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Preliminary communication

A novel deoxygenation of a carbonyl group of iron pentacarbonyl

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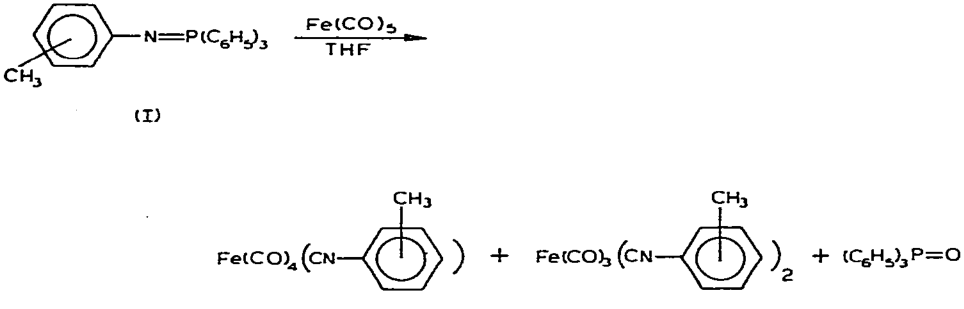
Iron pentacarbonyl is a useful reagent for effecting deoxygenation of sulfoxides[1] and various organic compounds containing the N–O linkage[2]. This communication reports a rare example of the reverse reaction: deoxygenation of a carbonyl group of $Fe(CO)_5$ without cleavage of the metal–carbon bond[★].

Reaction of each of the three *N*-tolyltriphenylphosphine imines (I, *o*-, *m*-, or *p*-CH_3–) and $Fe(CO)_5$ (1.15/1.00 mole ratio of $Fe(CO)_5$ to I) in refluxing dry tetrahydrofuran (THF) for 19–22 h affords the corresponding tolylisocyanideiron tetracarbonyl (II), bis(tolylisocyanide)iron tricarbonyl (III) (60–94% total yield of II and III) as well as triphenylphosphine oxide (IV, 97%)[★★]. Pertinent IR and ^1H NMR data for II and III are listed in Table 1.



[★] To our knowledge, the only other case of deoxygenation of $Fe(CO)_5$ without Fe–C cleavage results from treatment of the sodium salt of 1,1,1,3,3,3-hexamethyldisilazane with the metal carbonyl[3].
[★★] Satisfactory elemental analyses were obtained for new compounds.

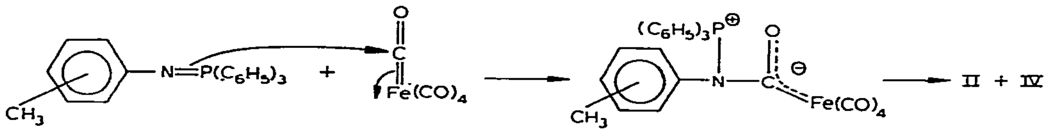
TABLE 1

IR AND ^{1}H NMR DATA FOR II AND III

	IR[a]		^{1}H NMR[b]	
Complex	ν(CN)	ν(CO)	CH_3(singlet)	Aromatic
II, o-CH_3–	2163	2055, 1992, 1963	1.90	6.50–6.85m
II, m-CH_3–[c]	2169[d]	2058, 1994, 1965	1.85	6.30–6.70m
II, p-CH_3–[c,e]	2175	2060, 1995, 1965	1.89	6.54s
III, o-CH_3–	2105	1998, 1934	2.07	6.69s
III, m-CH_3–[f,g]	2106	1993, 1937	1.83	6.50–6.67m
III, p-CH_3–[e]	2115	2000, 1955	1.86	6.62s

[a] Measured in methylene chloride solution. [b] ppm downfield of TMS, measured in C_6D_6. [c] Mass spectrum gave a molecular ion peak at m/e 285, followed by successive loss of four carbonyls. [d] A weak shoulder was also observed at 2153 cm^{-1}. [e] Taylor and Horrocks[4] have reported the preparation of II (p-CH_3–) and III (p-CH_3–) but no IR data was given. IR results for some related complexes have been published by Cotton and Parish[5]. [f] Molecular weight determined by vapor-phase osmometry (benzene) was 375 (calcd. 374). [g] IR shows weak bands due to II (m-CH_3–).

Complexes of type II probably result from initial attack of I at a metal carbonyl carbon to give the dipolar intermediate V. The latter can then collapse to II and the very stable IV, the formation of which is a driving force for this reaction. Complex (III) may arise from disproportionation of (II) at room temperature or under the reaction conditions.



Complexes II (p-CH_3–) and III (p-CH_3–) are also obtained by reaction of N-p-tolyltriphenylphosphine imine (I, p-CH_3–) with diiron enneacarbonyl [$Fe_2(CO)_9$] in benzene at room temperature. In addition, N,N′-di-p-tolylurea (44%), 4,4′-dimethyloxanilide (8%), and 4,4′-dimethylhydrazobenzene (5%) are organic products of the reaction. It should be noted that the same or analogous organic products were produced in lower yields in the $Fe(CO)_5$ reactions but we have not, as yet, attempted to optimize yields.

We are currently investigating the generality of this novel metal carbonyl deoxygenation reaction. For example, molybdenum hexacarbonyl reacts with I (m-CH_3–) in 1,2-dimethoxyethane to form m-tolylisocyanidemolybdenum pentacarbonyl and triphenylphosphine oxide.

ACKNOWLEDGMENT

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