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Fluorine in ligands: obvious and not-so obvious effects

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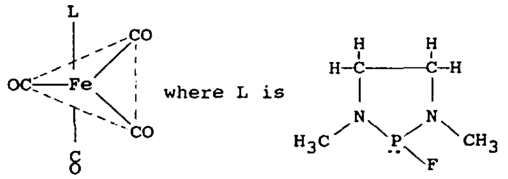
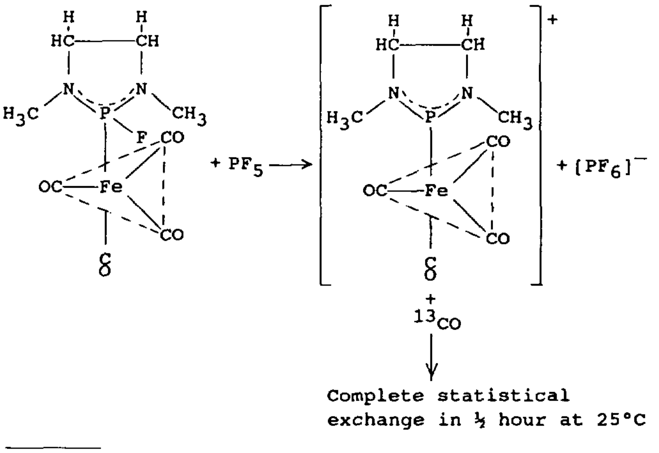
When electronegative fluorine replaces a group or element on a ligand, the change alters the coordinating properties of the ligand. For example, PF_3 is a π-acid ligand as opposed to $P(CH_3)_3$ which is a strong σ-donor. Today these effects are widely accepted and are considered obvious. This paper considers replacements of NR_2 groups by fluorines in $P(NR_2)_3$. The resulting compound is used as a ligand to attack $Fe(CO)_5$.

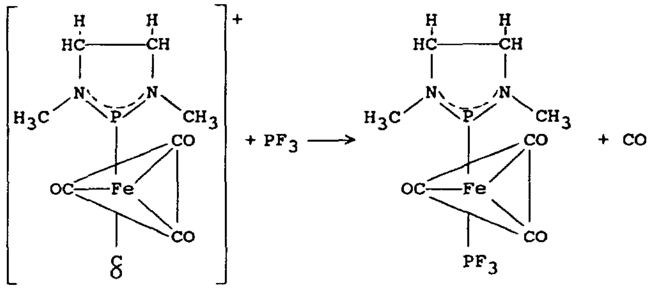
Carbon monoxide in $Fe(CO)_5$ is known to be kinetically inert as far as CO substitution is concerned. Thus, the exchange reaction $Fe(CO)_5 + {}^{13}CO$ has a half-life of 4 years [1]. Similarly, the substituted iron carbonyl shows no evidence of ^{13}CO exchange over a period of weeks at room temperature. On the other hand, *removal of fluoride* from the ligand, L, gives a cationic species which undergoes complete statistical exchange with ^{13}CO in 0.5 h at 25 °C.



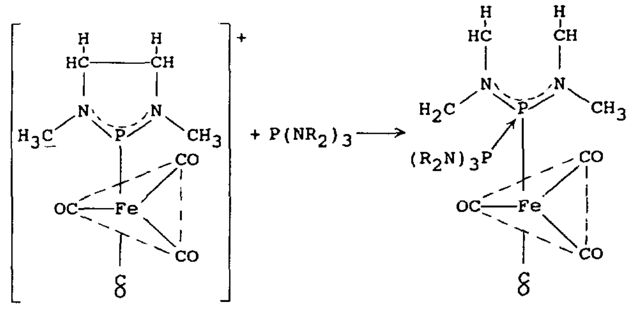


This can be rationalized in terms of the reduced multiple-bond character of the Fe–CO linkage and labilization of the CO which is axial to the cationic phosphorus ligand [2].

Since CO and PF_3 are both π-acid ligands, it appeared that the exchange reaction might be a useful route to introduce PF_3 into the coordination sphere of $Fe(CO)_5$ in place of CO. A reaction using PF_3 under conditions comparable to those used for CO exchange gave the product $Fe(CO)_4PF_3$ after 24 h. No further reaction was observed. Substitution of only one CO by PF_3 was somewhat unexpected even though PF_3 is known to react much more slowly than the CO in metal–carbonyl-type systems. The equation for the process is:



When $P[N(CH_3)_2]_3$ was used as the attacking ligand in place of PF_3 for the reaction with $[(CO)_4FeL]^+$ a different process was observed. The equation is:



The $P[N(CH_3)_2]_3$ attacked the *phosphorus* at −80 °C to give the compound shown (above). No CO dis-

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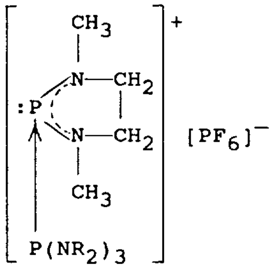
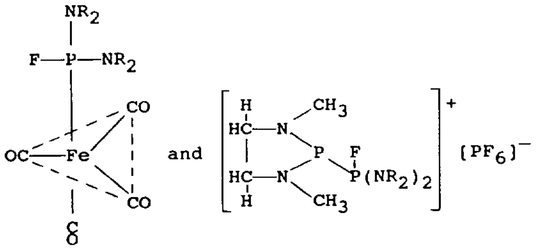
placement occurred under the conditions used. When the temperature was raised to −45 °C, the double-ligand was displaced by the excess $P(NR_2)_3$ to give $(CO)_4FeP(NR_2)_3$ and the ionic material:



When $PF(NR_2)_2$ was used as the attacking ligand instead of $P(NR_2)_3$, the reaction was similar to that for $P(NR_2)_3$. The final products were:



With PF_2NR_2 the reaction resembled the PF_3 reaction in part, but there were significant differences. The final product was $(F_2PNR_2)_3Fe(CO)_2$. Three intermediate products could be identified. All identifications were by ^{19}F and ^{31}P NMR. Differences are attributed to differences in both physical and chemical properties of the attacking ligands [3].

References

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