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Preliminary communication

SUBSTITUTED DERIVATIVES OF [$Fe_2(CO)_9$] AND [$Ru_2(CO)_9$] AND THEIR SUSCEPTIBILITY TO ELECTROPHILIC ATTACK: X-RAY CRYSTAL STRUCTURE OF [$Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(C_6H_5O)_2PN(C_2H_5)P(OC_6H_5)_2\}_2$]$PF_6$

GERARD DE LEEUW, JOHN S. FIELD, RAYMOND J. HAINES*, BETH McCULLOCH, ELSIE MEINTJIES, CHRISTIAAN MONBERG, KANDASAMY G. MOODLEY, GILLIAN M. OLIVIER, CLIFFORD N. SAMPSON and NICK D. STEEN

C.S.I.R. Unit of Metal Cluster Chemistry and Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg (Republic of South Africa)

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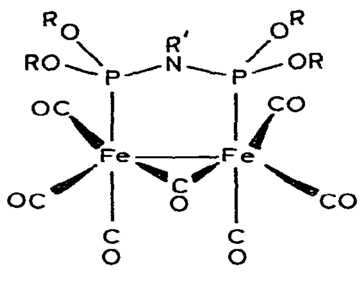
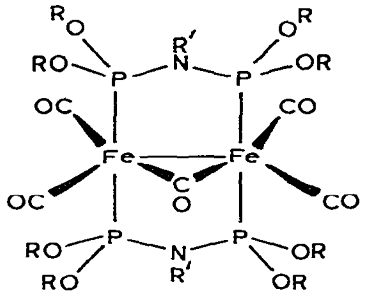
Summary

Bis- and, in particular, tetra-substituted ditertiary phosphine and diphosphazane derivatives of [$Fe_2(CO)_9$] and [$Ru_2(CO)_9$], readily synthesised by reaction of the appropriate bidentate ligand with [$Fe_2(CO)_9$] and [$Ru_3(CO)_{12}$], respectively, are very susceptible to electrophilic attack by reagents such as halogens and protons; the solid state structure of one of the products [$Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2$]$PF_6$ has been determined by X-ray crystallography.

Although [$Fe_2(CO)_9$] can be readily synthesised in high yield by irradiation of [$Fe(CO)_5$] with ultraviolet light in an appropriate solvent [1], it is unstable in solution degrading to [$Fe(CO)_5$] and [$Fe(CO)_4$] or [$Fe(CO)_4$(solvent)] [2]; its ease of preparation relies on its limited solubility in most solvents [1]. [$Ru_2(CO)_9$] is similarly very unstable in solution, and has only been detected transiently in the photolysis of [$Ru(CO)_5$] at temperatures of −40°C and less [3]. Earlier investigations in the authors' laboratories established that substituted derivatives of [$Fe_2(CO)_9$] can be stabilised by employing bidentate ligands with strong bridging properties and in particular by the pyrophosphite $(EtO)_2POP(OEt)_2$ [4]. Similar observations were made by Cotton et al. utilising $Ph_2PCH_2PPh_2$ [5] and by King et al. using $F_2PN(Me)PF_2$ [6]. We now report that the diphosphazane ligands $(RO)_2PN(R')P(OR)_2$ (R′ = alkyl group; R = alkyl or aryl group) afford not only stable bis- and tetra-substituted derivatives of [$Fe_2(CO)_9$] but also stable tetra-substituted derivatives of [$Ru_2(CO)_9$].



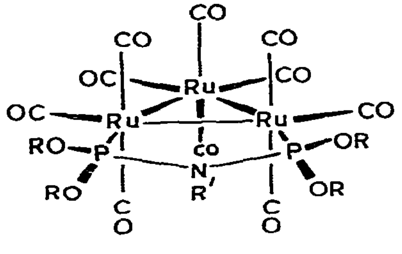
(I)



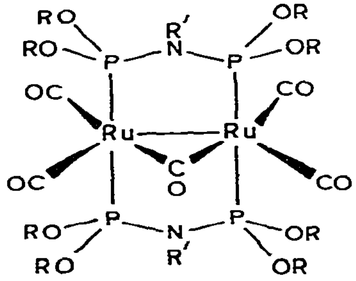
(II)

Treatment of $[Fe_2(CO)_9]$ with a half molar amount of $(RO)_2PN(R')P(OR)_2$ ($R' = Et$, $R = Me$ or Ph; $R' = Me$, $R = Et$ or i-Pr) followed by removal of the $[Fe(CO)_5]$ and irradiation of the resultant solution with ultraviolet light, affords bis-substituted derivatives of stoichiometry $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}(RO)_2\text{-}PN(R')P(OR)_2\}]$ (I)* and of structure analogous to that established for $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ [5] on the basis of infrared spectroscopic evidence (ν(C—O) for $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}Ph_2PCH_2PPh_2\}]$: 2040s, 1990s, 1973s, 1950(sh), 1940s, 1921(sh) and 1758ms cm^{-1}, measured in C_6H_{12}; $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}]$: 2060s, 2011s, 2001s, 1977m, 1969s, 1954m and 1777m cm^{-1}, measured in C_6H_{12}). Photochemical reaction of $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}(RO)_2PN(R')P(OR)_2\}]$ with an excess of $(RO)_2PN(R')\text{-}P(OR)_2$ readily leads to further substitution and the formation of tetrasubstituted derivatives of the type $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(R')P(OR)_2\}_2]$ (II). The band patterns of the peaks in the C—O stretching region of the infrared spectra of these species are very similar to those found for $[Fe_2(\mu\text{-}CO)(CO)_4\text{-}\{\mu\text{-}(EtO)_2POP(OEt)_2\}_2]$ [4] and $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}F_2PN(Me)PF_2\}_2]$ [6] (ν(C—O) for $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(EtO)_2POP(OEt)_2\}_2]$: 2010s, 1955vs, 1929s, 1910s, 1720(sh), 1710s and 1700(sh) cm^{-1}, measured in C_6H_{12}; $[Fe_2(\mu\text{-}CO)\text{-}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$: 1996m, 1952s, 1916s, 1903s, 1716(sh) and 1703m cm^{-1}, measured in C_6H_{12}) and on this basis the diphosphazane complexes are assumed to have structures analogous to those established crystallographically for the latter two compounds [4,6] viz. II.

Tetra-substituted derivatives of $[Ru_2(CO)_9]$ can also be synthesised but from $[Ru_3(CO)_{12}]$. Thus reaction of the latter with an equimolar amount of



(III)



(IV)

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*All new compounds were characterised by elemental analysis and by IR and ^{1}H NMR spectroscopy.

$(RO)_2PN(R')P(OR)_2$ ($R' = Et$, $R = Me$ or Ph; $R' = Me$, $R = Et$) affords $[Ru_3(CO)_{10}\{\mu\text{-}(RO)_2PN(R')P(OR)_2\}]$ (III) which on further reaction with excess $(RO)_2PN(R')P(OR)_2$ under photochemical conditions produces $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(R')P(OR)_2\}_2]$ (IV). The trinuclear compounds have been assigned structure III on the basis that this is the stereochemistry established for $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ [7] while the dinuclear derivatives are proposed to have the structure illustrated, IV, on the basis of the similar band patterns in the C—O stretching region of their infrared spectra with those for their iron analogues (ν(C—O) for $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$: 2000ms, 1970s, 1934s, 1921s, 1722w and 1708m cm^{-1}, measured in C_6H_{12}).

Not surprisingly these substituted derivatives of $[Fe_2(CO)_9]$ and $[Ru_2(CO)_9]$, particularly the tetra-substituted compounds, are very susceptible to electrophilic attack. Thus treatment of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ with halogens leads to the formation of the cationic species $[Fe_2(\mu\text{-}X)(CO)_4\text{-}\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]^+$ ($X = Cl$, Br or I), readily isolated as the hexafluorophosphate or tetraphenylborate salts. To establish the stereochemistry of these cationic species but, more important, to gain insight into the nature of the electrophilic attack on the neutral parent, the structure of $[Fe_2(\mu\text{-}Br)(CO)_4\text{-}\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]PF_6$ was determined by X-ray crystallography.

Crystal data: $[Fe_2Br(CO)_4\{(C_6H_5O)_2PN(C_2H_5)P(OC_6H_5)_2\}_2]PF_6\cdot$1acetone, $M = 1461$, orthorhombic, space group $Cmc2_1$, a 16.82(2), b 19.30(2), c 20.82(2) Å, V 6759.6 Å^3, D_m 1.47, D_c 1.44 g cm^{-3} for $Z = 4$; μ(Mo-K_α) 1.37 mm^{-1}, $\theta = 23°$. Data were collected on a Philips PW1100 diffractometer (NPRL, CSIR) with graphite-monochromated Mo-K_α radiation. Of the 2520 reflections measured 2060 with $I > 3\sigma(I)$ were used to solve the structure and refine it by full-matrix least-squares to $R = 0.079$; the Fe, Br and P atoms were refined using anisotropic temperature factors and the phenyl rings as perfect rigid hexagons*.

The molecular geometry of the compound is illustrated in Fig. 1. The two iron atoms which are separated by a distance corresponding to a formal metal—metal bond (2.725(5) Å), are bridged not only by the two diphosphazane ligands but by a bridging bromonium ion as well. Two of the terminal carbonyl groups are essentially orthogonal to the iron—iron vector while the other two are almost colinear with it. These carbonyl groups, together with the bromide and iron atoms, lie on a crystallographically imposed mirror plane. The structure of this cationic species is in fact very similar to that presumably adopted by $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ indicating that halogenation of the latter results in the replacement of a bridging carbonyl group by a bridging halogenonium ion.

$[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ similarly affords $[Fe_2(\mu\text{-}X)\text{-}(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ on reaction with halogens but in contrast to $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]^+$, the latter reacts further with halide ions and excess of the halogen to afford three new dinuclear compounds, one of them being characterised as a Michaelis-Arbuzov rearrangement product $[Fe_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}\{\mu\text{-}(MeO)_2PN(Et)\text{-}P(OMe)_2\}]$ (V) of structure analogous to $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)\text{-}$

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*Supplementary material is available from the authors.

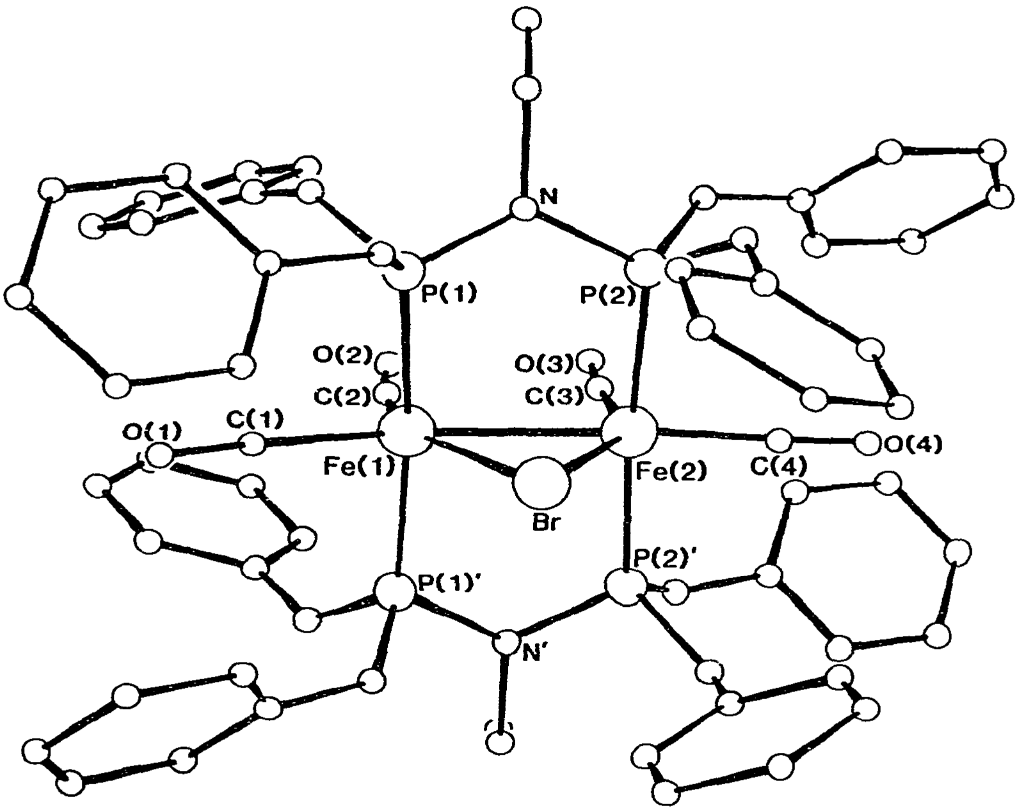
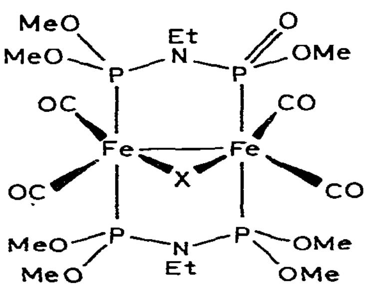
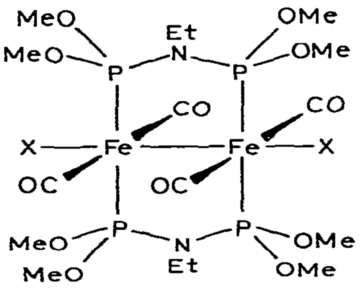


Fig. 1. The molecular structure of [$Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2$]. Hydrogen atoms were not located. Bond lengths: Fe(1)—Fe(2), 2.725(5); Fe(1)—Br, 2.391(4); Fe(2)—Br, 2.363(5); Fe(1)—P(1), 2.235(5); Fe(2)—P(2), 2.208(5); Fe(1)—C(1), 1.89(3); Fe(1)—C(2), 1.69(3); Fe(2)—C(3), 1.76(4); Fe(2)—C(4), 1.77(3) Å. Bond angles: Fe(1)—Br—Fe(2), 69.9(1); Fe(2)—Fe(1)—P(1), 91.7(2); Fe(1)—Fe(2)—P(2), 92.0(2); Fe(2)—Fe(1)—C(1), 167(1); Fe(2)—Fe(1)—C(2), 93(1); Fe(1)—Fe(2)—C(3), 89(1); Fe(1)—Fe(2)—C(4), 167(1)°.

$P(OPh)_2\}_2]^+$, on the basis of the infrared spectroscopic data (ν(C—O) for [$Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2$]$PF_6$: 2037m, 2006s, 1989ms, 1970m cm^{-1}, measured in CH_2Cl_2; [$Fe_2(\mu\text{-}I)(CO)_4$ $\{\mu\text{-}(MeO)_2PN(Et)P(O)(OMe)\}$-$\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}$]: 2009m, 1981s, 1954ms, 1932m cm^{-1}, measured

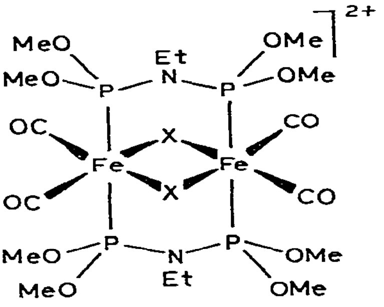


(V)

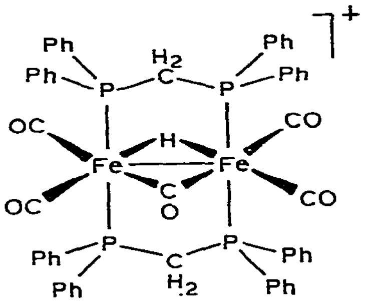


(VI)

in CH_2Cl_2). The other two are believed to be $[Fe_2X_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (VI) (ν(C—O) for $[Fe_2I_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$: 2057m, 1990s,br and 1952m cm^{-1}, measured in CH_2Cl_2) and $[Fe_2(\mu\text{-}X)_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^{2+}$ (VII) (ν(C—O) for $[Fe_2(\mu\text{-}Br)_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^{2+}$: 2076s and 2022s cm^{-1}, measured in $CHCl_3$) on the basis of elemental analysis and spectroscopic evidence.



(VII)



(VIII)

In contrast to halogenation, protonation of the tetra-substituted dinuclear compounds does not necessarily lead to carbonyl replacement but to simple addition across the metal atoms. Thus treatment of $[Fe_2(\mu\text{-}CO)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ with HBF_4. HPF_6, CF_3COOH, HCOOH, etc. leads to the reversible formation of a cationic species characterised as $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]^+$ (VIII) (ν(C—O): 2019m, 2004ms, 1945s, 1720ms, as a Nujol mull). This species is very susceptible to radical attack with dissolution in CH_2Cl_2 leading to the formation of $[Fe_2(\mu\text{-}Cl)(CO)_4\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]^+$.

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