Bis(μ-diphenylphosphido-μ'-carbonyl-π-methylcyclopentadienyl-carbonyliron)rhodium Hexafluorophosphate: A Non-closed Trinuclear Rhodium–Iron Complex

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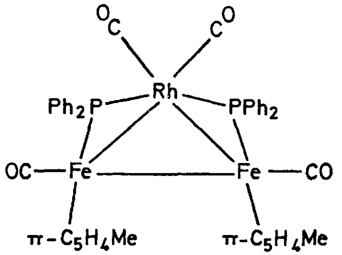
Summary The reaction of $[Rh(C_8H_{12})Cl]_2$, $[Rh(CO)_2Cl]_2$, or $RhCl_3,3H_2O$ in methanol or $[Rh(C_8H_{12})(thf)_2]^+$ in tetrahydrofuran with an excess of $[Fe(PPh_2)(CO)_2(\pi\text{-}C_5H_4Me)]$ in the presence of PF_6^- affords the title compound; an X-ray diffraction analysis shows the metals to be in a non-clustered configuration.

The synthesis of polynuclear complexes based on $[Rh(PPh_3)_3Cl]$, $[Rh(CO)(PPh_3)_2Cl]$, and $[Rh(C_8H_{12})(PPh_3)_2]SbF_6$ is of interest because of the potential of these species as homogeneous catalysts.[1] The compounds $RhCl_3,3H_2O$, $[Rh(CO)_2Cl]_2$, and $[Rh(C_8H_{12})Cl]_2$ were thus treated with the tertiary phosphine PPh_2M (I) [$M = Fe(CO)_2(\pi\text{-}C_5H_4R)$ (R = H, Me)] in methanol but the major product from these reactions when performed in the presence of large counteranions such as tetraphenylborate and hexafluorophosphate, as well as from the reaction of $[Rh(C_8H_{12})(thf)_2]SbF_6$ with (I) in tetrahydrofuran (thf), was characterised as $[Rh\{Fe(PPh_2)(CO)_2(\pi\text{-}RC_5H_4)\}_2][X]$ (II) ($X = BPh_4^-$, PF_6^-, or SbF_6^-); its i.r. spectrum showed it to contain both terminal and bridging carbonyl groups [ν(CO) = 2011s, 1845m, and 1817w cm^{-1}, in CH_2Cl_2].



(III)

Crystals of $[Rh\{Fe(PPh_2)(CO)_2(\pi\text{-}C_5H_4Me)\}_2]PF_6$ are orthorhombic with $a = 19{\cdot}92$, $b = 25{\cdot}96$, $c = 15{\cdot}82$ Å; $Z = 8$, space group *Pbca*. The structural analysis was based on 2541 independent reflexions ($I_{obs} > 3\sigma(I_{obs})$; Mo-$K_\alpha$) and R is presently 0·063. The essential stereochemistry of the cation is shown in the Figure; e.s.d.'s in the bond lengths average 0·002 Å (Rh—Fe), 0·004 Å (Rh—P and Fe—P) and 0·02 Å (Rh—C, Fe—C). The Fe_1RhFe_2 angle and the dihedral angles demonstrate an unusual stereochemistry about the rhodium ion.

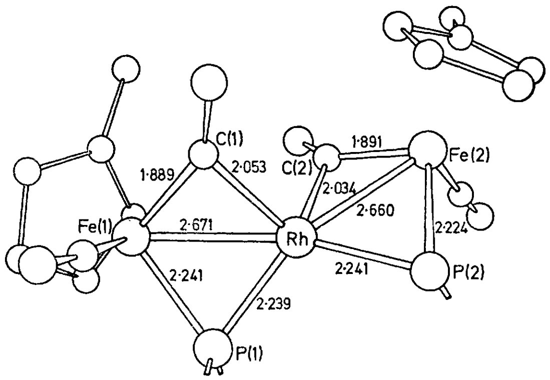


FIGURE. *Stereochemistry of* $[Rh\{Fe(PPh_2)(CO)_2(\pi\text{-}C_5H_4Me)\}_2]^+$ *about the rhodium and iron atoms. Relevant bond angles:* Fe_1RhFe_2, 145·0; P_1RhC_2; 136·3, C_1RhP_2, 137·3; Fe_1P_1Rh, 73·2; Fe_1C_1Rh, 85·2°. *Relevant interplanar angles:* Fe_1C_1Rh—Fe_1P_1Rh, 155·6; Fe_2C_2Rh–Fe_2P_2Rh, 153·5°.

Structure (III) might have been predicted as the thermodynamically preferred form on the basis of the 18-electron 'rule'. Mössbauer and i.r. spectroscopic data support triangular structures for $[RhFe_2(\pi\text{-}C_5H_5)(CO)_9]$ and $[Rh_2Fe(\pi\text{-}C_5H_5)_2(CO)_6]$[2] but for these species the relatively large number of carbonyl groups will reduce the population of antibonding orbitals which occur in 54-electron triangular clusters.[3] Structure (III) is suggested as being unstable with respect to the observed open arrangement as a result of the presence of the strongly basic phosphido-groups.

The rhodium in complex (II) is formally co-ordinatively unsaturated with the result that it reacts readily with donor ligands. For instance, treatment of (II) (R = H, X = BPh_4^-) with the ligands L = $P(OMe)_3$ and PPh_3 produces $[Rh\{Fe(PPh_2)(CO)_2(\pi\text{-}C_5H_5)\}_2L]BPh_4$ (IV) whose i.r. spectrum in the CO stretching region [L = $P(OMe)_3$: ν(CO) = 1997s, 1823ms, and 1796m cm^{-1}, in CH_2Cl_2] is very similar to that of (II), consistent with it being an adduct of (II). Complex (IV) (L = PPh_3) is also obtained by the reaction of $[Rh(C_8H_{12})(PPh_3)Cl]$ with $[Fe(PPh_2)(CO)_2(\pi\text{-}C_5H_5)]$ in ethanol in the presence of tetraphenylborate anions.

Complexes analogous to (II) have also been isolated from the reaction of $[Ir(C_8H_{12})(thf)_2]SbF_6$ and $[Rh(C_8H_{12})(thf)_2]SbF_6$ with $[Fe(PPh_2)(CO)_2(\pi\text{-}C_5H_5)]$ and $[Fe(SR)(CO)_2(\pi\text{-}C_5H_5)]$ (R = Et and Bu^t) respectively.

We thank the S.R.C. and the South African Council for Scientific and Industrial Research for support and Johnson Matthey Limited for the loan of rhodium and iridium salts to C.R.N.

(*Received, 28th June* 1972; *Com.* 1127.)

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