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X-ray crystal structure of $[FeRh(CO)_6(\mu\text{-}P^tBu_2)](Fe\text{-}Rh)$: a molecule with two semibridging carbonyl ligands

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Abstract

The structure of the phosphido-bridged heterobimetallic complex $[FeRh(CO)_6(\mu\text{-}P^tBu_2)]$ (**1**) has been established by X-ray analysis. **1** crystallizes in space group $P\bar{1}$ with four molecules per unit cell, the two crystallographically unrelated molecules are practically identical. By ignoring the Fe–Rh bond, the Fe atom has in good approximation a trigonal bipyramidal and the Rh atom an irregular coordination sphere. As indicated by the bonding geometry, two carbonyl ligands of the iron atom are weakly semibridging to the Rh atom.

Keywords: Iron; Rhodium; Phosphido-bridged; Carbonyl; X-ray structure

Recently, we reported on the synthesis of the phosphido-bridged heterobimetallic complex $[FeRh(CO)_6(\mu\text{-}P^tBu_2)]$ (**1**) by reaction of the anion $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}P^tBu_2)]^-$ with $[\{Rh(CO)_2Cl\}_2]$ [1]. At that time **1** was characterized by us only by spectroscopic methods owing to the lack of single crystals suitable for X-ray diffraction studies. Now we can obtain such crystals by cooling isopropanol solutions at −30°C overnight. Some other closely related binuclear phosphido-bridged FeRh complexes are known: $[FeRh(CO)_3(\mu\text{-}P^tBu_2)(HP^tBu_2)COD]$ (**2**) [2], $[FeRh(CO)_5(\mu\text{-}P^tBu_2)(HP^tBu_2)]$ (**3**) [3], $[FeRh(CO)_3(\mu\text{-}P^tBu_2)(PMe_3)_3]$ (**4**) [4] and $[FeRh(CO)_4(\mu\text{-}PCy_2)(PPh_3)_2]$ (**5**) [5]. In all these cases a semibridging carbonyl group bound to the iron atom was found. No crystal structure data are available for the complexes $[(CO)_3LFe(\mu\text{-}PR_2)RhL'L'']$($R=Ph$: $L=L'=PEt_3$, $L''=CO$ [6]; $L=L'=PPh_3$, $L''=CO$ [7]), a green isomer of **3** [4] and some other compounds containing Cp ligands [8–10]. Therefore, complex **1** is the first example of such a bimetallic phosphido-bridged FeRh core bearing only carbonyl ligands, whereas the compounds mentioned above contain at least one phosphine ligand. All the FeRh complexes which have been characterized by X-ray diffraction exhibit in their IR spectra a band for a semibridging carbonyl group. For **1** we observed IR spectra both in the solid (KBr, nujol mull) and in solution (hexane) with absorptions only for carbonyl ligands clearly indicating a terminal position (above 1900 cm^{-1}) [1]. This fact is, for instance, in contrast to compound **5** where in solution absorptions above 1900 cm^{-1} were observed, but in the solid a band at 1842 cm^{-1} appears [5]. Therefore, the coordination mode of the carbonyls in **1** was at first obscure and needed to be elucidated by X-ray analysis [11].

1 crystallizes in the triclinic space group $P\bar{1}$ with four molecules per unit cell. The two crystallographically independent molecules A and B have very similar geometries, therefore, only molecule A is shown in Fig. 1. As can be seen in Table 1, there are only a few significant differences in bond lengths and angles between molecules A and B. In the following discussion, values in square brackets are those for molecules B.

The molecular structure of **1** is closely related to those of compounds **2**–**5** containing an 18 e configuration on the iron atom and a formally coordinatively unsaturated 16 e rhodium center [2–5]. If one neglects the Fe–Rh bond, the iron atom has a trigonal bipyramidal coordination sphere with the phosphorus atom

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Table 1
Selected bond lengths (Å) and angles (°) for compound **1** (Molecules A and B)

	Molecule A	Molecule B		Molecule A	Molecule B
Rh-Fe	2.618(1)	2.620(1)	P-Rh-C(1)	100.00(7)	100.92(8)
Rh-P	2.278(1)	2.275(1)	P-Rh-C(2)	163.11(8)	161.55(8)
Fe-P	2.312(1)	2.319(1)	C(1)-Rh-C(2)	96.58(10)	97.43(11)
Rh-C(1)	1.859(3)	1.856(3)	P-Fe-C(3)	92.16(8)	94.61(8)
Rh-C(2)	1.925(3)	1.923(3)	P-Fe-C(4)	96.24(8)	93.48(8)
Fe-C(3)	1.825(3)	1.806(3)	P-Fe-C(5)	86.08(8)	86.63(8)
Fe-C(4)	1.799(3)	1.813(3)	P-Fe-C(6)	175.86(8)	176.83(9)
Fe-C(5)	1.770(3)	1.774(3)	C(3)-Fe-C(4)	126.3(1)	125.9(1)
Fe-C(6)	1.787(2)	1.787(2)	C(3)-Fe-C(5)	118.2(1)	112.7(1)
C1-O(1)	1.128(3)	1.136(3)	C(3)-Fe-C(6)	84.4(1)	88.5(1)
C2-O(2)	1.124(3)	1.121(3)	C(4)-Fe-C(5)	115.2(1)	121.1(1)
C3-O(3)	1.148(3)	1.151(3)	C(4)-Fe-C(6)	87.7(1)	84.4(1)
C4-O(4)	1.146(3)	1.142(3)	C(5)-Fe-C(6)	93.5(1)	92.4(1)
C5-O(5)	1.141(3)	1.138(3)	Rh-C(1)-O(1)	179.1(2)	179.0(2)
C6-O(6)	1.142(3)	1.139(3)	Rh-C(2)-O(2)	178.5(3)	177.0(3)
			Fe-C(3)-O(3)	166.4(2)	169.4(2)
			Fe-C(4)-O(4)	171.4(2)	169.0(2)
			Fe-C(5)-O(5)	178.4(2)	176.6(2)
			Fe-C(6)-O(6)	178.2(2)	177.4(2)

and carbon atom C(6) occupying the apical positions. There are only slight deformations of the idealized geometry, the greatest deviation of a bond angle from the theoretical values of 180°, 120° and 90°, respectively, amounts to 7,3° for C(3)–Fe–C(5) in molecule B. In contrast to that, the rhodium atom has a quite irregular coordination geometry. The Fe–Rh distance of 2.618(1) Å [2.620(1) Å] lies in the range observed for compounds **2** to **5**. As expected for a heterobimetallic complex, the phosphido-bridge is somewhat asymmetric, but surprisingly, the Rh–P distance is by 0.034(1) Å [0.044(1) Å] shorter than the Fe–P distance. However, the greater covalent radius of Rh is manifested by the values of the metal–carbon distances (mean ΔRh/Fe–C = 0.096 Å), cf. the empirical average values of M–C bond lengths in metal carbonyl complexes Fe–C = 1.782(30) and Rh–C = 1.847(40) Å given in literature [12].

Table 2
Atomic coordinates ($\times 10^4$) for **1** (Molecules A and B)

Atom	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
Rh	2295.7(2)	5757.4(1)	6247.9(1)	7688.0(2)	− 875.2(1)	8692.5(1)
Fe	2011.5(3)	4018.0(2)	7219.4(2)	7973.3(3)	924.7(2)	7837.1(2)
P	3021.4(5)	5288.9(4)	7661.7(4)	7024.2(6)	− 318.9(4)	7275.3(4)
O(1)	3222(3)	7789(2)	5832(2)	6782(2)	−2924(2)	8997(2)
O(2)	866(3)	5862(2)	4541(2)	9028(2)	−995(2)	10441(2)
O(3)	3846(2)	3601(2)	5352(1)	10730(2)	−321(2)	7865(2)
O(4)	−855(2)	5119(2)	7515(2)	5827(2)	1484(2)	9528(2)
O(5)	2847(3)	2785(2)	8863(2)	7890(2)	2041(1)	5999(1)
O(6)	961(2)	2321(2)	6586(2)	8983(2)	2597(2)	8546(1)
C(1)	2866(3)	7023(2)	5983(2)	7129(3)	−2147(2)	8889(2)
C(2)	1409(3)	5816(2)	5163(2)	8500(3)	−950(2)	9813(2)
C(3)	3186(3)	3877(2)	6070(2)	9611(3)	78(2)	7857(2)
C(4)	286(3)	4754(2)	7428(2)	6585(3)	1200(2)	8853(2)
C(5)	2526(3)	3280(2)	8222(2)	7886(3)	1596(2)	6716(2)
C(6)	1350(3)	2993(2)	6833(2)	8614(3)	1930(2)	8277(2)
C(7)	4934(2)	4969(2)	7645(2)	8001(2)	−1020(2)	6159(2)
C(8)	5294(3)	4580(2)	8615(2)	7625(3)	−456(2)	5243(2)
C(9)	5564(3)	5929(2)	7284(2)	7765(3)	−2142(2)	6215(2)
C(10)	5617(3)	4133(2)	6923(2)	9531(3)	−1078(2)	6110(2)
C(11)	2105(2)	6069(2)	8749(2)	5127(2)	24(2)	7237(2)
C(12)	1944(3)	5366(2)	9650(2)	4798(3)	1027(2)	6633(2)
C(13)	2843(3)	6934(2)	8897(2)	4630(3)	−847(2)	6838(2)
C(14)	678(3)	6584(3)	8587(2)	4324(3)	180(3)	8254(2)

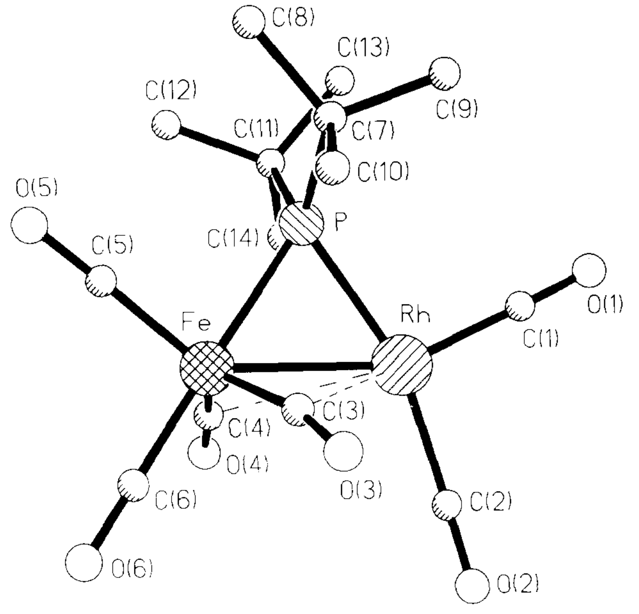

Fig. 1. The molecular structure of [FeRh(CO)$_6$(μ-P^{t}Bu$_2$)] (**1**, Molecule A).

An inspection of the four Fe–C bond lengths gives the result that the distances of Fe to C(5) and C(6) are only a little but significantly shorter than those to C(3) and C(4). Moreover, angles Fe–C(3)–O(3) = 166.4(2)° [169.4(2)°] and Fe–C(4)–O(4) = 171.4(2)° [169.0(2)°] deviate considerably from linearity whereas the bond angles at C(5) and C(6) are approximately 180° (cf. Table 1). These observations indicate the existence of two semibridging carbonyl groups in **1**. As the formal geometric criterion for a semibridging interaction generally the 'asymmetry parameter' α (defined as $\alpha = (d_2 - d_1)/d_1$; where d_1 is the shorter and d_2 is the longer M–C distance, with $0.1 \leq \alpha \leq 0.6$) is used [13]. With α-values of 0.35 [0.43] and 0.58 [0.51] for C(3)–O(3) and C(4)–O(4), respectively, this criterion is fulfilled. However, the distances Rh ··· C(3) = 2.467(3) Å [2.577(3) Å] and Rh ··· C(4) = 2.851(3) Å [2.738(3) Å] are rather long, compared with corresponding values in complexes **2**–**5** which contain only one semibridging CO group and the Fe–C–O angles are less bent in **1**. Therefore, the semibridging carbonyl group interactions in **1** have to be classified as rather weak.

The observed interatomic distance between the Fe and Rh atom indicates an Fe–Rh single bond. The bonding situation in the similar heterobimetallic complex [FeRh(CO)$_4$(μ-PCy$_2$)(PPh$_3$)$_2$] (**5**) has been discussed by Jenkins et al. [5]. The structure of the latter in solution can be formulated as containing an Fe to Rh dative bond and a Rh center that is coordinatively unsaturated, while in the solid state the compound can be better described as containing a semibridging CO group accompanied by a metal–metal bond. An indication for the existence of such a semibridging carbonyl in **5** in the solid is the appearance of a low band at 1842 cm^{-1} in the IR spectrum which cannot be observed in the solution spectra [5]. Although we could not find such a band for **1** we believe the complex to have similar bonding situations as described for **5**. The reality could be anywhere between the extreme views as discussed before; however, in this case the structural data, especially the M–P bond lengths, strongly suggest that the Fe–Rh bond is a donor–acceptor interaction. Usually, a 16 e configuration at rhodium(I) centers is sufficient and the rule, but in our case we assume an increased electron density on the rhodium because of the presence of the bulky μ-P^{t}Bu$_2$ group. This increased electron density could be compensated by the two semibridging CO groups bound to the iron and accepting electron density from the filled rhodium d orbitals. A certain 'coordinative saturation' of the Rh center is also well proved by the fact that no reaction of **1** with CO (80 bar, 7 h, pentane, room temperature) has been observed.

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[11] Crystal data for **1**: C$_{14}$H$_{18}$FeO$_6$PRh, $M = 472.0$, space group $P\bar{1}$; $a = 10.141(2)$, $b = 13.142(3)$, $c = 14.257(3)$ Å; $\alpha = 85.60(1)$, $\beta = 78.71(2)$, $\gamma = 78.30(1)°$; $V = 1823.2(7)$ Å^3; $Z = 4$; $D_{calc} = 1.720$ g cm^{-3}; $F(000) = 944$; λ(MoKα) = 0.71073 Å, μ(MoKα) = 18.12 cm^{-1}.

The intensity data were collected on a Stoe STADI-4 diffractometer, using the ω/θ-scan technique at 200 K (Oxford CRYOSTREAM low-temperature equipment). 5694 unique reflections with 2θ in the range 3–48° were measured and 5692 of them used in refinement. The structure was solved by direct methods [14] and refined by full-matrix least-squares on F^2 [15] with anisotropic displacement parameters for the non-H atoms. The hydrogen atoms were placed at their geometrically calculated positions and the methyl groups were treated as rigid groups. Empirical corrections for absorption and extinction were applied. Final $R(F)$, $wR(F^2)$ and $S(F^2)$ amount to 0.027, 0.058 and 1.08, respectively, for all data.

Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-400677, the names of the authors, and the journal citation.

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