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Preliminary communication

Hindered rotation in phosphorus trifluoride substituted trimethylenemethaneirontricarbonyl

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Only a very limited number of studies have been made of the substitution of Lewis bases for carbon monoxide in metal carbonyls of the sort $LFe(CO)_3$ where L represents four-electron donors such as butadiene, cyclobutadiene and trimethylenemethane[1]. A ligand capable of such a substitution is phorphorus trifluoride which is unique among ligands that can replace carbonyl groups[2]. It does so readily, yielding all possible compositions and frequently all possible isomers while causing little change in the physical properties and bonding in the new compounds when they are compared with the parent compound. Phosphorus trifluoride is an excellent model for carbon monoxide.

Trimethylenemethaneirontricarbonyl [$TMMFe(CO)_3$] was prepared from $Fe_2(CO)_9$ and 3-chloro-2-methylpropene according to the procedure of Ehrlich[3]. Phosphorus trifluoride reacts photochemically with hexane solutions of $TMMFe(CO)_3$ at 0° in Pyrex containers to yield all possible compounds of the type $TMMFe(PF_3)_x(CO)_{3-x}$ where $x = 1,2$ and 3. No sign of isomerization of the trimethylenemethane group to butadiene is observed under the irradiation conditions used. The individual $TMMFe(PF_3)_x(CO)_{3-x}$ species are light-yellow, low melting solids that are isolated on short GLC columns. The purified compounds are identified by a variety of methods. Their sequence of formation as a function of the time of reaction, the elution pattern, their parent ion molecular weight and mass spectral fragmentation pattern, their infrared spectra and their ^{19}F NMR spectra are all used to identify the species. The manner in which these techniques are employed has been illustrated previously[2].

The parent carbonyl with C_{3v} symmetry has two carbonyl bands at 2064 and 1994 cm^{-1} (hexane solvent). The monophosphine also has two carbonyl stretching frequencies at 2041 and 1992 cm^{-1}. Its ^{19}F NMR spectrum shows a doublet (^1J(P–F) 1310 Hz) centered at 6.38 ppm upfield from $CFCl_3$. The diphosphine has only one carbonyl stretching frequency at 2014 cm^{-1}. Its ^{19}F NMR spectrum shows a typical $AA'X_3X_3'$ pattern indicative of a diphosphine with two equivalent PF_3 groups[4]. The ^{19}F NMR spectrum of the triphosphine shows a typical $AA'A''X_3X_3'X_3''$ pattern characteristic of a triphosphine with three equivalent PF_3 groups[5]. The fluorine spectra for all species remain sharp and unchanged throughout a temperature range from +30° to −110°.

The non-rigid character of the substituted trimethylenemethaneirontricarbonyl system is revealed in the proton spectra. The ^{1}H NMR of TMMFe(CO)$_3$ is a single sharp peak 2.01 ppm from TMS as expected for six equivalent hydrogens. However, as shown in Fig. 1, the spectrum of TMMFe(CO)$_2$(PF$_3$) is broad at room temperature. As the temperature is raised the pattern sharpens to a doublet with a splitting of about 2.9 Hz. As the temperature is lowered the spectrum reveals a more complex pattern due to three types of protons in a 1/1/1 ratio. The situation most probably responsible for these spectral changes can be understood by an examination of the structure from a projection down the iron–methane-carbon axis. One of the simplest explanations seems to be that there is hindered motion of the PF$_3$ group relative to the trimethylenemethane ligand. The resulting transformation is as if a rotation had occurred about the Fe–C bond analogous to the hindered rotation in substituted ethanes[6].

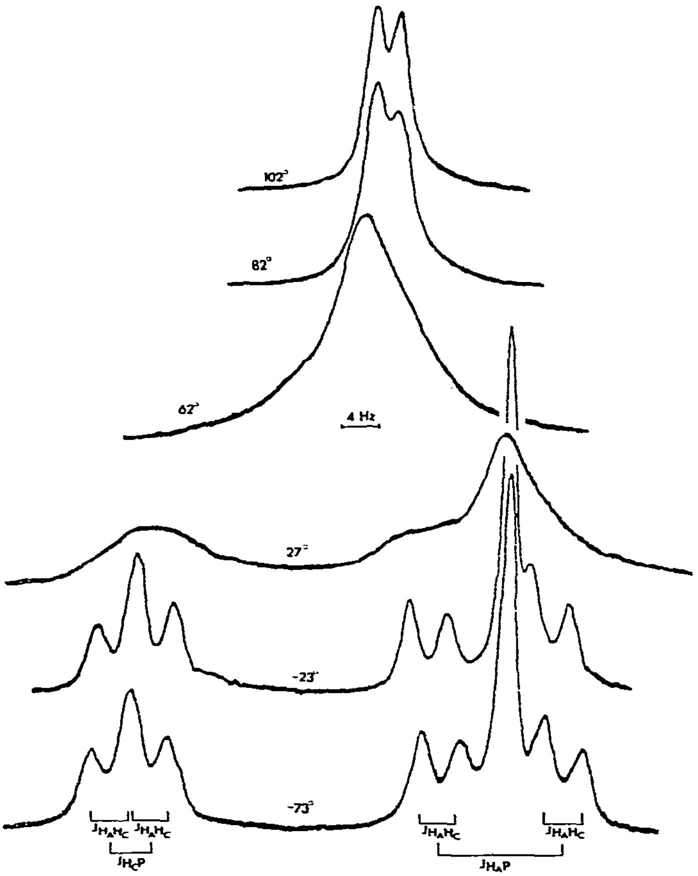
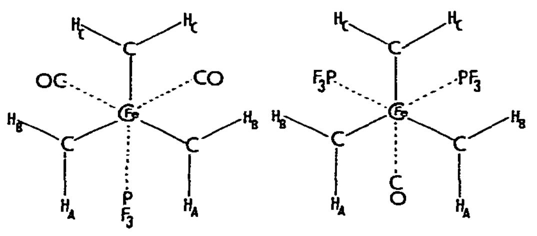


Fig. 1. Variable temperature 90 MHz proton NMR spectra of TMMFe(CO)$_2$(PF$_3$).



Thus, at the high temperature limit, the proton spectrum of the monophosphine can be interpreted as resulting from rapid rotation of the TMM and $Fe(CO)_2(PF_3)$ moieties relative to one another such that all six protons become equivalent and are coupled equally to one phosphorus atom. At low temperatures, when the motion is slow compared to the NMR time scale, the protons are no longer equivalent and give the pattern illustrated by the −73° spectrum.

Ehrlich[3] has explained the NMR pattern of several $(CHR)C(CH_2)_2Fe(CO)_3$ compounds by invoking only 'W' coupling, *i.e.*, coupling of the protons that are at the ends of a W as viewed from any of the three perspectives. This kind of interpretation reduces the complexity expected for the $TMMFe(CO)_2(PF_3)$ spectral pattern since most of the coupling constants become equal to zero.

The low temperature spectrum shows two doublets, a singlet and a triplet. Spin decoupling experiments reveal that the single peak in the upfield region is not coupled to any other part of the spectrum and must be assigned to the B protons. The low-field triplet is actually a doublet of doublets coupled to a high field doublet of doublets with $J(H_A{-}H_C)$ 4.0 Hz. The larger coupling in the high-field doublet of doublets is 13.3 Hz which must be due to the phosphorus atom. Proton splitting patterns in the butadieneiron–carbonyl–triflurophosphine system indicate that the largest P–H coupling occurs between the *'anti'* protons on the butadiene ligand and the apical phosphorus atom, *i.e.* the protons and phosphorus atom in closest proximity, and is equal to ~10–15 Hz[7]. The high-field doublets in the $TMMFe(CO)_2(PF_3)$ spectrum are therefore assigned to the A protons while the low-field doublets with a smaller P–H coupling of 4.4 Hz are assigned to the C protons. The average J(P–H) value at high temperatures of 2.9 Hz is equal to an averaging of 13.3, 4.4 and ~0 Hz if $J(P{-}H_C)$ and $J(P{-}H_A)$ have opposite signs. The relative signs of the constants are confirmed by spin decoupling[8].

The proton spectrum of the diphosphine compound broadens at temperatures which are slightly lower than those for the monophosphine. Those for the triphosphine are lower still. For the di- and triphosphine species the high temperature spectra reveal a triplet and a quartet respectively, indicating a coupling of equivalent protons to two and three phosphorus atoms. The low temperature spectra for these species are second order and quite complex.

These studies will be reported more fully later, along with a study of the monomethyl- and α,α-dimethyltrimethylenemethaneirontricarbonyls. In these later cases the various staggered rotamers are not expected to be energetically equivalent. Preliminary results indicate that some of these rotational isomers do exist.

It is not clear whether the barrier to rotation is a steric one, attributable to interaction between the ligands, or an alectronic one, caused by the nature of the bonding between the iron and the ligands. Our present results show that, in any event, the substitution of methyl groups into TMM causes little change in the temperatures for which broadening is seen in the proton NMR spectra of the phosphorus trifluoride substituted species when compared with $\mathrm{TMMFe(PF_3)_x(CO)_{3-x}}$.

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