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**Preliminary communication**

# $\eta^2$-ACYLIRON COMPLEXES. CRYSTAL STRUCTURE OF $[Fe(I)(\eta^2\text{-}C(O)\text{-}i\text{-}Pr)(CO)(PEt_3)_2]$

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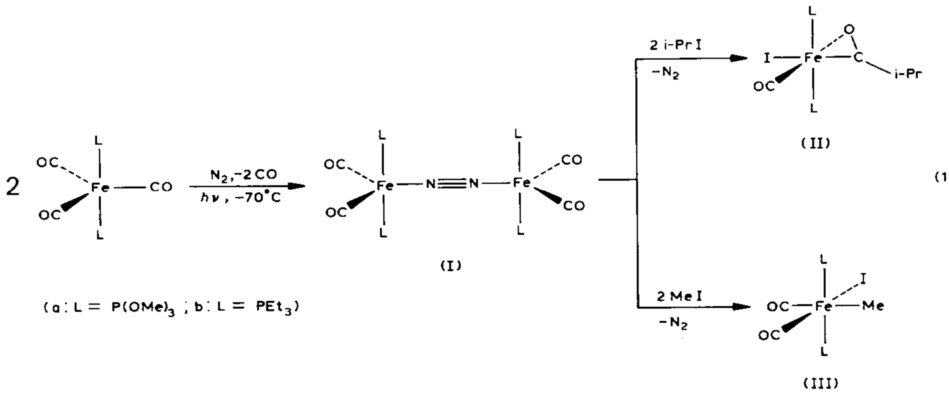
## Summary

The syntheses of $\eta^2$-isobutyrylcarbonyliodobis(phosphorus donor)iron (IIa, IIb) and dicarbonyliodomethylbis(phosphorus donor)iron complexes ($L = P(OMe)_3$, $PEt_3$) (IIIa, IIIb) are reported. IIb has been characterized by an X-ray structure analysis.

$\eta^2$-Acyl complexes have been structurally characterized for actinide and early transition metals [1], Group VI metals [2] and ruthenium [3]. We have now found that this binding mode can also operate in iron(II) complexes.

The complexes II are easily prepared by oxidative addition of isopropyl iodide to $(OC)_2FeL_2$ fragments, $L = P(OMe)_3$ $PEt_3$, generated from the corresponding isolable $\mu$-dinitrogen derivatives I (eq. 1) [4,5].



Complex Ia separates from ether [4] and Ib from pentane upon irradiation of the corresponding $(OC)_3FeL_2$ compound (4–8 h, −70°C). Addition of $i\text{-}C_3H_7I$ to Ia, Ib in ether at room temperature produces deep red brown solutions, from which

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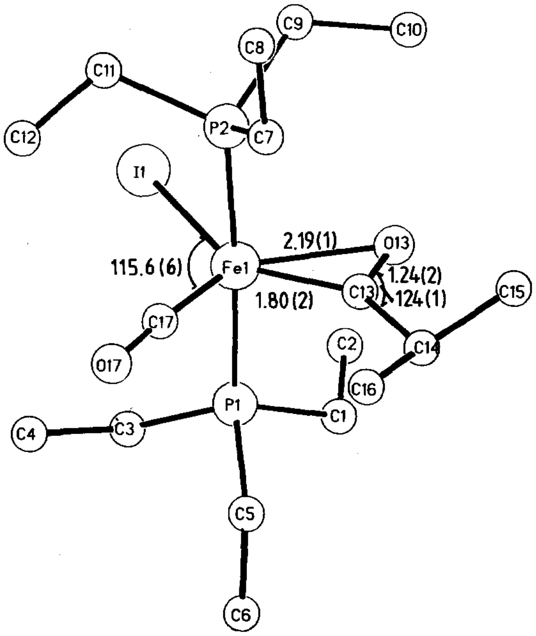

Fig. 1. Coordination geometry of $(PEt_3)_2(CO)IFe(\eta^2\text{-}C(O)\text{-}i\text{-}Pr)$ (IIb).

crystals of IIa, IIb are isolated when the solutions are concentrated and kept at −80°C. The $\eta^2$-structure of compounds II was initially assigned on the basis of spectroscopic data, and then confirmed in the case of IIb by X-ray structural analysis.

The IR spectra of II exhibit characteristic broad bands at 1586 $cm^{-1}$ in the region expected for $\eta^2$-bound acyl moieties. Among the NMR spectroscopic data the downfield $^{13}C_{acyl}$ resonances also indicate this type of bonding. The crystal structure analysis of IIb reveals that as for the comparable ruthenium systems [3], there is a relatively long Fe–O bond and a short Fe–C bond (Fig. 1).

In consequence of the $\eta^2$-bonding mode of the acyl ligand an angle of the CO and I ligands close to 120° is observed. The overall coordination geometry is almost trigonal bipyramid.

In contrast to the reaction of I with i-PrI the addition of methyl iodide to I leads to the formation of methyliodoiron complexes III. The methyl group is obviously firmly bound to the metal and shows no tendency to migrate spontaneously to the CO group. Complex IIIa has been synthesized before [5] and was identified by spectroscopic means. The attachment of the methyl moiety to the iron center in IIIb is confirmed by the observation of a phosphorus coupling of 7.7 Hz to the $CH_3$ protons. The fact that the methyl group remains bound to the metal is in accord with earlier observations and a theoretical analysis of the migrating abilities of alkyl ligands [6,7].

### *X-Ray structure*

Syntex-Nicolet P3 diffractometer, $\lambda(\text{Mo-}K_\alpha)$ 71.069 pm, $T$ −35°C, $2 \leq 2\theta \leq 42°$, space group $P2_1/c$, $a$ 1906(3), $b$ 1309(2), $c$ 2283(4) pm; $\beta$ 128.4(1); $Z = 8$;

ω-scan, 3452 reflections ($I \geq 2\ \sigma\ (I)$). Structure solution SHELXTL [8], $R_1 = 0.075$, $R_2 = 0.086$. The two independent molecules within the asymmetric unit have essentially identical geometries. Detailed structural data are available from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldszentrum 2, upon quotation of deposit No. CSD 51891, the authors, and the journal reference for this article.

*Selected spectroscopic data.* IIa: $\nu$(CO) (n-Pentane): 1936s, 1586w,br cm$^{-1}$; $^{1}$H NMR ($CD_3COCD_3$): 3.86 (t, *J*(P–H) 5.3 Hz, 2 $P(OMe)_3$), 3.06 (sept, *J*(H–H) 6.6 Hz, 1CH), 0.86 (d, *J*(H–H) 6.6 Hz, 2-$CH_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$): 155.2 ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$): 53.44 (s, 2$P(OMe)_3$), 43.65 ppm (t, *J*(P–C) 3.5 Hz, CH), 18.47 (s, 2-$CH_3$), 219.65 (t, *J*(P–C) 51.6 Hz, CO), 283.03 ppm (t, *J*(P–C) 25.8 Hz, $\eta^2$-CO).

IIb: $\nu$(CO) (n-Pentane): 1899s, 1586w,br cm$^{-1}$; $^{1}$H NMR ($(CDCl)_3$: 1.95 (sept, *J*(P, H–H) 3.7 Hz, P–$CH_2$–$CH_3$, 12H), 1.1 (quint., *J*(P, H–H), 7.1 Hz, P–$CH_2$–$CH_3$, 18H), 2.72 (sept, *J*(H–H) 6.9 Hz, CH), 1.56 ppm (d, *J*(H–H) 6.9 ppm, 2-$CH_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$): 32.06 ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$): 8.4 ppm (s, P–$CH_2$–$CH_3$), 18.6 ppm (t, *J*(P–C) 12.5 Hz, P–$CH_2$–$CH_3$), 19.3 ppm (s, $CH_3$), 44.28 (s, CH), 222.4 ppm (t, *J*(P–C) 34.7 Hz, CO), 285.9 ppm (t, *J*(P–C) 19.4 Hz, $\eta^2$-CO).

IIIb: $\nu$(CO) (n-Pentane): 1986s, 1923s cm$^{-1}$; $^{1}$H NMR ($C_6D_6$): 1.86 (sept, *J*(P, H–H), 3.4 Hz, P–$CH_2$–$CH_3$), 12H), 0.91 (quint, *J*(P,H–H) 7.1 Hz, P–$CH_2$–$CH_3$, 18H), 0.96 ppm (t, *J*(P–H) 7.7 Hz, $CH_3$); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): 31.9 ppm.

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