Intermediate Complex in the Reduction of Trimethylamine Oxide by Pentacarbonyl Iron: Its Use as Catalyst in the Addition of Carbon Tetrachloride to Carbon–Carbon Double Bonds

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Summary The intermediate compound in the reduction of Me_3NO by $Fe(CO)_5$, a reaction used for the synthesis of diene–tricarbonyl iron complexes, was intercepted and identified as the trimethylamino–tetracarbonyl iron complex; its potential as catalyst for the addition of CCl_4 to unsaturated substrates has been shown.

AMINE OXIDES can be converted into the corresponding amines by using $Fe(CO)_5$ as reducing agent.[1] Although no evidence is given for the existence of possible intermediates, $Fe(CO)_4$ is believed to be produced in this reaction, which has recently been used for preparing diene–tricarbonyl iron complexes.[2] We present here results concerning the interception of the intermediate complex (**1**) in this reaction, as well as its potential as a catalyst in the addition of CCl_4 to olefins.

When $Fe(CO)_5$ in tetrahydrofuran (THF) solution was added dropwise to a suspension of a two-fold excess of Me_3NO in THF at -30 °C, the solution instantaneously turned red and evolution of CO_2 occurred.† After work-up an orange–red solid was obtained (45% yield) which was identified as complex (**1**)† on the basis of the following spectroscopic data: *m/e* 226·991 (M^+) (calc. *M* 226·988), 199, 171, 143, and 115 (successive loss of 4 CO groups); ν 2050, 1960, and 1940—1920 cm^{-1} (CO); ^{1}H n.m.r.: δ (C_6D_6, 35 °C) 1·87 (s); ^{13}C n.m.r.: δ (C_6D_6, 10 °C) 217·5 (s, CO), 61·4 (q, *J* 137 Hz, NMe_3) p.p.m. Compound (**1**) has been mentioned in an i.r. investigation of tetracarbonyl iron complexes; no experimental details were given.[3] A possible mechanism leading to the formation of complex (**1**) is shown in the Scheme; upon warming to 50 °C the complex decomposes with formation of Me_3N as reported previously.[1]

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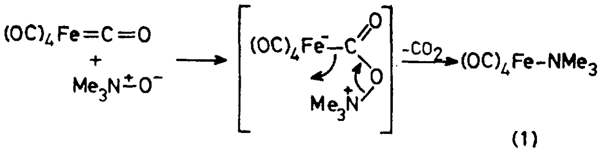
† Shown by obtaining a white precipitate with $Ba(OH)_2$ solution.



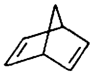
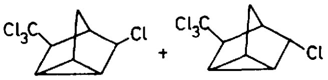
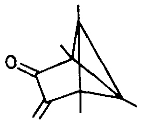
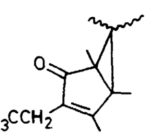
(1)

SCHEME

The reaction between $Fe(CO)_5$ and amine oxides, reported by Alper and Edward,[1] and the present synthesis of (**1**) indicate that amino-tetracarbonyl iron complexes can be generally prepared by this route. Direct syntheses of these complexes from $Fe(CO)_5$ and amines, either thermally[4] or photochemically[5] give low yields and/or formation of side products occurs. Pyridine–tetracarbonyl iron complex has been prepared in *ca.* 45% yield by the reaction between $Fe_2(CO)_9$ and pyridine in THF.[6] Treating (**1**) with an equimolar amount of cyclo-octatetraene at 60 °C in benzene solution gave the corresponding tricarbonyl iron complex (55% yield), which is consistent with the intermediacy of (**1**) in the preparation of diene–tricarbonyl iron complexes from dienes, Me_3NO, and $Fe(CO)_5$.[2]

The chance observation of the rapid decomposition of complex (**1**) in CCl_4 solution has been applied successfully to a procedure, in which (**1**) acts as catalyst for the addition of CCl_4 to olefins. This is illustrated by the three examples in the Table (10 mol % of catalyst, room temperature).

TABLE

Substrate	Products	Reaction time/h	% Yield
CH_2=CH$[CH_2]_4$Me	$Cl_3CCH_2CHCl[CH_2]_4Me$	15	50[a]
	 ratio 2:1	15	90[b]
		2	80[c]

[a] Ref. 7. [b] The reaction products were identified by a comparison with products obtained by the free radical addition of CCl_4 to norbornadiene [D. I. Davies and L. T. Parfitt, *J. Chem. Soc.* (*C*), 1967, 2691]. [c] R. F. Heldeweg and H. Hogeveen, *Tetrahedron Letters*, 1975, 1517.

It is of interest to note that $Fe_2(CO)_9$ shows a similar catalytic behaviour in the addition of CCl_4 to olefins. Catalysis by organochromium complexes in the addition of CCl_4 to olefins under mild conditions has been reported recently.[7]

(*Received*, 30*th June* 1977; *Com.* 659.)

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