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Preliminary communication

PHOTOLYTIC GENERATION OF $Fe(CO)_4MeTHF$, $Fe(CO)_3(MeTHF)_2$, (2 ISOMERS), AND $Fe(CO)_4NEt_3$; RELEVANCE TO REACTIONS OF $Fe_2(CO)_9$

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Summary

The title compounds have been prepared from $Fe(CO)_5$ by glassy matrix photolysis; there is evidence for pre-photolytic ligand $Fe(CO)_5$ interaction.

Some years ago the species $Fe(CO)_4$ (I) was invoked as an intermediate in the reactions of $Fe_2(CO)_9$ [1] and this interpretation is broadly confirmed by studies of species $Fe(CO)_4$(olefin) in hydrocarbon solution [2]. It has recently been shown that the behaviour of $Fe_2(CO)_9$ in tetrahydrofuran (THF) is different from that in other reaction media, and $Fe(CO)_4THF$ (II) has been suggested as an intermediate [3]. We now describe the results of some experiments in which $Fe(CO)_5$ was photolysed in the presence of potential ligands. These results support the proposed intermediate I and explain some apparent anomalies.

The IR spectrum of $Fe(CO)_5$ in hydrocarbon glasses molar in MeTHF* is considerably different from that in pure hydrocarbon glass. We ascribe the differences to loose coordination of MeTHF, probably to one or more equatorial CO groups of $Fe(CO)_5$ [4]. Photolysis produces initially free CO and a species which we assign as $Fe(CO)_4MeTHF$ (substituent axial) on the basis of its infrared spectrum (2062m (A_1), 1963s (A_1), 1946vs, 1940(sh) (E)). The splitting of the E band which is more pronounced in pure MeTHF glass, is also shown by the E' mode of $Fe(CO)_5$ under our conditions**. In hydrocarbon glass with lower concentration of MeTHF (~0.1 M) there are also bands present similar to those formed when $Fe(CO)_5$ is photolysed in methane [5] or undoped hydrocarbon glass [6]. Further photolysis gives rise to two species III and IV which we assign

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*4/1 methylcyclohexane—isopentane 10^{-2} molar in $Fe(CO)_5$, (nominal 77 K, liq. N_2) in VLT-2 FH-01 cell assembly with sapphire windows unless otherwise stated. MeTHF = 2-methyltetrahydrofuran.

**We have considered and rejected an assignment of I as $Fe(CO)_4MeTHF$(equatorial). The band pattern is qualitatively highly reminiscent of those we have observed in several species of type $Fe(CO)_4L$ (L = e.g. $P(C_6H_4CH_3)_3$ [1], $P(OMe)_3$, $P(NMe_2)_3$ [7]), and the forms of the split E bands are extremely similar to those of the E' band of $Fe(CO)_5$ in both the environments discussed.

as $Fe(CO)_3(MeTHF)_2$ (bis-axial and axial—equatorial[*] respectively) from their IR spectra [in hydrocarbon glass, III: 1900 (E'); IV: 1990, 1882, 1865; in pure MeTHF glass, III: 2012vw (A'_1) 1895(br) (E'); IV: 1980 (A'), 1877 (A'), 1855 (A'') cm^{-1}]. III gave the strongest secondary photolysis band in hydrocarbon, while in MeTHF the spectrum of IV was more pronounced than that of III; these differences are consistent with our assignments and with the expected effects of a polar solvent, which should facilitate the less symmetrical reaction pathway. Reactions in THF-doped hydrocarbon glass are similar.

Spectra of $Fe(CO)_5$ in hydrocarbon glass 1 *M* in triethylamine also showed distortion before photolysis. On photolysis at least two new species were formed. One of these V persisted after warm up to 175 K and refreezing and is assigned as $Fe(CO)_4NEt_3$ (substituent axial) [ν(CO) 2045 (A_1), 1954 (A_1), 1925, 1920 (collapsing to 1924 on warming and refreezing) (E)]. The other species (ν(CO) 1945, 1892) disappears on warming, and is presumably an unsaturated fragment of some kind.

We note that in some circumstances (e.g. IV) an equatorial position in substituted $Fe(CO)_5$ can be occupied by a σ-donating, non-π-accepting ligand; this lends credence to the suggestion [3] that $Fe(CO)_4L$ (equatorial) (L = pyridine, pyrazine) are possible pseudorotation intermediates in the axial—equatorial CO exchange of $Fe(CO)_4L$ (axial), if this proceeds by a true Berry mechanism. We note also the facile formation of species $Fe(CO)_3(MeTHF)_2$ and $Fe(CO)_3(THF)_2$; these could possibly explain the complexity of the spectrum of $Fe_2(CO)_9$/THF/amine reaction mixtures [3] and the role of a CO atmosphere. We suggest that lighting conditions should be controlled and specified in all work relating to substitution reactions of metal carbonyls.

References

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[*] Relative intensities are not consistent with the assignment of this species as bis-equatorial, although other arrangements of ligands, not based on a trigonal bipyramid, cannot be ruled out. Both III and IV are presumably coordinatively saturated, since they form in donor solvent glass.