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A Novel Synthesis of Neutral Dinitrosyl Iron Complexes. Their Catalytic Behaviour

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Dinitrosyl complexes such as $[Fe(NO)_2Cl]_2$ and $[Co(NO)_2Cl]_2$ lead to catalytic precursors when the chloro ligand is expelled out of the coordination sphere by a metathetical reaction with salts of non coordinating anions like PF_6^-, BF_4^-, ClO_4^-, BPh_4^- [1, 2]. The catalytic activity mainly originates from the existence of at least two easily accessible coordination sites. Another way to obtain such coordination sites is to abstract the chloro ligand by a reductive pathway. The work reported below is concerned with the catalytic behaviour of such complexes.

Reduction of $[Fe(NO)_2Cl]_2$ with copper or zinc powder leads to catalytic precursors which are very active and selective for the cyclodimerisation of representative unsaturated hydrocarbons such as norbornadiene, butadiene, isoprene and phenylacetylene. The reduction is achieved on adding an excess of the metal powder (molar ratio = 4) to $[Fe(NO)_2Cl]_2$ dissolved in a solvent S (Table I). The reduction reaction is rapid (< 1 hr at –20 °C) and leads to neutral complexes which contain the dinitrosyl iron moiety. The compounds $Fe(NO)_2(PPh_3)_2$ and $Fe(NO)_2(dppe)$ have been isolated quantitatively when the reaction was conducted in the presence of triphenylphosphine or 1,2-bis(diphenylphosphino)ethane (dppe).

Table I reports catalytic results for various S and unsaturated hydrocarbons under a standard set of experimental conditions, *i.e.* [Fe]/[unsaturated hydrocarbon] = 0.01, [S]/[unsaturated hydrocarbon] = 5, reaction temperature = –20 °C, reaction time = 22 hr. Under these experimental conditions $Fe(NO)_2(PPh_3)_2$, $Fe(NO)_2dppe$, $[Fe(NO)_2Cl]_2$ and metal powders are inactive.

TABLE I. Catalytic Behaviour of Reduced $[Fe(NO)_2Cl]_2$ Complex *versus* the Cyclodimerisation of Norbornadiene (nbd), Butadiene (bd), Isoprene (is) and Phenylacetylene (acet).

S	Olefin	Conversion (%)	Selectivity (%)
Bulk	nbd	3	exo-*trans*-exo dimer (81)
Toluene	nbd	33	exo-*trans*-exo dimer (80)
Diethyl-ether	nbd	66	exo-*trans*-exo dimer (89)
Thf	nbd	100	exo-*trans*-exo dimer (87)
Acetone	nbd	100	exo-*trans*-exo dimer (87)
Aceto-nitrile	nbd	35	exo-*trans*-exo dimer (84)
Methanol	nbd	26	exo-*trans*-exo dimer (88)
Thf	bd	100	4-vinylcyclohexene (100)
Thf	is	74	1,4(2,4)-dimethyl-4-vinylcyclohexene (96)
Thf	acet	20	1,2,4-triphenylbenzene (55)

Norbornadiene (nbd) is dimerised selectively to the exo-*trans*-exo dimer (85%), butadiene (bd) to 4-vinylcyclohexene (100%), isoprene (is) to 1,4(2,4)-dimethyl-4-vinylcyclohexene (96%) and phenylacetylene (acet) to 1,2,4-triphenylbenzene (55%). The dimerisation is solvent dependent: the activity increases with the medium polarity. The more active systems are obtained with dichloromethane, tetrahydrofuran and acetone. We are currently investigating the origin of this solvent dependency. It may be pointed out that the decrease of catalytic activity when S = acetonitrile, methanol are certainly related to a competition within the coordination sphere between S and the unsaturated substrate. The selectivity is temperature independent (–20 °C to +20 °C) and is slightly lowered, in the case of norbornadiene, when the medium polarity is low (bulk and toluene).

The catalytic behaviour of $Fe(NO)_2(CO)_2$ has already been reported [3, 4] for the cyclodimerisation of norbornadiene, butadiene and isoprene but under more severe conditions (reaction temperatures up to 100 °C in Carius tubes). The $Fe(NO)_2$ moiety was claimed to be the active species [4]. This work points out a new method of preparation of the $Fe(NO)_2$ moiety in a less coordinating medium which leads to a dramatic increase of the activity, the selectivity being identical. The work is being actually extended to the study of electrochemical reduction and oxidation. Preliminary measurements show that, starting from $[Fe(NO)_2Cl]_2$, an irreversible one electron reduction takes place in dimethylformamide or tetrahydrofuran.

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