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COMMUNICATION

THE PREPARATION AND X-RAY CRYSTAL STRUCTURE OF $[RhPh(OCOCF_3)(C_{10}H_4NO_2)\{P(p\text{-}FC_6H_4)_3\}(H_2O)]$, AN OCTAHEDRAL COMPLEX CONTAINING A σ-RhPh BOND

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Abstract—New complexes containing a σ-RhPh bond have been obtained by elimination of Hg from the intermediate heterobimetallic complexes $[Rh(OCOCF_3)(HgPh)(quin)(CO)\{P(p\text{-}RC_6H_4)_3\}]$ (quin = 2-quinaldinate ($C_9NH_6COO^-$), R = Cl, F, CH_3 and CH_3O). The heterobimetallic complexes were prepared by reactions of $[Rh(quin)(CO)\{P(p\text{-}RC_6H_4)_3\}]$ with $PhHg(OCOCF_3)$. The crystal structure of $[RhPh(OCOCF_3)(quin)\{P(p\text{-}FC_6H_4)_3\}(H_2O)]$ has been determined.

In a previous paper we have shown that complexes of the type $[Rh(pyC)(CO)\{P(p\text{-}RC_6H_4)_3\}]$ (pyC = $2\text{-}C_5NH_4COO^-$) react with PhHgCl to give $[RhCl(HgPh)(pyC)(CO)\{P(p\text{-}RC_6H_4)_3\}]$.[1] Related reactions with $PhHg(OCOCF_3)$ yield unstable heterobimetallic complexes, which after deposition of metallic mercury give new compounds with RhPh bonds. So, we propose the synthesis of σ-organometallic RhPh compounds using heterobimetallic Rh—Hg complexes as intermediates.

In this paper we describe the reactions of $[Rh(quin)(CO)\{P(p\text{-}RC_6H_4)_3\}]$ with $PhHg(OCOCF_3)$ and the formation of new σ-organometallic compounds. The crystal structure of the complex $[RhPh(OCOCF_3)(quin)\{P(p\text{-}FC_6H_4)_3\}(H_2O)]$ has been determined and is shown in Fig. 1.†

The reactions of $[Rh(quin)(CO)\{P(p\text{-}RC_6H_4)_3\}]$ with $PhHg(OCOCF_3)$ yielded the new products $[Rh(OCOCF_3)(HgPh)(quin)(CO)\{P(p\text{-}RC_6H_4)_3\}]$. The addition of HgPh and $OCOCF_3$ groups to the rhodium atom is in agreement with the related reactions with PhHgCl.[1] The complexes were stable in the solid state, but when treated in acetone decarbonylated products were observed. The new decarbonylated complexes were characterized as $[RhPh(OCOCF_3)(quin)\{P(p\text{-}RC_6H_4)_3\}]$ on the basis of analytical and spectroscopic data.

We have solved the crystal structure for one

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† Crystal data: $C_{36}F_6H_{25}NO_5PRh$, triclinic, $a = 15.846(3)$, $b = 11.585(3)$, $c = 10.804(5)$ Å, $\alpha = 64.27(3)$, $\beta = 103.68(3)$, $\gamma = 113.15(2)°$, $U = 1638(1)$ Å^3, space group $P\bar{1}$, $Z = 2$, $M_r = 799.5$, $D_c = 1.62$ g cm^{-3}. Data were measured on an Enraf–Nonius CAD4 diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) using ω–2θ scans. The structure was solved by the heavy-atom method and refined anisotropically using absorption corrected data to give $R = 0.049$, $R_w = 0.054$, for 5472 independent observed reflections $[|I_o| \geqslant 2\sigma(|I|)]$, $1 < \theta < 26$. The atomic coordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by a full literature citation for this communication.

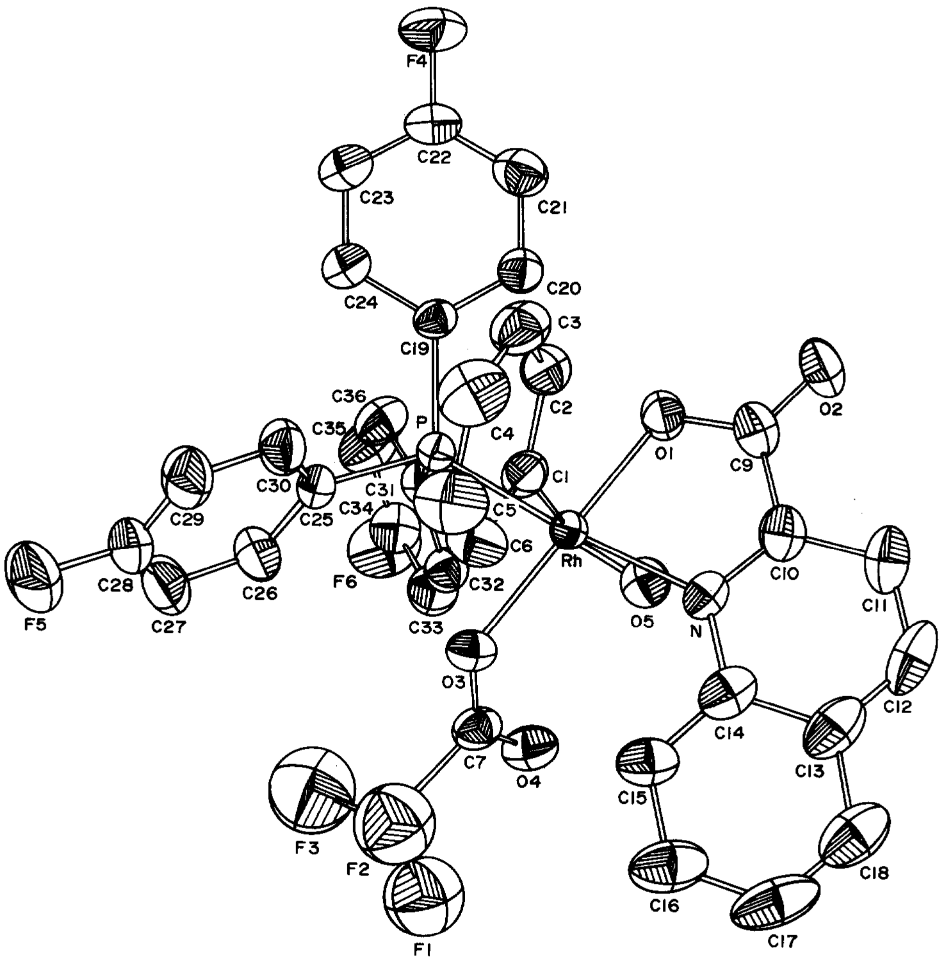

Fig. 1. The X-ray crystal structure of [RhPh(OCOCF$_3$)(quin){P(p-FC$_6$H$_4$)$_3$}(H$_2$O)]. Important bond distances (Å) and angles (°):

Bond distances

Rh—P	2.305(2)	Rh—C(1)	2.011(7)	N—C(14)	1.374(8)
Rh—N	2.164(5)	P—C(19)	1.815(6)	O(1)—C(9)	1.283(8)
Rh—O(1)	1.100(3)	P—C(25)	1.828(6)	O(2)—C(9)	1.221(6)
Rh—O(3)	2.067(3)	P—C(31)	1.829(6)	O(3)—C(7)	1.266(9)
Rh—O(5)	2.243(6)	N—C(10)	1.318(6)	O(4)—C(7)	1.215(9)

Angles

O(5)—Rh—C(1)	168.1(2)	N—Rh—C(1)	91.0(2)	P—Rh—O(3)	84.2(1)
O(3)—Rh—C(1)	90.9(2)	N—Rh—O(5)	78.6(2)	P—Rh—O(1)	95.9(1)
O(3)—Rh—O(5)	96.9(2)	N—Rh—O(3)	100.3(2)	P—Rh—N	175.5(2)
O(1)—Rh—C(1)	89.9(2)	N—Rh—O(1)	79.6(2)	Rh—P—C(31)	115.0(2)
C(1)—Rh—O(5)	82.61(2)	P—Rh—C(1)	88.5(2)	Rh—P—C(25)	112.2(2)
O(1)—Rh—O(3)	179.2(2)	P—Rh—O(5)	101.4(1)	Rh—P—C(19)	118.2(2)

of these derivatives, [RhPh(OCOCF$_3$)(quin){P(p-FC$_6$H$_4$)$_3$}], and a six-coordinated distorted octahedral for the rhodium atom has been observed (Fig. 1). The phenyl and OCOCF$_3$ groups are in *cis* positions and a molecule of water is coordinated as the sixth ligand. The water molecule is attached to a non-coordinated oxygen atom (O$_4$) of the trifluoroacetate ligand through an intramolecular hydrogen bond and to the non-coordinate oxygen atom (O$_2$) of the quinaldinate ligand through an intermolecular hydrogen bond. The bond lengths and angles are as expected.$^{2-4}$

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