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Preliminary communication

The *in situ* preparation and utilization of a novel bidentate ligand

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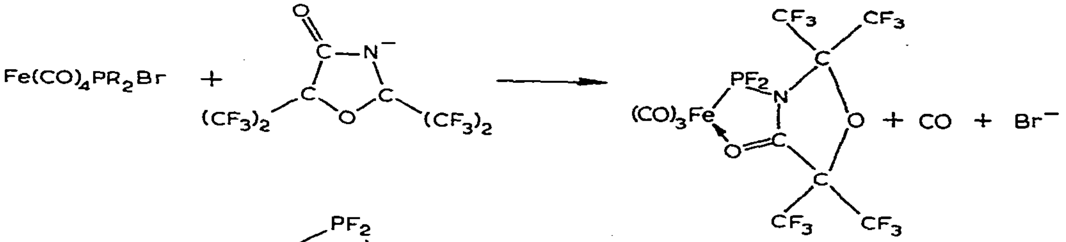
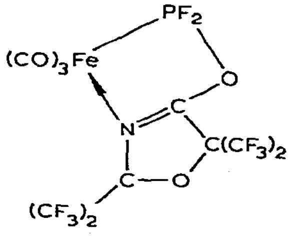
The bromine in the complex $Fe(CO)_4PF_2Br$ has been found to undergo nucleophilic displacement by several anions (*e.g.* F^-, SCN^-, N_3^-)[1]. Thus it was of interest to attempt bromide displacement with the ambident anion of 2,2,5,5-tetrakis(trifluoromethyl)-4-oxazolidone[2]. The expected mixture of the P–O and P–N bonded isomers was not obtained (compounds I and Ia) when the reaction was carried out in acetonitrile at 25°. Instead only P–N bonding occurred and the oxazolidone group was also found to coordinate to the iron via the carbonyl oxygen (compound I). No evidence for compound Ia was found. The product obtained, as the only volatile component of the reaction mixture, (yellow oil, b.p. 40–42°/0.03 mm, 91% yield) had the empirical composition $Fe(CO)_3PF_2NC(CF_3)_4O_2$. This was confirmed by elemental analyses (Found: C, 21.5; Fe, 10.1; N, 2.69, calcd.: C, 21.1; Fe, 9.88; N, 2.46%.) The molecular weight of the product (calcd. 567) was found to be 567 by mass spectrometry, which also indicated the presence of only three CO groups.



(I)



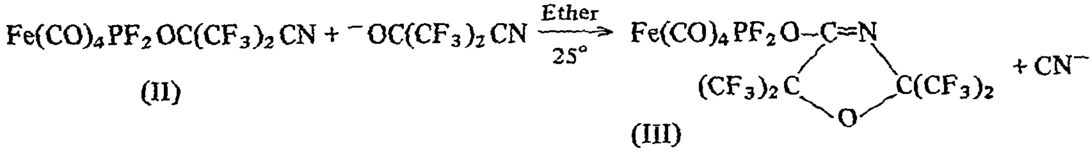
(Ia)

The assignment of the P–N bonded configuration depended upon spectroscopic and other synthetic studies. The ^{31}P NMR spectrum of I was a triplet (δ $-$ 50.8, J(PF) 1264 Hz) while the ^{19}F NMR spectrum consisted of a doublet (δ 13.0 ppm, J(PF) 1264 Hz) and two singlet trifluoromethyl group resonances (δ 72.0 and 76.5 ppm). The relative intensities were 1/3/3 respectively*. The NMR studies demonstrate the presence of a PF_2 group and two nonequivalent sets consisting of two trifluoromethyl groups each.

An important aspect of the infrared spectrum of I** is the presence of ν(C=O) stretching frequency at 1669 cm^{-1} and the absence of a band attributable to ν(C=N) stretch. In addition, metal ν(C=O) stretches were found at 2107, 2096, 2090, 2042, 2032, and 2017 cm^{-1} and PF stretches could be assigned to bands at 893 and 874 cm^{-1}. The band at 1669 cm^{-1} did not uniquely eliminate configuration Ia for the complex since *O*-alkylation of the ambident anion of the oxazolidone with ethyl iodide resulted in a ν(C=N) frequency at 1672 cm^{-1} whereas *N*-alkylation resulted in a ν(C=O) frequency at 1785 cm^{-1}. However, coordination of the oxygen in a ketone function to a metal where π-bonding is possible can reduce the ν(C=O) frequency[3] by as much as 180 cm^{-1}. Models of both isomers (I and Ia) demonstrated that an unstrained ring could exist only for structure I. This can occur only if a P–N bond is formed.

In order to further support the assigned configuration of I the related P–O bonded complex was synthesized. Since attempts to prepare the free ligand, $PF_2ONC_3(CF_3)_4O$ by reactions of PF_2Br with the ambident oxazolidone anion proved unsatisfactory an indirect method was developed. Reaction of $Fe(CO)_4PF_2Br$ with $NaOC(CF_3)_2CN$[2,4] in diethyl ether produced the intermediate complex $Fe(CO)_4PF_2OC(CF_3)_2CN$ (II) which was isolated by trapping in a −45° trap at 10^{-2} mm. in 89% yield (Found: C, 22.6; Fe, 12.98; N, 3.33. Calcd.: C, 22.4; Fe, 13.01; N, 3.26%.) The presence of four CO groups bonded to iron was clearly observed in the mass spectrum of II as well as the presence of a parent molecular ion peak at 429 *m/e*. The infrared spectrum of II in the ν(C≡O) region (2102, 2094, 2028, 2011 and 1998 cm^{-1}) was very similar to that reported for $Fe(CO)_4PF_3$[5]. In addition, the expected ν(C≡N) bond was found at 2267 cm^{-1}. The ^{31}P and ^{19}F spectra (triplet, δ(P) −54.3; doublet δ(PF) 10.5; singlet $\delta(CF_3)$ 76.2 ppm and J(PF) 1178 Hz) were compatible with the above formulation since the integrated ratio PF/CF_3 was 1/3.

Complex II was found to undergo further reaction with excess $NaOC(CF_3)_2CN$ to produce a new complex, $Fe(CO)_4PF_2OC_3N(CF_3)_4$ (III), (Found: C, 21.8; N, 2.80. Calcd.: C, 22.2; N, 2.45%.) as a liquid in low yield. The mass spectrum of III exhibited a parent molecular ion at 595 *m/e* demonstrated the presence of four CO groups. This was confirmed by the lack of CO evolution during its preparation.



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* All ^{31}P spectra are relative to external P_4O_6 and all ^{19}F spectra are relative to internal CCl_3F. All samples were run as neat liquids.

** All infrared spectra were taken on cyclohexane solutions using a PE Model 621 spectrometer.

The infrared spectrum of complex III in the metal $\nu(C\equiv O)$ region was almost identical to that found for complex II but rather different from that due to complex I (2102, 2095, 2020, 2003, and 1996 cm^{-1}). The band assigned to the $\nu(C=N)$ frequency occurred at 1676 cm^{-1} while no band was observed in the region of 1750 to 1800 cm^{-1}. The latter would be expected if this monodentate ligand was P—N bonded since an uncomplexed carbonyl group would be present. The similarity of the infrared spectra in the $\nu(C=O)$ region of complexes II and III and the fact that a P—O to P—N rearrangement is likely under the mild reaction conditions argue for the above structural assignment for III. Although the ^{31}P and ^{19}F spectra of III demonstrate the presence of a PF$_2$ group (triplet, δ(P)—55.3 ppm and J(PF) 1189 Hz) the fluorines in the CF$_3$ groups appear as a singlet at δ 75.4 ppm. Since the CF$_3$ groups appear to be in different environments it is not obvious why this should occur unless the chemical shifts are accidentally degenerate. However, the phosphorus—fluorine coupling constants for complexes II and III are close but quite different than that of I, suggesting a similarity in bond hybridization of the phosphorus in II and III. Thus it is concluded that the oxazolidone ring is *N*-bonded to phosphorus in complex I but is *O*-bonded to phosphorus in complex III. This difference must be attributed to the difference in the substrate and ligand precursors employed. The formation of complex I represents a nucleophilic displacement of bromide bonded to phosphorus by nitrogen followed by chelation whereas the formation of complex III can probably be considered as nucleophilic displacement of cyanide ion bonded to carbon, followed by an intramolecular cyclization and a Chapman rearrangement[6].

The infrared spectra of all three complexes in the metal carbonyl region exhibit too many bands to be assigned to one isomer (assuming a trigonal bipyramid configuration around iron). This problem has been discussed by Clark *et al.*[5] for Fe(CO)$_4$PF$_3$ and Fe(CO)$_3$(PF$_3$)$_2$ and more recently by Odom[7]. The monosubstituted complexes (II and III) are apparently undergoing an intramolecular axial—equatorial exchange on a time scale not observed by ^{31}P and ^{19}F NMR. Complex I is also undergoing isomerization since only three $\nu(C=O)$ bands would be expected for a single isomer. This type of isomerization has also been observed for the complex Fe(CO)$_3$[(CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$][7].

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