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Preliminary communication

PROTONATION OF A SERIES OF DIPHOSPHAZANE- AND DIPHOSPHINE-BRIDGED DERIVATIVES OF IRON AND RUTHENIUM: DEPENDENCE OF THE NATURE OF THE HYDRIDE LIGAND ON THE METAL AND THE BRIDGING DIPHOSPHORUS LIGAND

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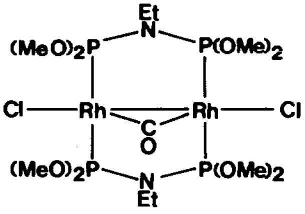
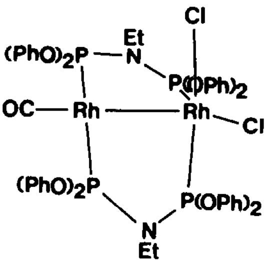
Summary

Protonation of the dinuclear compounds $[M_2(\mu\text{-CO})(CO)_4(\mu\text{-}R_2PYPR_2)_2]$ by HBF_4 or HPF_6 leads to the formation of crystalline cationic hydrido products $[M_2H(CO)_5(\mu\text{-}R_2PYPR_2)_2]X$ and $[M_2(\mu\text{-H})(\mu\text{-CO})(CO)_4(\mu\text{-}R_2PYPR_2)_2]X$ ($X = BF_4$ or PF_6) in which the hydride ligand is terminal for M = Ru, Y = N(Et) and R = OMe or OPr^i and bridging for M = Fe, Y = CH_2 and R = Me or Ph, for M = Fe, Y = N(Et) and R = OMe, OEt, OPr^i or OPh and for M = Ru, Y = CH_2 and R = Ph; the fluxional behaviour of $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (R = Me or Pr^i) in solution is described.

It is becoming increasingly evident that the structures of related homodinuclear compounds bridged by two diphosphorus ligands are dependent on both the donor/acceptor and the stereochemical properties of these ligands. Thus $[Rh_2Cl_2(CO)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ is a symmetrical molecule with the carbonyl bridging the two rhodium atoms for R = Me, while it is asymmetric with the carbonyl coordinating terminally to the one rhodium and both chlorines bonding terminally to the other rhodium atom for R = Ph (I and II) [1,2]. Furthermore, treatment of $[Pt_2(\mu\text{-H})H_2(\mu\text{-}R_2PCH_2PR_2)_2]^+$ with $R_2PCH_2PR_2$ leads to

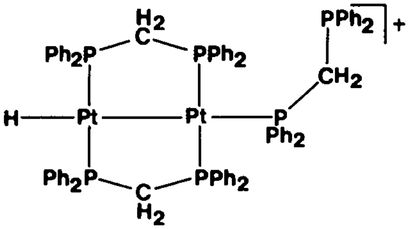


(I)

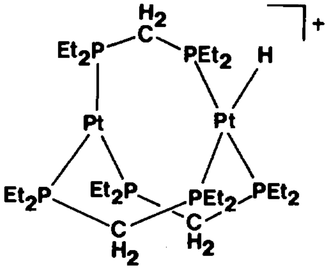


(II)

the formation of one of two different products depending on the choice of R; for R = Ph, $[Pt_2H(\mu\text{-}R_2PCH_2PR_2)_2(\eta^1\text{-}R_2PCH_2PR_2)^+]$ (III), containing a mono-ligated $R_2PCH_2PR_2$ ligand, is formed [3], while for R = Et, the Pt^0–Pt^{II} mixed oxidation state complex, $[Pt_2H(\mu\text{-}R_2PCH_2PR_2)_3]^+$ (IV) is produced [4]. We now



(III)

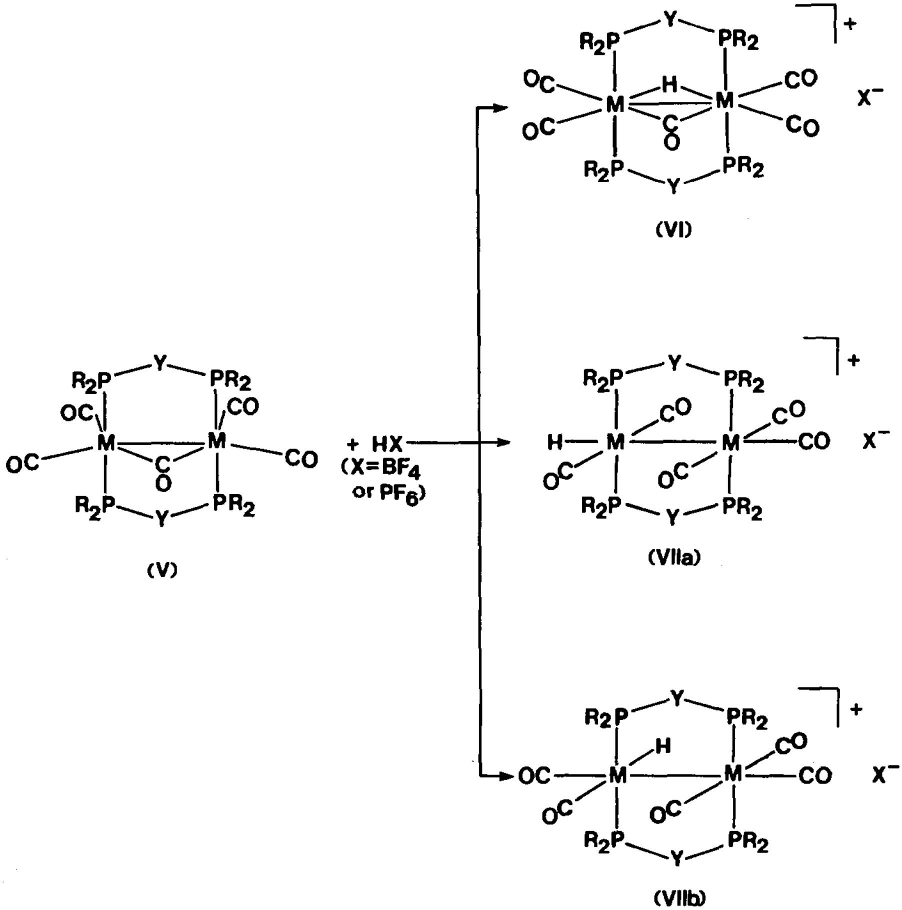


(IV)

report that the nature of the products from the protonation of $[M_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PYPR_2)_2]$ (V) (M = Fe or Ru; Y = CH_2 or NEt; R = Me, Ph, OMe, OEt, OPr^i or OPh) [5] is dependent on the metal as well as on the ligand bridging the two metal atoms.

Reaction of the bridged di-iron derivatives $[Fe_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PCH_2PR_2)_2]$ (R = Me or Ph) [5], $[Fe_2(\mu\text{-}CO)(CO)_4(\mu\text{-}Me_2PCH_2PMe_2)(\mu\text{-}Ph_2PCH_2PPh_2)]$ [5] and $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(R'O)_2PN(Et)P(OR')_2\}_2]$ (R′ = Me, Et, Pr^i or Ph) [5] with $HBF_4 \cdot Et_2O$ in ether or benzene gives the hydrido species, $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PCH_2PR_2)_2]BF_4$, $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(\mu\text{-}Me_2PCH_2PMe_2)(\mu\text{-}Ph_2PCH_2PPh_2)]BF_4$ and $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4\{\mu(R'O)_2PN(Et)P(OR')_2\}_2]BF_4$, respectively, which according to infrared and NMR spectroscopic evidence, contain a bridging hydride as well as bridging carbonyl and bridging diphosphorus ligands (VI; X = BF_4; M = Fe; Y = CH_2, R = Me or Ph; Y = NEt, R = OMe, OEt, OPr^i or OPh) in both solution and the solid state *.

The protonation is reversible, although in the case of the ditertiary phosphine products the deprotonation could only be effected by strong bases such as $NaBH_4$. In contrast the diphosphazane species $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]BF_4$ were found to be readily deprotonated by solvents in the absence of excess acid, with the ease of deprotonation increasing along the series R = Et < Pr^i < Me < Ph.



SCHEME 1. For VI: M = Fe, Y = CH_2, R = Me or Ph; M = Fe, Y = N(Et), R = OMe, OEt, OPr^i, or OPh; M = Ru, Y = CH_2, R = Ph. For VII: M = Ru, Y = N(Et), R = OMe or OPr^i.

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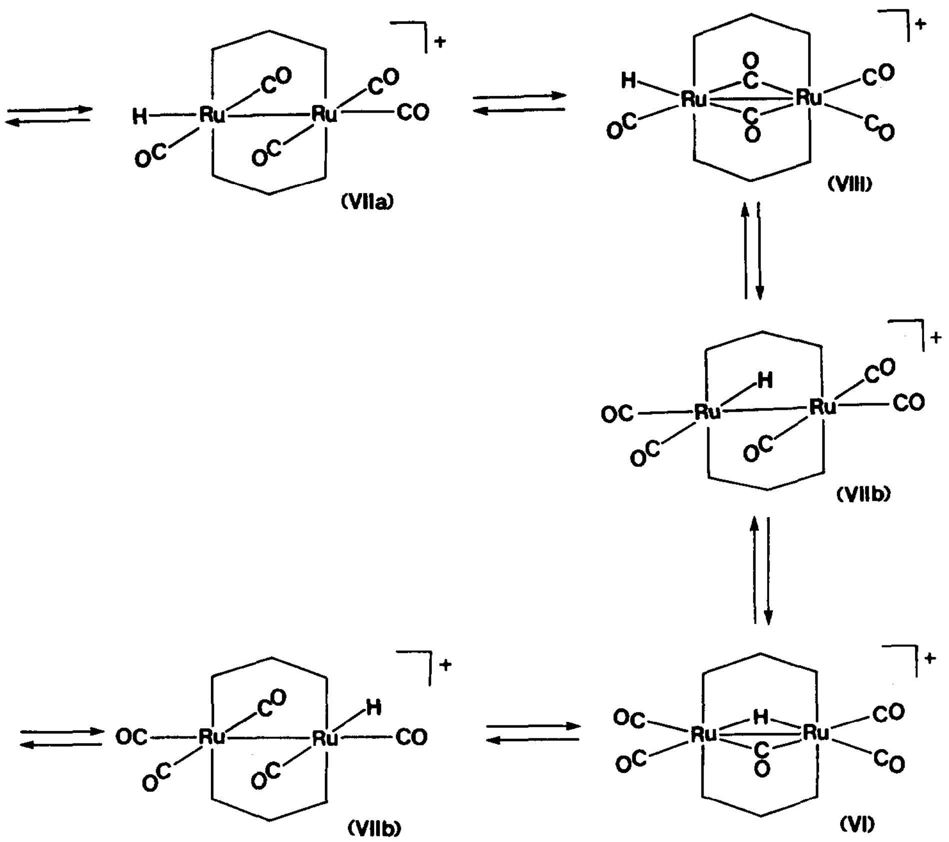
* $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(\mu\text{-}Me_2PCH_2PMe_2)_2]BF_4$: IR: ν(C–O): 1999vs, 1945s, 1935s, 1705ms cm^{-1} (nujol mull); 1998s, 1953vs, 1720ms cm^{-1} (in CH_2Cl_2); ^1H NMR: δ −12.64q ppm (Fe–H–Fe, in acetone-d_6); $^{31}P\{^1H\}$ NMR: 109.9s ppm (rel. H_3PO_4, in acetone-d_6). $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]BF_4$: IR: ν(C–O): 2040ms, 2003ms, 1948s, 1935s, 1720s cm^{-1} (nujol mull); 2010s, 1957vs, 1730 cm^{-1} (in CH_2Cl_2); ^1H NMR: δ −11.44q ppm (Fe–H–Fe, in acetone-d_6); $^{31}P\{^1H\}$ NMR: 128.2s ppm (rel. H_3PO_4, in acetone-d_6). $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(\mu\text{-}Me_2PCH_2PMe_2)(\mu\text{-}Ph_2PCH_2PPh_2)]BF_4$: IR: ν(C–O): 2060w, 1995s, 1990s, 1952vs, 1727m cm^{-1} (nujol mull); 2002ms, 1959vs, 1725ms cm^{-1} (in CH_2Cl_2); ^1H NMR: δ −11.99q ppm (Fe–H–Fe, in acetone-d_6): $^{31}P\{^1H\}$ NMR: 66.6 ppm (centre of AA′BB′ pattern, rel. H_3PO_4, in acetone-d_6). $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]BF_4$: IR: ν(C–O): 2025s, 2000vs, 1978vs, 1747s, 1725s cm^{-1} (nujol mull); 2010sh, 1995vs, 1765ms cm^{-1} (in CH_2Cl_2). $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(EtO)_2PN(Et)P(OEt)_2\}_2]BF_4$: IR: ν(C–O): 2010s, 1985vs, b, 1744m cm^{-1} (nujol mull); 2020sh, 1990vs, 1755m cm^{-1} (in CH_2Cl_2); ^1H NMR: δ −10.78q ppm (Fe–H–Fe, in acetone-d_6). $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]BF_4$: IR: ν(C–O): 2000s, 1960vs, 1730m cm^{-1} (nujol mull); 2000s, 1975vs, 1760m cm^{-1} (in CH_2Cl_2). $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]BF_4$: IR: ν(C–O): 2010s, 1990vs, 1760m cm^{-1} (in CH_2Cl_2).



SCHEME 2.

The diruthenium ditertiary phosphine derivative $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ was also found to afford a protonated product in which the proton has effectively added across the two ruthenium atoms. On the other hand the diphosphazane-bridged compounds $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ ($R = Me$ and Pr^i) [5] gave, on protonation by HBF_4 or HPF_6, a crystalline product $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ ($X = BF_4$ or PF_6) (VII; $X = BF_4$ or PF_6; $M = Ru$; $Y = N(Et)$; $R = OMe$ or OPr^i), which from IR and NMR spectroscopic data is judged to contain a terminally coordinated hydride ligand in both solution and the solid state *. These compounds can also be deprotonated, but, in contrast to the iron analogues, they require strong bases.

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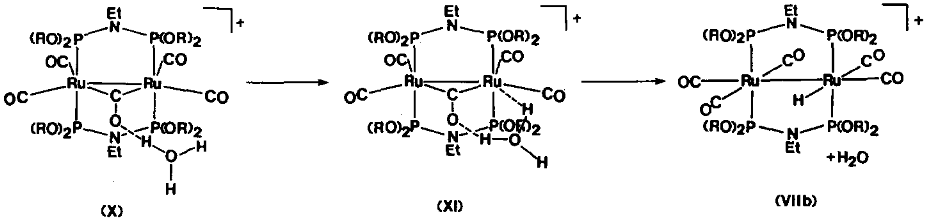
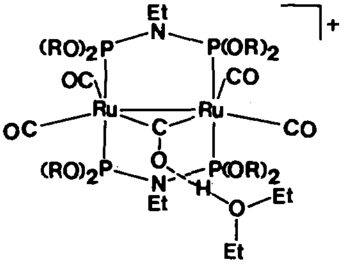
* $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]PF_6$: IR: ν(C–O): 2052sh, 2042ms, 1991ms, 1978s, 1946m, 1688m cm^{-1} (nujol mull); 2049ms, 2031s, 1992s, 1963ms, 1704m, br cm^{-1} (in CH_2Cl_2); ^1H NMR: δ −9.36q ppm (Ru–*H*–Ru, in CD_2Cl_2); $^{31}P\{^1H\}$ NMR: 26.8s, b ppm, rel. H_3PO_4, in CD_2Cl_2). $[Ru_2H(CO)_5\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]SbF_6$: IR: ν(C–O): 2096w, 2082m, 2035vs, 2014vs, 1986s, 1971s cm^{-1} (nujol mull); 2079w, 2037s, 2016s, 1985ms cm^{-1} (in CH_2Cl_2); ^1H NMR: δ −8.17q ppm (Ru–*H*, in CD_2Cl_2); $^{31}P\{^1H\}$ NMR: 150.7s ppm (rel. H_3PO_4, in CD_2Cl_2). $[Ru_2H(CO)_5\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$: IR: ν(C–O): 2072m, 2035s, 2017ms, 2000s, 1981ms cm^{-1} (nujol mull); 2064w, 2031s, 2000s, 1995sh, 1975sh cm^{-1} (in CH_2Cl_2); ^1H NMR: δ −7.57q ppm (Ru–*H*, in acetone-d_6); $^{31}P\{^1H\}$ NMR: 137.7s ppm (rel. H_3PO_4, in acetone-d_6).

The room temperature $^{31}P\{^1H\}$ NMR spectra of $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]X$ ($R = Me$ or Pr^i, $X = BF_4$ or PF_6) were found to exhibit a single resonance corresponding to the diphosphazane ligands which is inconsistent with a terminally coordinated hydride unless the latter is rapidly exchanging coordination sites. Lowering of the temperature led to broadening of the singlet and the formation of a set of resonances with an AA′BB′ pattern, while a further decrease in temperature resulted in the collapse of the singlet and the appearance of two symmetrical sets of resonances each corresponding to AA′BB′ patterns. When the solution was raised to room temperature only a sharp singlet was again observed. This variable temperature spectroscopic data are interpreted in terms of the presence of predominantly two isomers in solution, VIIa and VIIb, and the fluxional process illustrated in Scheme 2. The hydride ligand is proposed to migrate around the two ruthenium atoms in a plane perpendicular to that defined by the two ruthenium and four phosphorus atoms via VIIa, VIII, VIIb and VI as shown.



SCHEME 3

Earlier investigations have revealed that protonation of $[M_3H(\mu\text{-}CO)(CO)_{10}]^-$ ($M = Fe$, Ru, or Os) at low temperatures under anhydrous conditions gives the O-protonated products $[M_3H(\mu\text{-}COH)(CO)_{10}]$ which at slightly higher temperatures rearrange to the dihydride $[M_3(\mu\text{-}H)H(CO)_{11}]$ and subsequently to $[M_3(CO)_{12}]$ in the case of the iron and ruthenium hydrides [6–8]. The addition of $HBF_4 \cdot$ etherate to an anhydrous pale yellow solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ ($R = Me$ or Pr^i) in ether was found to lead to spontaneous formation of an intense red mixture, which slowly decolourised with formation of the pale yellow hydride $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$. It is assumed that the site of the initial attack of the proton is at the oxygen of the bridging carbonyl group and that



(IX)

the intense red colour is due to the initial formation of a species $[Ru_2(\mu\text{-}COHOEt_2)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ (IX) of the charge-transfer type in which $[HOEt_2]^+$ is weakly bound to the oxygen of the bridging carbonyl via a hydrogen bond as shown. Significantly, the rate of formation of $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ can be markedly increased by the addition of water to the reaction mixture. This rate increase can be readily explained in terms of Scheme 3, with the water catalysing the proton transfer from the bridging carbonyl oxygen to the ruthenium via the six-membered transition state (XI).

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