

Journal of Organometallic Chemistry, 171 (1979) 85–88
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CHEMISTRY OF IRON CARBONYL ANIONS

SELECTIVE REDUCTION OF NITROARENES AND α , β -UNSATURATED CARBONYL COMPOUNDS, AND REDUCTIVE DEHALOGENATION OF ORGANIC HALIDES BY $(C_2H_5)_4N^+ HFe_3(CO)_{11}^-$

GIAN PAOLO BOLDRINI, ACHILLE UMANI-RONCHI*,

Istituto Chimico "G. Ciamician", Università di Bologna, via Selmi 2, Bologna 40126 (Italy)

and MAURO PANUNZIO

Laboratorio dei Composti del Carbonio Contenenti Eteroatomi, CNR, 40064 Ozzano Emilia, Bologna (Italy)

(Received December 16th, 1978)

Summary

The tetraethylammonium undecacarbonylhydridotriferrate $[(C_2H_5)_4N^+ HFe_3(CO)_{11}^-]$ (I), which can be easily prepared in a two-step sequence from iron pentacarbonyl, triethylamine and tetraethylammonium chloride, selectively reduces nitroarenes to amines and α , β -unsaturated carbonyl compounds to the corresponding saturated compounds both in good yield. I reacts with some organic halides to give dehalogenated products.

There are many important applications of $Na_2Fe(CO)_4$ and $NaHFe(CO)_4$ in organic synthesis [1]. The tetracarbonylferrate dianion and the corresponding monohydride were recently shown to be useful in the synthesis of aldehydes [2], unsymmetrical ketones [1], carboxylic acid derivatives [3], in the hydroacylation [4], dehalogenation [5], desulphuration [6] and reduction of the carbon-carbon double bond of α , β -unsaturated carbonyl compounds [7]. Moreover we found that treating an aldehyde, a ketone, or an active methylene compound with an aldehyde in the presence of potassium tetracarbonylhydridoferrate in ethanol or water results in high yield reductive alkylation of the carbonyl compound or the active methylene compound [8]. Under similar conditions using a variety of aldehydes we were able to alkylate primary and secondary amines [9] and indole [10].

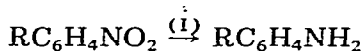
Extending these studies on applications of iron complexes, we have investigated novel approaches to the application of transition metal clusters in organic

synthesis. Transition metal clusters offer the possibility of reaction paths involving adjacent metal centers acting on a single substrate. Although there have been many studies of the structure, bonding and fluxional behaviour of carbonyl cluster compounds and their hydrides, little is known about their reactions.

Recently Collman reported synthetic and preliminary mechanistic studies of the reduction of the olefinic bond in α , β -unsaturated carbonyl compounds by the binuclear hydride, $\text{NaHFe}_2(\text{CO})_8$ [11], while Landesberg and co-workers found that refluxing equimolar amounts of a nitroarene and $\text{Fe}_3(\text{CO})_{12}$ for 10–17 h in benzene containing methanol gave the corresponding aniline [12]. More recently Alper reported that anilines are formed in good to excellent yields by treatment of nitroarenes with $\text{Fe}_3(\text{CO})_{12}$ in aqueous sodium hydroxide, benzene, and benzyltriethylammonium chloride [13].

We describe below the specific reduction of the nitro group in nitroarenes and the olefinic bond in α , β -unsaturated carbonyl compounds, and the reductive dehalogenation of organic halides by means of the trinuclear iron hydride complex $[(\text{C}_2\text{H}_5)_4\text{N}^+ \text{HFe}_3(\text{CO})_{11}^-]$ (I). This salt is easily prepared by treating iron pentacarbonyl with triethylamine, since the solid salt $[(\text{C}_2\text{H}_5)_3\text{NH}^+ \text{HFe}_3(\text{CO})_{11}^-]$ so obtained reacts rapidly with tetraethylammonium chloride in dichloromethane to give I [14]. It is a dark red solid, relatively stable to air and can be stored indefinitely at room temperature; it is easier to handle than iron pentacarbonyl and other iron carbonyl salts [15].

We have now shown that the treatment of aromatic nitro compounds with I in tetrahydrofuran gives the corresponding primary amines in very good yields.



R = CH_3 , CHO, OCH_3 , OC_6H_5 , Cl

Specific examples are listed in Table 1. To ensure maximum yield equimolar amounts of nitroarene and iron complex are necessary. A potentially useful feature of the $[(\text{C}_2\text{H}_5)_4\text{N}^+ \text{HFe}_3(\text{CO})_{11}^-]$ reagent is the tolerance of other functional groups. This is illustrated (Table 1) by the conversion of *p*-nitrobenzaldehyde into *p*-aminobenzaldehyde. Tetrahydrofuran is the best solvent for this reduction, I being satisfactorily soluble in this solvent. Compounds containing activated double bonds also react with the salt I to give the corresponding saturated

TABLE 1
REDUCTION OF NITROARENES BY $(\text{C}_2\text{H}_5)_4\text{N}^+ \text{HFe}_3(\text{CO})_{11}^-$

Substrate	Product ^a	Yield (%) ^b
$\text{C}_6\text{H}_5\text{NO}_2$	$\text{C}_6\text{H}_5\text{NH}_2$	95
<i>m</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_3$	<i>m</i> - $\text{NH}_2\text{C}_6\text{H}_4\text{CH}_3$	95
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{CHO}$	<i>p</i> - $\text{NH}_2\text{C}_6\text{H}_4\text{CHO}$	90
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{OCH}_3$	<i>p</i> - $\text{NH}_2\text{C}_6\text{H}_4\text{OCH}_3$	95
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{Cl}$	<i>p</i> - $\text{NH}_2\text{C}_6\text{H}_4\text{Cl}$	70
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{OC}_6\text{H}_5$	<i>p</i> - $\text{NH}_2\text{C}_6\text{H}_4\text{OC}_6\text{H}_5$	90

^a Products were identified by comparison with authentic samples. ^b Yields indicated refer to pure isolated compounds.

TABLE 2

SELECTIVE REDUCTION OF α , β -UNSATURATED CARBONYL COMPOUNDS BY $(C_2H_5)_4N^+ HFe_3(CO)_{11}^-$

Carbonyl compound	Product ^a	Yield (%) ^b
$C_6H_5CH=CHCOCH_3$	$C_6H_5CH_2CH_2COCH_3$	80
$C_6H_5CH=CHCOOC_2H_5$	$C_6H_5CH_2CH_2COOC_2H_5$	50

^a Products were identified by comparison with authentic samples. ^b Yields indicated refer to pure isolated compounds.

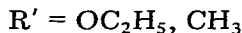
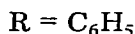
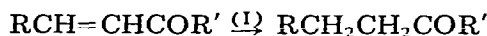
TABLE 3

RECUTIVE DEHALOGENATION BY $(C_2H_5)_4N^+ HFe_3(CO)_{11}^-$

Alkyl halide	Product ^a	Yield (%) ^b
$C_6H_5COCH_2Br$	$C_6H_5COCH_3$	75
$C_6H_5CH(Br)CH(Br)C_6H_5$ ^c	<i>trans</i> - $C_6H_5CH=CHC_6H_5$	94

^a Products were identified by comparison with authentic samples. ^b Yields indicated refer to pure isolated compounds. ^c *meso* form.

compounds in excellent yields. As shown in Table 2 and in the Experimental



section, the best results are obtained when a 3/1 molar ratio of reagent to substrate is used.

We have also found that the reaction of the complex I with the ω -bromoacetophenone or *meso*-1,2-dibromodiphenylethane in THF at 50°C gives acetophenone or *trans*-1,2-diphenylethane in very good yields (Table 3).

We conclude that the readily accessible salt I provides a useful alternative reagent to others recently reported for the reduction of nitroarenes to amines and α , β -unsaturated carbonyl compounds to the corresponding saturated species. The only limitation to the use of I is the difficulty which is sometimes encountered of separating the iron containing by-products from the organic compounds.

Experimental

All reactions were carried out under dry, oxygen-free argon. Tetrahydrofuran (THF) was obtained in anhydrous and oxygen-free form by distillation over sodium benzophenone ketyl under argon. $Fe(CO)_5$ was purchased from Merck.

Preparation of $[(C_2H_5)_4N^+ HFe_3(CO)_{11}^-]$ (I)

In a 1 l argon-filled three necked flask, equipped with a magnetic stirrer and a reflux condenser, were placed air-free water (240 ml), iron pentacarbonyl (110 ml, 0.82 mol), and triethylamine (83 ml, 0.59 mol), and the mixture was stirred and heated at 80°C overnight. After cooling, filtering off, and washing with

water, the solid triethylammonium hydrogen undecacarbonylhydridotriferrate $[(C_2H_5)_3NH^+ HFe_3(CO)_{11}^-]$ (102.4 g, 65%) was obtained. A mixture of $[(C_2H_5)_3NH^+ HFe_3(CO)_{11}^-]$ (22 g, 38 mmol) and $(C_2H_5)_4NCl$ (8 g, 49.3 mmol) was stirred in dichloromethane at room temperature for 30 min and the solvent was then removed under reduced pressure. The red solid residue was washed with water, dried under vacuum, and recrystallized from methanol to give the pure $[(C_2H_5)_4N^+ HFe_3(CO)_{11}^-]$ (18.2 g, 81%).

Aniline from nitrobenzene (general procedure)

To a solution of $[(C_2H_5)_4N^+ HFe_3(CO)_{11}^-]$ (3 g, 5 mmol) in dry THF (30 ml) was added nitrobenzene (0.61 g, 5 mmol) in dry THF (10 ml). The mixture was stirred for 2 h at 50°C, acidified with aqueous HCl and extracted with diethyl ether. The aqueous solution was separated and made basic with aqueous sodium hydroxide, and then re-extracted with ether. The organic layer was dried (Na_2SO_4), filtered, and evaporated under vacuum. Bulb to bulb distillation of the residue gave aniline (0.44 g, 95%).

Benzylacetone from benzalacetone (general procedure)

To a solution of $[(C_2H_5)_4N^+ HFe_3(CO)_{11}^-]$ (9 g, 15 mmol) in dry THF (90 ml), benzalacetone (0.73 g, 5 mmol) in dry THF (10 ml) was added dropwise. The mixture was heated for 2 h at 50°C, poured into water and extracted with diethyl ether. The organic layer was dried (Na_2SO_4), filtered, and evaporated under vacuum. The residue was chromatographed on silica gel with hexane/ether to give benzylacetone (0.59 g, 80%).

Acetophenone from ω -bromoacetophenone (general procedure)

To a solution of $[(C_2H_5)_4N^+ HFe_3(CO)_{11}^-]$ (3 g, 5 mmol) in dry THF (30 ml), ω -bromoacetophenone (0.99 g, 5 mmol) in dry THF (10 ml) was added dropwise. The mixture was heated for 2 h at 50°C, poured into water, and extracted with diethyl ether. The organic layer was dried (Na_2SO_4), filtered, and evaporated under vacuum. The residue was chromatographed on silica gel with hexane/ether to give acetophenone (0.45 g, 75%).

References

- 1 J.P. Collman, *Acc. Chem. Res.*, 8 (1975) 342 and references therein.
- 2 M.P. Cooke, *J. Amer. Chem. Soc.*, 92 (1970) 6080; G. Cainelli, F. Manescalchi, M. Panunzio and A. Umani-Ronchi, *J. Org. Chem.*, 43 (1978) 1598.
- 3 J.P. Collman, S.R. Winter and R.G. Komoto, *J. Amer. Chem. Soc.*, 95 (1973) 249.
- 4 T. Mitsudo, Y. Watanabe, M. Yamashita and Y. Takegami, *Chem. Lett.*, (1974) 1385.
- 5 H. Alper, *Tetrahedron Lett.*, (1975) 2257.
- 6 H. Alper and Hang-Nam Paik, *J. Org. Chem.*, 42 (1977) 3522.
- 7 R. Noyori, I. Umeda and T. Ishigami, *J. Org. Chem.*, 37 (1972) 1542.
- 8 G. Cainelli, M. Panunzio and A. Umani-Ronchi, *J. Chem. Soc. Perkin Trans.*, 1 (1975) 1273.
- 9 G.P. Boldrini, M. Panunzio and A. Umani-Ronchi, *Synthesis*, (1974) 733.
- 10 G.P. Boldrini, M. Panunzio and A. Umani-Ronchi, *Chem. Commun.*, (1974) 359.
- 11 J.P. Collman, R.G. Finke, P.L. Matlock, R. Wahren, and J.I. Brauman, *J. Amer. Chem. Soc.*, 98 (1976) 4685.
- 12 J.M. Landesberg, L. Katz and C. Olsen, *J. Org. Chem.*, 37 (1972) 930.
- 13 H. des Abbayes and H. Alper, *J. Amer. Chem. Soc.*, 99 (1977) 98.
- 14 E.E. Isaacs and W.A.G. Graham, *J. Organometal. Chem.*, 85 (1975) 237.
- 15 T.E. Cole and R. Pettit, *Tetrahedron Lett.*, (1977) 781.