0 mmol of methyllithium in 6 mL of ether. The solution was slowly warmed to room temperature, stirred for 30 min, again cooled to −78 °C, and treated with 1.0 mmol of $[C_5H_5M(CO)I_2]$. After being warmed to 25 °C, the reaction mixture was stirred for 3 h, and then the solvent was removed. The residue was extracted with pentane (3 × 10 mL), the pentane solution was filtered, concentrated in vacuo to ca. 5 mL, and chromatographed on Al_2O_3 (see above). With pentane–ether (20:1), a red fraction was eluated that was brought to dryness in vacuo. The residue was recrystallized from pentane to give red (17) or red-brown (18) crystals; yield 5–10%.

17: mp 140 °C dec; MS, m/e (I_r) 528 (100, M^+), 513 (68, $M^+ - CH_3$), 360 (12, $C_5Me_5RhP_2Me_4^+$), 303 (34, $C_5Me_5RhC_5H_5^+$). Anal. Calcd for $C_{19}H_{32}P_2Rh_2$: C, 43.20; H, 6.11; Rh, 38.96. Found: C, 43.47; H, 6.31; Rh, 39.03.

18: mp 147 °C dec; MS, m/e (I_r) 484 (100, M^+), 469 (27, $M^+ - CH_3$), 360 (14, $C_5Me_5RhP_2Me_4^+$), 303 (34, $C_5Me_5RhC_5H_5^+$), 259 (29, $C_5Me_5CoC_5H_5^+$). Anal. Calcd for $C_{19}H_{32}CoP_2Rh$: C, 47.13; H, 6.66; Rh, 21.25. Found: C, 47.28; H, 6.52; Rh, 21.05.

Preparation of $[C_5Me_5Rh(\mu\text{-}PMe_2)_2RuC_6H_6]$ (19). This compound was prepared analogously as described for 17, 18, starting with $[C_5Me_5Rh(PMe_2H)_2]$ (362 mg, 1.0 mmol) and $[C_6H_6RuCl_2]_2$ (250 mg, 0.5 mmol): yield 48 mg (9%); mp 151 °C dec; MS, m/e (I_r) 540 (100, M^+), 525 (57, $M^+ - CH_3$), 237 (13, $C_5Me_4CH_2Rh^+$). Anal. Calcd for $C_{20}H_{33}P_2RhRu$: C, 44.53; H, 6.17; Rh, 19.08; Ru, 18.74. Found: C, 44.78; H, 6.08; Rh, 19.18; Ru, 18.64.

Preparation of $[C_5Me_5Ir(PMe_2H)Cl_2]$ (20). This compound was prepared analogously as described for 4, starting with 398 mg (0.5 mmol) of $[C_5Me_5IrCl_2]_2$ and 1.0 mmol of PMe_2H: yield almost quantitative; mp 197 °C dec; MS, m/e (I_r) 460 (36, M^+), 425 (21, $M^+ - Cl$), 398 (36, $M^+ - PMe_2H$), 363 (100, $C_5Me_5IrCl^+$); ^1H NMR ($CDCl_3$) δ 1.70 [d, J(PH) = 2.7 Hz, C_5Me_5], 1.65 [dd, J(PH) = 9.5 Hz, J(HH) = 6.2 Hz, PMe_2H]. Anal. Calcd for $C_{12}H_{22}Cl_2IrP$: C, 31.31; H, 4.82. Found: C, 31.07; H, 4.99.

Crystallographic Structural Determination of 15. Crystals of 15 were obtained by crystallization from pentane and mounted on a glass fiber. Photographic data and the cell reduction program TRACER revealed no symmetry higher than triclinic. Lattice constants (see Table III) were calculated from the angular settings of 25 reflections ($22° \le 2\theta \le 30°$) including Friedel-related sets. A learned profile routine was used to improve the accuracy in measurement of weak reflections. Data were corrected for Lp effects, but not for absorption. The locations of the Rh and P atoms were obtained from an interpreted Patterson map. The centrosymmetric alternative $P\bar{1}$ was initially assumed correct (Z = 2) and later supported by the chemically reasonable and computationally stable results of refinement.

All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom contributions were idealized (d_{HH} = 0.95 Å, U = 1.2 × attached C's U); the rotational orientations of the Cp methyl groups were determined from formal H-atom positions. Atom coordinates are given in Table IV and selected

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 15

	x	y	z	U^a
Rh(1)	611.2 (3)	2232.0 (3)	3024.5 (2)	34.5 (1)
Rh(2)	2793.3 (3)	4746.2 (3)	2601.4 (2)	32.0 (1)
P(1)	365 (1)	4066 (1)	2838 (1)	39 (1)
P(2)	1938 (1)	2871 (1)	1862 (1)	37 (1)
C(1)	−844 (5)	4175 (5)	2100 (3)	62 (2)
C(2)	−232 (5)	4817 (5)	3716 (3)	63 (2)
C(11)	−1174 (5)	214 (4)	3254 (3)	55 (2)
C(12)	−1235 (5)	1070 (4)	3895 (3)	56 (2)
C(13)	111 (6)	1538 (4)	4299 (3)	60 (2)
C(14)	1002 (5)	954 (4)	3908 (3)	54 (2)
C(15)	203 (5)	144 (4)	3261 (3)	51 (2)
C(16)	−2425 (6)	−604 (6)	2729 (4)	101 (3)
C(17)	−2575 (6)	1277 (6)	4147 (4)	93 (3)
C(18)	505 (8)	2390 (6)	5048 (3)	103 (4)
C(19)	2439 (6)	1074 (6)	4208 (4)	91 (3)
C(20)	619 (7)	−747 (5)	2720 (4)	85 (3)
C(21)	4282 (5)	6248 (4)	3494 (3)	55 (2)
C(22)	5111 (5)	5658 (4)	3096 (3)	59 (2)
C(23)	5222 (5)	5905 (4)	2280 (3)	62 (2)
C(24)	4455 (5)	6674 (4)	2155 (3)	64 (2)
C(25)	3882 (5)	6890 (4)	2922 (4)	60 (2)
C(26)	3997 (8)	6278 (7)	4385 (3)	120 (4)
C(27)	5896 (7)	4982 (7)	3502 (5)	114 (4)
C(28)	6159 (7)	5576 (7)	1641 (4)	116 (4)
C(29)	4478 (8)	7303 (7)	1385 (4)	140 (4)
C(30)	3162 (7)	7785 (5)	3098 (5)	118 (4)
C(31)	3649 (6)	1944 (5)	800 (3)	64 (3)
C(32)	4737 (7)	1501 (6)	648 (3)	83 (3)
C(33)	5430 (6)	1302 (6)	1247 (4)	77 (3)
C(34)	5089 (5)	1563 (5)	2031 (3)	67 (2)
C(35)	4007 (5)	2027 (5)	2193 (3)	55 (2)
C(36)	3284 (5)	2217 (4)	1580 (3)	45 (2)
C(41)	−62 (7)	1582 (6)	653 (4)	86 (3)
C(42)	−721 (8)	1551 (9)	−57 (4)	115 (5)
C(43)	−245 (9)	2695 (10)	−480 (4)	110 (6)
C(44)	825 (8)	3824 (8)	−224 (3)	90 (4)
C(45)	1486 (6)	3859 (6)	464 (3)	68 (3)
C(46)	1081 (5)	2754 (4)	922 (3)	50 (2)

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

Table V. Selected Bond Parameters of 15[a]

(a) Bond Distances (Å)

Rh(1)–Rh(2)	2.7952 (4)	Rh(2)–P(2)	2.230 (1)
Rh(1)–P(1)	2.230 (1)	Rh(1)–CNT(1)	1.896 (4)
Rh(1)–P(2)	2.240 (1)	Rh(2)–CNT(2)	1.892 (4)
Rh(2)–P(1)	2.221 (1)		

(b) Bond Angles (deg)

Rh(1)–P(1)–Rh(2)	77.81 (4)	CNT(1)–Rh(1)–P(1)	137.5 (1)
Rh(1)–P(2)–Rh(2)	77.39 (4)	CNT(1)–Rh(1)–P(2)	141.6 (1)
P(1)–Rh(1)–P(2)	80.01 (5)	CNT(2)–Rh(2)–P(1)	138.5 (1)
P(1)–Rh(2)–P(2)	80.39 (5)	CNT(2)–Rh(2)–P(2)	140.3 (1)
CNT(1)–Rh(1)–Rh(2)	151.7 (1)	C(1)–P(1)–C(2)	98.8 (3)
CNT(2)–Rh(2)–Rh(1)	151.2 (1)	C(36)–P(2)–C(46)	102.6 (2)

(c) Torsion Angle (deg)

CNT(1)–Rh(1)–Rh(2)–CNT(2) 2.5 (2)

(d) "Butterfly" Dihedral (deg)

[P(1)–Rh(1)–Rh(2)]–[P(2)–Rh(1)–Rh(2) 111.5 (2)

[a] CNT = centroid of Cp* ring.

bond distances and angles in Table V.

All computation used the SHELXTL program system (version 5.1), Nicolet Corp., Madison, WI. Atomic coordinates and selected bond distances and angles are given in Tables IV and V, respectively.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support, and Degussa AG for generous gifts of chemicals. We also thank U. Neumann and R. Schedl for the elemental analyses, Dr. G. Lange for the mass spectra, and Dr. W. Buchner and C. P. Kneis for NMR measurements.

Registry No. **2**, 12354-85-7; **3**, 67841-74-1; **4**, 87882-77-7; **5**, 112654-36-1; **6**, 87897-87-8; **7**, 87897-88-9; **8**, 112654-37-2; **9**, 87882-79-9; **10**, 87882-78-8; **11**, 112654-38-3; **13**, 87882-88-0; **14**, 112654-39-4; **15**, 112654-40-7; **16**, 112654-41-8; **17**, 112654-42-9; **18**, 112680-31-6; **19**, 112654-43-0; $[C_5He_5Rh(PMe_2H)_2]$, 86224-84-2; $[C_5H_5Rh(CO)I_2]$, 12192-49-3; $[C_5H_5Co(CO)I_2]$, 12012-77-0; $[C_6H_6RuCl_2]_2$, 37366-09-9; $[C_5Me_5Ir(PMe_2H)Cl_2]$, 112654-44-1; $[C_5Me_5IrCl_2]_2$, 12354-84-6; Rh, 7440-16-6; Co, 7440-48-4.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages); a listing of structure factors (30 pages). Ordering information is given on any current masthead page.

Phosphido-Bridged Diiron Complexes from Low-Coordinate Phosphorus Compounds

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Received August 24, 1987

The (methylene)phosphido-bridged diiron complex $[\mu\text{-}(Me_3Si)_2C{=}P](\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (**2**) was prepared by the reaction of $Li[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$ (**1**) with $(Me_3Si)_2C{=}PCl$, and the structure was determined by X-ray diffraction. Treatment of **1** with $(Me_3Si)_2NP{=}C(H)SiMe_3$ (**3**) yielded two new phosphido-bridged complexes, $\{\mu\text{-}[Me_3Si(H)N][(Me_3Si)_2CH]P\}(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (**4**) and $\{\mu\text{-}[(Me_3Si)_2N][Me_3SiCH_2]P\}(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (**5**). While the major product of **1** and **3** was **4**, complex **5** was the major product when **3** was treated with $Et_3NH[(\mu\text{-}t\text{-}BuS)(\mu\text{-}CO)Fe_2(CO)_6]$. Characterization of these new complexes by ^1H, ^{31}P, and ^{13}C NMR spectroscopy, elemental analysis, and IR spectroscopy is discussed.

Introduction

Low-coordinate phosphorus compounds, RP=NR′ and RP=CR′$_2$, are interesting ligands because there are several sites for bonding to transition metals, i.e., through the phosphorus lone pair[1] as is typical for ordinary phosphines, R_3P, through the P=E π system[2] as is typical for alkenes, through direct σ P–M bonds,[3] or through combinations of these.[4] Another type of phosphine bonding mode is that found in phosphido-bridged systems where the phosphorus is essentially bonded to the two metals through both a simple σ covalent bond and a coordinate covalent bond involving the phosphorus lone pair.[5] The only examples of this type of bonding mode for low-coordinate phosphorus are $\{[\mu\text{-}P{=}C(SiMe_3)_2]_2Fe_2(CO)_6\}$ which has been prepared by treatment of $(Me_3Si)_2C{=}PCl$ with $Na_2Fe(CO)_4$[6] and $\{(\mu\text{-}P{=}ML_n)_2Fe_2(CO)_6\}$ [ML_n = $Cr(CO)_5$, $Cp(CO)_2Mn$] which has been prepared from $Fe_2(CO)_9$ and $L_nM\text{–}PX_3$.[7] In this paper we report the preparation and X-ray crystallographic structure of another low-coordinate phosphido-bridged diiron complex as well as the preparation of two sterically hindered phosphido-bridged complexes that are derived from a low-coordinate (methylene)phosphine.

Results and Discussion

A novel diiron complex with the metal atoms bridged by one [bis(trimethylsilyl)methylene]phosphido moiety, $P{=}C(SiMe_3)_2$, and by the bulky *tert*-butylthio group, *t*-

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