

### Preliminary communication

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## NOVEL DIETHYLAMINO MIGRATIONS IN THE REACTION OF DIETHYLAMINODICHLOROPHOSPHINE WITH SODIUM TETRACARBONYLFERRATE(– II)

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### Summary

Reaction of  $\text{Et}_2\text{NPCl}_2$  with  $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5$  dioxane in diethyl ether below  $0^\circ\text{C}$  gives deep orange  $(\text{Et}_2\text{N})_2\text{PP}[\text{Fe}(\text{CO})_4]_2[\text{Fe}(\text{CO})_4]\text{OC}(\text{NEt}_2)\text{Fe}(\text{CO})_3$ , shown by X-ray diffraction (monoclinic, space group  $P2_1/n$ ;  $a$  17.071(7),  $b$  19.117(8),  $c$  10.853(3) Å,  $\beta$  96.82(3)°,  $Z = 4$ ) to have a four-membered  $\text{FeP}_3$  ring bonded to two isolated  $\text{Fe}(\text{CO})_4$  groups, a four-membered  $\text{FeOPC}$  ring formed by a diethylcarbamoyl group bridging an  $\text{Fe}-\text{P}$  bond, an  $(\text{Et}_2\text{N})_2\text{P}$  unit formed by diethylamino migration, but no  $\text{Fe}-\text{Fe}$  bonds. This complex undergoes facile decarbonylation in solution at room temperature to form  $[(\text{Et}_2\text{N})_2\text{PP}[\text{Fe}(\text{CO})_4]_2\text{PCO}-\text{NEt}_2]_2\text{Fe}_2(\text{CO})_6$ . Structure determination of this product by X-ray diffraction (monoclinic, space group  $P2_1/n$ ;  $a$  9.054(4),  $b$  38.752(34),  $c$  19.737(8) Å,  $\beta$  104.05(3)°,  $Z = 8$ ) indicates that this decarbonylation reaction involves conversion of a bridging diethylcarbamoyl group to a terminal diethylcarbamoyl group, formation of an  $\text{Fe}-\text{Fe}$  bond, and formation of a new  $\text{Fe}-\text{P}$  bond.

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Recently we reported reactions of diisopropylaminodichlorophosphine with  $\text{Na}_2\text{Fe}(\text{CO})_4$  to give the phosphorus-bridging carbonyl derivatives  $(i\text{-Pr}_2\text{NP})_2\text{CO}-\text{Fe}_2(\text{CO})_6$  [1] and  $(i\text{-Pr}_2\text{NP})_3\text{COFe}_2(\text{CO})_6$  [2] and the triphosphine complex  $(i\text{-Pr}_2\text{NP})_3\text{Fe}_2(\text{CO})_6$  [2] depending upon the reaction conditions. We have now found that use of a much less sterically hindered dialkylaminodichlorophosphine, namely diethylaminodichlorophosphine, in such reactions leads to totally different products arising from dialkylamino migration both from one phosphorus to another to give an  $(\text{R}_2\text{N})_2\text{P}$  unit and from phosphorus to carbon to give a dialkylcarbamoyl group,  $\text{R}_2\text{NCO}$ .

A suspension of 180 mmol of  $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5$  dioxane [3] in 1400 ml of diethyl ether was treated with 160 mmol of  $\text{Et}_2\text{NP}(\text{Cl})_2$  [4] at  $-78^\circ\text{C}$ . After stirring at  $0^\circ\text{C}$  for 20 h the reaction mixture was filtered as rapidly as possible without taking any special precautions to exclude air. Removal of solvent at  $0^\circ\text{C}$  from the filtered reaction mixture followed by chromatography on a  $20 \times 4$  cm silica gel column in hexane solution gave 16 g (37% yield) of deep orange air-stable crystals, m.p.  $101\text{--}102^\circ\text{C}$ , of the composition  $(\text{Et}_2\text{NP})_3\text{Fe}_3(\text{CO})_{12}$  [5] after elution with a mixture of dichloromethane and hexane and crystallization at  $-10^\circ\text{C}$ .

This product was found by X-ray diffraction to have structure I [6]. This structure (Fig. 1) contains a bent triphosphine unit (P(1)–P(3): 2.122(4) Å; P(2)–P(3): 2.183(4) Å; P(1)–P(3)–P(2):  $85.5(2)^\circ$ ) with two diethylamino groups bonded to one of the terminal phosphorus atoms and  $\text{Fe}(\text{CO})_4$  units coordinated both to the center (Fe(2)–P(3): 2.270(3) Å and other terminal (Fe(3)–P(1): 2.223(4) Å) phosphorus atoms. In addition an  $\text{Fe}(\text{CO})_3$  unit bridges the terminal phosphorus atoms to form a four-membered  $\text{FeP}_3$  ring (Fe(1)–P(1): 2.302(3) Å; Fe(1)–P(2): 2.312(4) Å; P(2)–Fe(1)–P(1):  $78.6(1)^\circ$ ; Fe(1)–P(1)–P(3):  $96.4(1)^\circ$ ; Fe(1)–P(2)–P(3):  $94.4(1)^\circ$ ). Most unusual, however, is the bridging of a diethylcarbamoyl group across the Fe(1)–P(1) bond to form a four-membered  $\text{FePOC}$  ring (Fe(1)–C(14): 2.00(1) Å; C(14)–O(1): 1.35(1) Å; P(1)–O(1): 1.746(7) Å; P(1)–Fe(1)–C(14):  $67.7(3)^\circ$ ; Fe(1)–C(14)–O(1):  $107.4(7)^\circ$ ; P(1)–O(1)–C(14):  $101.4(6)^\circ$ ; Fe(1)–P(1)–O(1):  $83.4(2)^\circ$ ). The short C(14)–N(3) bond length of 1.30(1) Å suggests C=N double bond character and the bond orders indicated in structure I. All iron and phosphorus atoms in I have the rare gas electronic configurations. The three-coordinate phosphorus atom P(3) has a pyramidal configuration (P(1)–P(3)–Fe(2):  $124.2(2)^\circ$ ; Fe(2)–P(3)–P(2):  $129.2(2)^\circ$ ) and an uncoordinated lone pair. There are no iron–iron bonds in this structure.

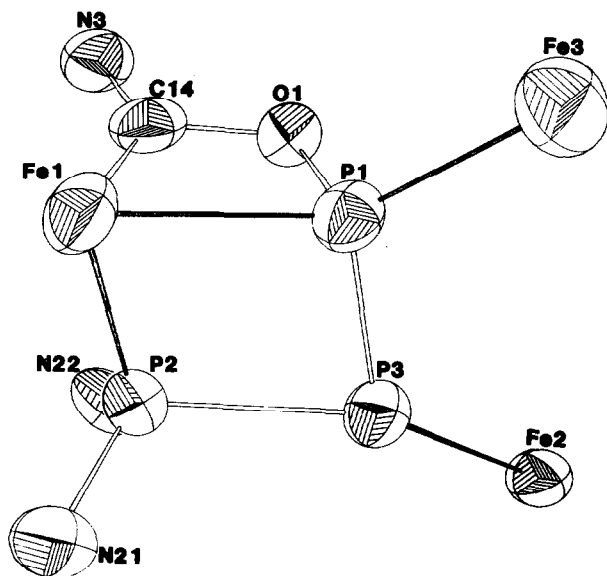


Fig. 1. ORTEP diagram of the complex  $(\text{Et}_2\text{NP})_3\text{Fe}_3(\text{CO})_{12}$  (I). For clarity the eleven metal carbonyl groups and the six ethyl groups are not shown.

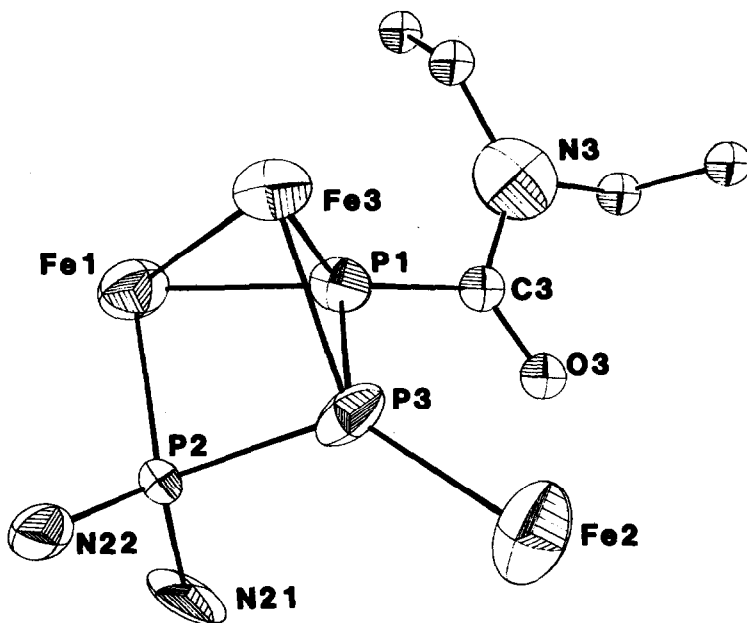
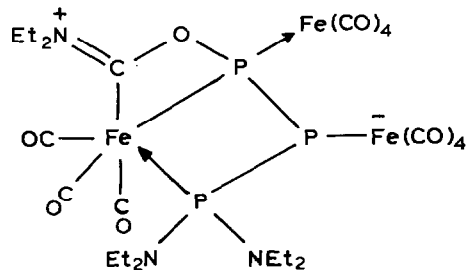
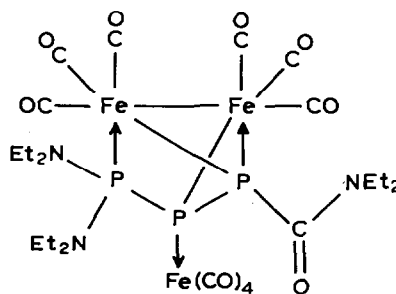


Fig. 2. ORTEP diagram of the complex  $(\text{Et}_2\text{NP})_3\text{Fe}_3(\text{CO})_{11}$  (II). For clarity the ten metal carbonyl groups and the six ethyl groups are not shown.

Complex I when dissolved in organic solvents such as  $\text{CDCl}_3$ ,  $\text{C}_6\text{D}_6$ ,  $\text{CH}_2\text{Cl}_2$ , or  $\text{Et}_2\text{O}$  undergoes a major change at ambient temperature over a period of hours to form a second complex II, as indicated by following the  $^{31}\text{P}$  NMR spectra of such solutions. Complex II, an orange solid, m.p.  $75\text{--}80^\circ\text{C}$ , of stoichiometry  $(\text{Et}_2\text{NP})_3\text{Fe}_3(\text{CO})_{11}$  [7] can be isolated in 35% yield from the original reaction of  $\text{Et}_2\text{NP}(\text{CO})_2\text{Fe}(\text{CO})_4$  with  $\text{Na}_2\text{Fe}(\text{CO})_4$  if the reaction mixture is stirred at  $25^\circ\text{C}$  rather than  $0^\circ\text{C}$  for 24 h, before product isolation by a procedure similar to that described above for I. The structure of II was determined by X-ray diffraction [8]. This structure (Fig. 2) reveals that the facile conversion of I to II involves conversion of the bridging diethylcarbamoyl group to a terminal diethylcarbamoyl group ( $\nu(\text{CO})$ :  $1648\text{ cm}^{-1}$ ), formation of an iron–iron bond ( $\text{Fe}(1)\text{--}\text{Fe}(3)$ :  $2.733(19)\text{ \AA}$ ), and formation of a new iron–phosphorus bond ( $\text{Fe}(3)\text{--}\text{P}(3)$ :  $2.315(14)\text{ \AA}$ ) by displacement of a carbonyl group on  $\text{Fe}(3)$  by the lone pair on  $\text{P}(3)$  in I.



(I)



(II)

Supplementary material (positional parameters, anisotropic thermal parameters, bond angles, and bond distances for I and II) is available from the authors.

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## References

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- 5 Found: C, 35.5; H, 3.9; N, 5.2.  $C_{24}H_{30}Fe_3N_3O_{12}P_3$  calcd.: C, 35.4; H, 3.7; N, 5.2%. Infrared  $\nu(\text{CO})$  in  $\text{CHCl}_3$ : 2080 m, 2055 s, 2037 s, 2007 m, 1957 s br, 1941 s br  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR in  $\text{CHCl}_3$ :  $\delta$  228.5 dd (367, 37 Hz), 156.1 dd (367, 301 Hz), 118.6 dd (301, 37 Hz) ppm;  $^{13}\text{C}$  NMR at 67.8 MHz in  $\text{CD}_3\text{CN}$ : CO at  $\delta$  217.3 s, 214.4 d (9 Hz), 208.7 dd (29, 20 Hz), and 205.0 dt (45, 20 Hz) ppm.
- 6 Crystal data for  $(\text{Et}_2\text{NP})_3\text{Fe}_3(\text{CO})_{12}$  (I):  $\text{Fe}_3\text{P}_3\text{C}_{24}\text{H}_{30}\text{N}_3\text{O}_{12}$ , mol. wt. 813.0, monoclinic crystals: space group  $P2_1/n$ ;  $a$  17.071(7),  $b$  19.117(8),  $c$  10.853(3) Å,  $\beta$  96.82(3)°,  $V$  3516.6(23) Å<sup>3</sup>,  $D_{\text{calc}}$  1.535  $\text{g}/\text{cm}^3$ ,  $Z = 4$ . Anisotropic least squares refinement (Mo- $K_\alpha$  radiation,  $\mu(\text{Mo-}K_\alpha)$  14.11  $\text{cm}^{-1}$ ,  $F(000) = 1656$ , 3238 observed reflections,  $R = 0.071$ ).
- 7 Found: C, 35.2; H, 3.9; N, 5.3.  $C_{23}H_{30}Fe_3N_3O_{11}P_3$  calcd.: C, 35.2; H, 3.8; N, 5.4%. Infrared  $\nu(\text{CO})$  in hexane: 2070 m, 2048 s, 2025 s, 1998 s, 1990 m, 1983 m, 1973 m, 1960 m, 1955 m sh, 1948 m, 1648 w ( $\text{Et}_2\text{NCO}$ )  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR in  $\text{CHCl}_3$ :  $\delta$  123.0 dd (195, 54 Hz), 97.7 dd (264, 54 Hz), 85.8 dd (264, 195 Hz) ppm;  $^{13}\text{C}$  NMR at 67.8 MHz in  $\text{CDCl}_3$ : CO at  $\delta$  215.3 s, 211.3 s, 210.3 s, and 165.3 s ( $\text{Et}_2\text{NCO}$  carbonyl) ppm.
- 8 Crystal data for  $(\text{Et}_2\text{NP})_3\text{Fe}_3(\text{CO})_{11}$  (II):  $\text{Fe}_3\text{P}_3\text{C}_{23}\text{H}_{30}\text{N}_3\text{O}_{11}$ , mol wt. 785.0, monoclinic crystals: space group  $P2_1/n$ ;  $a$  9.054(4),  $b$  38.75(3),  $c$  19.737(8) Å,  $\beta$  104.05(3)°,  $V$  6717.8(70) Å<sup>3</sup>,  $D_{\text{calc}}$  1.552  $\text{g}/\text{cm}^3$ ,  $Z = 8$ . Refinement using anisotropic thermal parameters for Fe, P, N, O, and CO groups and isotropic thermal approximations for  $\text{C}_2\text{H}_5$  carbons (Mo- $K_\alpha$  radiation,  $\mu(\text{Mo-}K_\alpha)$  14.72  $\text{cm}^{-1}$ ,  $F(000) = 3200$ , 2524 observed reflections,  $R = 0.109$ ). Bond distances given in the text are the averages of the values obtained for the two independent molecules in the unit cell, one of which showed disorder in the position of the ethyl groups.