Preliminary communication

The formal umpolung behaviour of protonic acids containing coordinating anions towards diphosphazane-bridged derivatives of nonacarbonyldiruthenium

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Abstract

Reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) with the protonic acids HCl, HBr, HNO_3, H_2BO_2F, CF_3COOH, $PhSH/HPF_6$, and H_2CO_3/HPF_6 produces $[Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and/or $[Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (A = Cl, Br, ON(O)O, OB(F)OH, OC(CF_3)O, SPh, and OC(OH)O) via $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ as intermediate; the structure of $[Ru_2\{\mu\text{-}OB(F)OH\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ has been established X-ray crystallographically.

A recognised procedure for the synthesis of dinuclear metal hydrides involves the protonation of appropriate dinuclear compounds. Typical examples illustrating this method are provided by the protonation reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2(CO)_2]$ [1–4], $[Rh_2(CO)_3(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ [5], $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2\text{-}PPh_2)]$ [6], $[Pt_2(\mu\text{-}Et_2PCH_2PEt_2)_3]$ [7], and $[MPt(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)(CO)_3(PPh_3)]$ (M = Mo or W) [8] which afford $[Fe_2(\mu\text{-}H)(\eta\text{-}C_5H_5)_2(CO)_4]^+$, $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]^+$, $[Rh_2(\mu\text{-}H)(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2\text{-}PPh_2)]^+$, $[Pt_2H_2(\mu\text{-}Et_2PCH_2PEt_2)_3]^{2+}$, $[MoPt(\mu\text{-}H)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)(CO)_3\text{-}(PPh_3)]^+$, and $[WPtH(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)(CO)_3(PPh_3)]^+$, respectively. It is also known that "protonation" of metal hydrides by hydrogen halides may lead to the formal substitution of the hydride ligands and the formation of the corresponding halides. In particular it has been shown that treatment of dinuclear $[Rh_2(\mu\text{-}H)_2\text{-}(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ with HCl and HBr leads to the liberation of hydrogen and the formation of $[Rh_2Cl_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ and $[Rh_2Br_2(CO)_2(\mu\text{-}Ph_2\text{-}PCH_2PPh_2)_2]$ and $[Rh_2(\mu\text{-}H)Br_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_2]Br$, respectively [9]. We have previously communicated that reaction of $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PYPR_2)_2]$ (Y = CH_2, R = Ph; Y = N(Et), R = OMe or OPr^i) with $HBF_4 \cdot OEt_2$ or HPF_6/H_2O

produces $[Ru_2H(CO)_5(\mu\text{-}R_2PYPR_2)_2]^+$ [10]. We now wish to report that protonation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) by acids with conjugate bases with ligating properties is accompanied by formal oxidation of the ruthenium atoms and the coordination of the conjugate base.

Treatment of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ with solutions of the hydrogen halides HCl and HBr in ether was found to lead to the formation and separation of products characterised as $[Ru_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P\text{-}(OMe)_2\}_2]Cl$ (I,Cl) and $[Ru_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]Br$ (II,Br) respectively. These compounds in which the two ruthenium atoms are bridged by a halogeno group as well as by two diphosphazane ligands have been previously synthesised by direct halogenation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)\text{-}P(OMe)_2\}_2]$ [11]. Similarly reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN\text{-}(Et)P(OMe)_2\}_2]$ with HNO_3 in thf, gives the bridged nitrato species $[Ru_2(\mu\text{-}ON(O)O)(CO)_4\{\mu\text{-}MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (III), characterised fully, including by FD mass spectrometry, as the hexafluorophosphate salt. In contrast, protonation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) by H_2SO_4 in thf gave the protonated species $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (IV) [10] as the sole product.
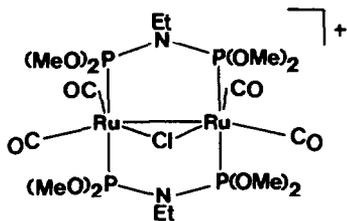
(I)
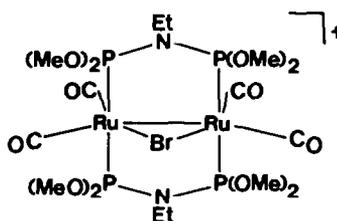
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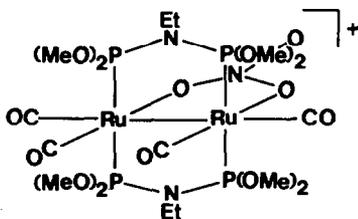
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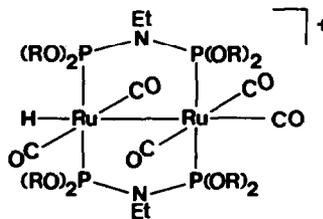
(IV)

Carboxylic acids were also found to react with $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ with the nature of the product being dependent on the strength of the carboxylic acid. Thus trifluoroacetic acid produced the pentacarbonyl species $[Ru_2(CF_3COO)(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ (V), in which the trifluoroacetato group is terminally bonded to one of the ruthenium atoms, on addition to $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. Decarbonylation of the hexafluorophosphate salt of this cation could be readily achieved both thermally and photochemically affording the tetracarbonyl compound $[Ru_2\{\mu\text{-}OC(CF_3)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ (VI,PF_6) which contains the CF_3COO ligand in the bridging coordination mode. On the other hand the equilibrium shown below was established with the weaker carboxylic acids R'COOH

(R′ = H, Me, and Ph). This equilibrium could be pushed to the right by using excess of the carboxylic acid but attempts to isolate the protonated species $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ as the carboxylate salt led to its deprotonation by the anion and the formation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$.

(V)   (VI)

$$[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2] + R'COOH \rightleftharpoons$$

$$[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]R'COO$$
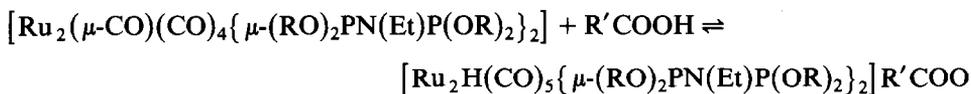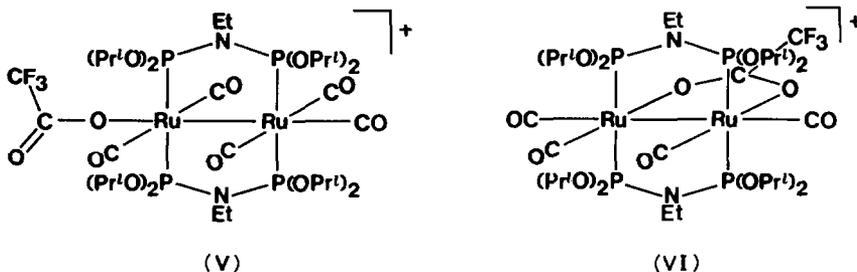
(R′ = Me, Pr^i; R′ = H, Me, or Ph)

Protonation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ with impure tetrafluoroboric acid diethyl etherate resulted in the formation of a somewhat unexpected product. While pure $HBF_4 \cdot Et_2O$ gave $[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ in virtually quantitative yield [10] the impure acid afforded a product characterised by conventional methods as well as by X-ray crystallography as the fluoroborato derivative $[Ru_2\{\mu\text{-}OB(F)OH\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]BF_4$ (VII,BF$_4$). This species was subsequently synthesised by employing an excess of $HBF_4 \cdot Et_2O$ in the presence of water and a reaction time of 5 days. The stereochemistry of VII is illustrated in Fig. 1 *. The two ruthenium atoms, which are separated by a distance of 2.814(1) Å, corresponding to a formal ruthenium–ruthenium bond, are bridged by an OB(F)OH group as well as by two diphosphazane ligands. The two ruthenium atoms, the four carbonyls and the oxygen, boron and fluorine atoms of the OB(F)OH group lie in a plane which is orthogonal to a plane containing the two ruthenium and four phosphorus atoms. The ^{31}P NMR spectrum of VII exhibits a single resonance indicating that the OB(F)OH hydrogen, identified by means of ^1H NMR spectroscopy, is rapidly exchanging sites or is coordinated symmetrically, with the two oxygens being potential bridging sites.

Fig. 1. The molecular stereochemistry of $[Ru_2\{\mu\text{-}OB(F)OH\}(CO)_4\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ (VII) showing the atom labelling. Relevant interatomic distances and angles: Ru(1)–Ru(2), 2.814(1); Ru(1)–P(1), 2.349(3); Ru(1)–P(4), 2.351(2); Ru(2)–P(2), 2.345(3); Ru(2)–P(3), 2.334(3); Ru(1)–O(6), 2.148(6); Ru(2)–O(5), 2.145(7); B(1)–O(5), 1.23(2); B(1)–O(6), 1.21(2); B(1)–F(1), 1.35(2) Å; Ru(2)–O(5)–B(1), 121(1); Ru(2)–O(6)–B(1), 126(1); O(5)–B(1)–O(6), 129(1)°.

A number of aspects of these protonation reactions warrant particular comment:
(i) The formation of $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ is dependent on the strength of the acid, HA, employed; the conjugate bases of the weaker acids deprotonate $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ under appropriate conditions and treatment of the protonated species with sodium acetate in methanol for instance gives $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$.
(ii) $[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OR)_2\}_2]^+$, as well as $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$, affords $[Ru_2(CF_3COO)(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ on reaction with CF_3COOH.
(iii) Treatment of $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ with A^- does not lead to the formation of $[Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and/or $[Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$; $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ must be converted to $[Ru_2H(CO)_4(solvent)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ by treatment with Me_3NO before nucleophilic substitution can occur. Thus reaction of BH_4^- with $[Ru_2H(CO)_4(MeCN)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ gives $[Ru_2H_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ [13] whereas with $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ it leads to deprotonation.
(iv) The formation of $[Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and/or $[Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ only occurs for those acids which are sufficiently strong to protonate $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ to a diproto-
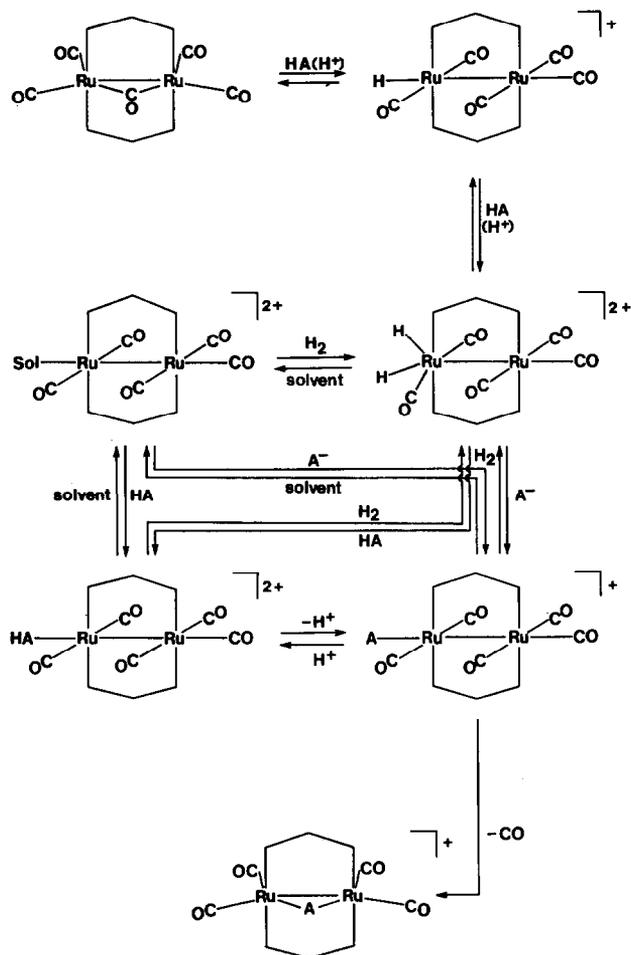
Scheme 1

nated species and for which the conjugate base is sufficiently nucleophilic to substitute H_2 in this species.

(v) Products of the type $[Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ have only been isolated for those systems in which the Ru_2A moiety occurs as either a three- or five-membered dimetallocyclic ring. Furthermore, five-membered dimetallocycles were only obtained for those conjugate bases which can afford delocalised unsaturated rings, e.g. NO_3^-, CF_3COO^- and HBO_2F^- but not for HSO_4^- or $H_2PO_4^-$.

The products of the reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ with HA are formally derived by addition of A^+ to this dinuclear species and as such the acid formally exhibits umpolung behaviour. However, the results indicate that the hydride $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ is an intermediate in the reaction and a reaction pathway which will account for the formation of $[Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and/or $[Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ is summarised in Scheme 1. Although a product from the reaction of $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ with HBF_4, HPF_6, or H_2SO_4

was detected spectroscopically it was only found to exist in appreciable quantities in the presence of excess of these acids and all attempts to isolate it led to the isolation of the mono-protonated species instead. The proposal that this product is a diprotonated species and is a second intermediate in the reactions involving HA is not unreasonable in that Eisenberg et al. have established that hydrogen is liberated on reaction of $[Rh_2(\mu-H)_2(CO)_2(\mu-Ph_2PCH_2PPh_2)_2]$ with protons [9]. Furthermore a cationic complex with an η^2-H_2 ligand has been reported to be formed in the protonation of $[Ru(\eta-C_5H_5)H(PPh_3)(CNBu^t)]$ by HPF_6 [14]. The final step in the reaction involves the nucleophilic substitution of H_2 by HA and/or A^-. Significantly, the solvento species $[Ru_2(CO)_5(acetone)\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ has been synthesised by treatment of $[Ru_2(\mu-CO)(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]$ with a twice molar amount of $AgSbF_6$ in acetone and found to react with OH^-, OMe^- and $MeCO_2^-$ to afford $[Ru_2(\mu-OR)(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^+$ (R = H and Me) and $[Ru_2\{\mu-OC(Me)O\}(CO)_4\{\mu-(RO)_2PN(Et)P(OMe)_2\}_2]^+$, respectively [13].

It was anticipated that this reaction could be developed for the synthesis of a wide range of compounds of the type $[Ru_2A(CO)_5\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^+$ or $[Ru_2(\mu-A)(CO)_4\{\mu-RO)_2PN(Et)P(OR)_2\}_2]^+$ by addition of HA (or A^-) to $[Ru_2(\mu-CO)(CO)_4(\mu-(RO)_2PN(Et)P(OR)_2\}_2]$ in the presence of a strong acid. Thus phenyl mercaptan which is unreactive towards $[Ru_2(\mu-CO)(CO)_4\{\mu-(RO)_2PN(Et)P-(OR)_2\}_2]$ at room temperature readily affords $[Ru_2(\mu-SPh)(CO)_4\{\mu-(MeO)_2-PN(Et)P(OMe)_2\}_2]^+$ (VIII) on reaction with $[Ru_2(\mu-CO)(CO)_4\{\mu-(MeO)_2PN(Et)-P(OMe)_2\}_2]$ or $[Ru_2H(CO)_5\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ in the presence of HPF_6. Likewise, while CO_2 is unreactive towards $[Ru_2H(CO)_5\{\mu-(Pr^iO)_2PN(Et)-P(OPr^i)_2\}_2]^+$ under anhydrous conditions it readily produces $[Ru_2\{\mu-OC(OH)O\}(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ (IX) in the presence of water and a strong acid *. On the other hand $[Ru_2H(CO)_5\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^+$ proved "unreactive" towards MeOH and PhCOOH in the presence of HPF_6 indicating that the systems $OMe^-/MeOH$ and $PhCO_2^-/PhCOOH$ are not sufficiently nucleophilic to replace the H_2 in $[Ru_2H_2(CO)_5\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$.
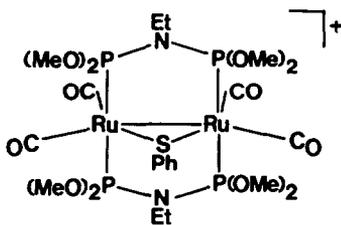
(VIII)
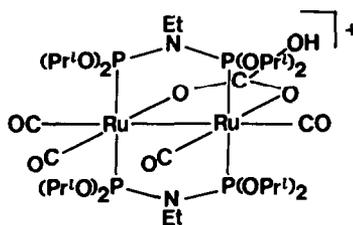
(IX)

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* Attempts to obtain crystals of $[Ru_2\{\mu-OC(OH)O\}(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$ from acetone/ether or CH_2Cl_2/hexane always led to the separation of oils but crystallisation from methanol/H_2O gave yellow crystals of a product characterised as $[Ru_2\{\mu-OC(OMe)O\}(CO)_4\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$.

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AUTHOR INDEX