

TITLE

PREPARATION OF TRANSITION METAL IMINE COMPLEXES

FIELD OF THE INVENTION

Preparation of imine complexes of certain
5 transition metals from selected metal compounds and
organic compounds which are precursors of imines in
essentially a single step are described. The imine
complexes are useful in the polymerization of olefins,
and may be used directly without isolation.

10 TECHNICAL BACKGROUND

Imine complexes of certain transition metals such
as iron, palladium, cobalt, nickel and others are
important parts of catalyst systems for the
polymerization of olefins, see for instance U.S. Patent
15 5,714,556, World Patent Applications 96/23010,
97/48737, 97/48735, 97/38024, and U.S. Patent
Application 08/991372, filed Dec. 16, 1997 all of which
are hereby included by reference. These and other
references generally describe the synthesis of these
20 types of imine complexes as the reaction of the imine
containing ligand with various types of transition
metal compounds to form the transition metal imine
complex. These methods usually involve the use of
substantially anhydrous conditions to avoid hydrolysis
25 of the starting transition metal compound and/or any
intermediates or the desired final complex.

For the most part, the imines themselves are not
commercially available, usually being made from the
corresponding carbonyl compound, such as a ketone or
30 aldehyde, and an amine, often an aromatic amine. When
made by this method, water is a byproduct. Since this
imine forming reaction is usually considered to be an
equilibrium, to drive the reaction to completion the
water is often removed during the synthesis of the
35 imine, for example by distillation, preferably
azeotropic distillation, or by formation of a hydrate,
preferably an inorganic hydrate.



Thus imine complexes of transition metals are often made in two step processes, imine synthesis, and then synthesis of the metal complex. A simpler, especially one step, synthesis would be preferable if they used the same starting materials since they would usually be cheaper than a two step synthesis.

Many complexes of imines and transition metals have been synthesized and reported in the literature. In addition to the above references, see for instance: H. tom Dieck et al., Inorg. Chim. Acta, vol. 177, p. 191-197 (1990); R. van Asselt, et al., J. Am. Chem. Soc., vol. 116, p. 977-985 (1994); H. tom Dieck, et al., Z. Naturforsch. B, vol. 33, p. 1381 et seq. (1978); H. G. von Schnering, et al., Chem. Ber., vol. 109, p. 1665 et seq. (1976); and H. tom Dieck et al., Chem. Ber., vol. 109, p. 1657 et seq. (1976).

R. van Asselt, et al., Recl. Trav. Chim. Pays-Bas., vol. 113, p. 88-98 (1994) describes the synthesis of certain zinc and nickel α -diimine complexes from the diketone and aromatic amine. In many of the syntheses, (glacial) acetic acid is present.

SUMMARY OF THE INVENTION

This invention concerns a process for the production of a transition metal complex of an imine, comprising, contacting under imine forming conditions in an aprotic solvent, a transition metal compound, a first organic compound containing at least one aldehyde or ketone group, and a second organic compound which is a primary amine to form said transition metal complex of said imine, and provided that said transition metal is nickel, palladium, iron and cobalt.

DETAILS OF THE INVENTION

It is well known that imines can be made by the reaction of a carbonyl group such as a ketone or aldehyde with a primary amine, the reaction being:





Since (1) is generally thought of as being an equilibrium reaction, it is usually driven to completion (formation of the imine) by removing the byproduct water that is formed. This can be done in a variety of ways, for instance removing the water by azeotropic distillation or as a hydrate of an inorganic salt. In order to efficiently utilize carbonyl compound and amine used in (1), they should preferably be present in the reaction in approximately the same ratio as they are in the product.

It has surprisingly been found that imine complexes [the imine(s) in the complex may contain one or more imine groups] of certain transition metals can be made in an aprotic solvent by addition of salts of those metals to a process in which reaction (1) is being carried out, even though water is generated as a byproduct. Thus reaction (1) is carried out in the presence of a suitable salt of the desired transition metal. The ratio of transition metal salt to the other ingredients is not critical, but in order to efficiently utilize all of the ingredients the ratio of moles transition metal compound to moles of the other reactants is such that they are approximately the same as they are in final desired imine complex. The transition metal compound is preferably present at the beginning of the process, but may be added at any time during the formation of the imine.

Useful transition metal compounds include metal halides, especially chlorides and bromides, and carboxylates. Zerovalent metal compounds that are not too sensitive to water may be used in conjunction with a suitable oxidizing agent (which are known in the art). Preferred transition metal compounds are halides, especially chlorides and bromides.

Any transition metal may be used. Transition metals are those metals in Groups 3-12 (IUPAC



notation), and metals in Groups 3-11 are preferred and metals in Groups 8-10 are especially preferred. Specific preferred transition metals are nickel, cobalt, iron and palladium, and nickel is especially preferred.

Process conditions for forming imines are well known and will be found in the various references cited in the Technical Background section, and also in R. L. Reeves in S. Patai, Ed., The Chemistry of the Carbonyl Group, Interscience Publishers, London, 1966, p. 608-619, and J. K. Whitesell in B. M. Trost, et al., Ed., Comprehensive Organic Synthesis, Vol. 6, Pergamon Press, Oxford, 1991, p. 719, which are both hereby included by reference.

The present process is preferably performed at a temperature of about 0°C to about 250°C, more preferably about 20°C to about 130°C. While pressure is not critical, and the process will probably be most often be carried out at ambient pressure, higher or lower pressures (than atmospheric pressure) may be used, for example to control the process temperature while distilling off byproduct water.

Preferred primary amines in the process are aryl amines, i.e., R^1 is an aryl or substituted aryl group. Aryl herein includes groups that have one or more aromatic rings which may be fused, as in naphthyl, or connected by a covalent bond, as in 2-phenylphenyl (o-biphenyl). It is preferred that the aromatic rings of the aryl group are carbocyclic rings, and it is more preferred that R^1 is phenyl or substituted phenyl. Useful substituents on a substituted phenyl group are alkyl, especially alkyl containing 1 to 4 carbon atoms, halo, especially chloro, phenyl, and halo substituted alkyl, especially fluoro substituted alkyl. It is also preferred that the phenyl group be substituted in the 2, or 2 and 6, positions.

The reaction is conducted in an aprotic solvent. By aprotic is meant the solvent has no protons whose



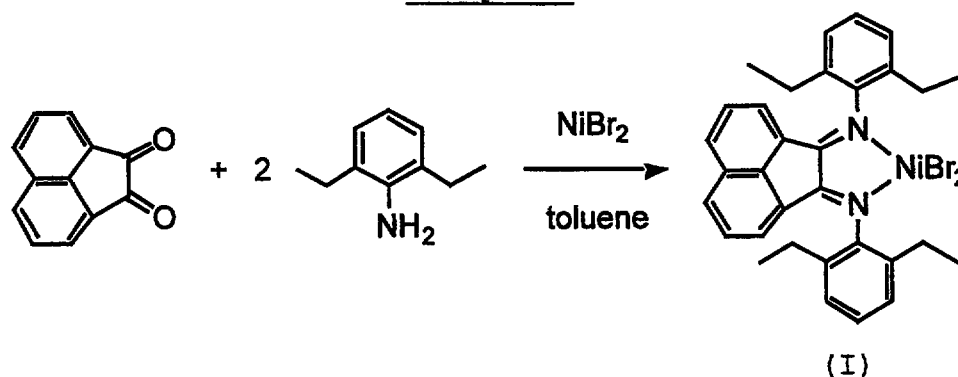
pKa is about 20 or more, more preferably about 25 or more. Useful solvents include aromatic hydrocarbons such as benzene and toluene, xylene, chlorobenzene and o-dichlorobenzene. Since the transition metal complex
5 may often be used in conjunction with other types of compounds (such as alkyl aluminum compounds) as a catalyst system for the polymerization of olefin, the absence of protic solvents is an advantage, since the solvent need not be removed before adding an alkyl
10 aluminum compound.

The carbonyl compound may contain more than one carbonyl group which may form an imine. Useful carbonyl compounds include α,β -diones, 2,6-pyridinedicarboxyaldehydes, 2,6-diacetylpyridines,
15 cyclic α,β -diones, 1,3-diones and ketoaldehydes. Specific useful carbonyl compounds include glyoxal, 2,3-butanedione, acenaphthenequinone, 2,6-diacetylpyridine, 2,6-pyridinedicarboxaldehyde, 1,2-cyclohexanedione, and pyruvaldehyde.

20 The transition metal imine complex, after it is made, may be isolated, as by removing the solvent under vacuum or by crystallization, or the solution may be used directly (i.e., without isolation of the complex, but the solution may be filtered to remove any
25 insoluble impurities) in a polymerization of one or more olefins. Olefins which may be polymerized with various transition metal complexes of imines, and the conditions for polymerizations will be found in U.S. Patent 5,714,556, World Patent Applications 96/23010,
30 97/48737, 97/48735, 97/38024, and U.S. Patent Application 08/991372, filed Dec. 16, 1997, and other references.

In the Examples, all pressures are gauge pressures.



Example 1

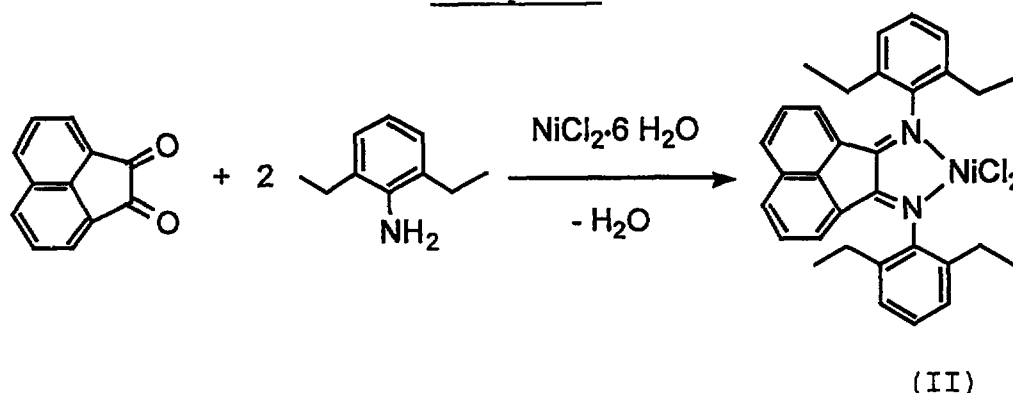
Nickel dibromide was purified of insoluble
 5 material by dissolving 2.22 g anhydrous nickel
 dibromide in 100 mL ethanol containing 1 mL water,
 filtering through diatomaceous earth and rotary
 evaporating dry. A mixture of 1.84 g (10.1 mmol)
 acenaphthenequinone, 3.00 g (20.0 mmol)
 10 2,6-diethylaniline, 2.1 g (9.6 mmol) nickel dibromide
 and 50 mL toluene was refluxed under nitrogen with
 water removal for 24 h to give a deep red-black
 reaction mixture. The mixture was rotary evaporated to
 remove toluene and the concentrate was stirred with 50
 15 mL methylene chloride and filtered through diatomaceous
 earth to remove unreacted nickel bromide. The filtrate
 was rotary evaporated and then held under high vacuum
 to yield 4.84 g dark red, waxy solids. The product was
 crushed and slurried in 40 mL hexane and
 20 suction-filtered. Drying under nitrogen yielded 3.95g
 (I) as a brown, methylene chloride-soluble powder.

Example 2

A suspension of 2.0 mg (0.0030 mmol) (I) of
 Example 1 in 5 mL dry, deaerated toluene was mixed with
 25 1.0 mL 1.7M modified methylaluminoxane in toluene
 (contains about 30% isobutyl groups) in a septum vial
 under nitrogen, swirling occasionally over 5 min,
 resulting in a dark maroon solution. A 600-mL stirred
 autoclave was loaded with 200 mL dry toluene. The
 30 solvent was stirred and saturated with ethylene at 50°C
 and 0.7 MPa for 10 min. The autoclave was vented and
 the toluene solution of catalyst was taken up into a

10-mL syringe and was injected into the autoclave through a head port. The autoclave was immediately pressured to 1.0 MPa with ethylene and was stirred for 30 min in a 50°C water bath as ethylene was fed to maintain pressure. After 30 min the ethylene was vented and resulting clear polymer gel was extracted with acetone and vacuum-oven dried (70°C/nitrogen purge) to yield 6.7 g polyethylene.

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Example 3

A mixture of 1.84 g (10.1 mmol) acenaphthenequinone, 3.00 g (20.0 mmol) 2,6-diethylaniline, 2.25g (9.5 mmol) nickel dichloride hexahydrate, 30 mg p-toluenesulfonic acid and 50 mL toluene was refluxed for 48 h under nitrogen with water removal. The deep red-brown reaction mixture was suction-filtered on a glass fritted funnel to remove unreacted nickel dichloride. The black filtrate solution was sparged with nitrogen before using as a catalyst.

Example 4

A mixture of 20 mL dry, deaerated toluene and 1.0 mL 1.7M modified methylalumoxane was magnetically stirred at room temperature under 41 kPa ethylene in a 50-mL Schlenk flask for a few minutes to saturate the solvent with ethylene. Then 1.5 mL of the solution of (II) made in Example 10 was added; a black solution immediately resulted. This solution was stirred under 41 kPa ethylene for 16 h; it remained black but became

more viscous with time. The ethylene was vented and the solution was stirred with 25 mL 6N HCl and 20 mL additional toluene, and the toluene layer was separated, water-washed and rotary-evaporated to yield, 5 after washing with methylene chloride and acetone and vacuum-oven drying (70°C), 0.96 g of soft, tacky polyethylene.

CLAIMS

What is claimed is:

1. A process for the production of a transition metal complex of an imine, comprising, contacting under
5 imine forming conditions in an aprotic solvent, a transition metal compound, a first organic compound containing at least one aldehyde or ketone group, and a second organic compound which is a primary amine to form said transition metal complex of said imine, and
10 provided that said transition metal is nickel, palladium, iron, or cobalt.
2. The process as recited in claim 1 wherein byproduct water is removed by distillation or formation of a hydrate.
- 15 3. The process as recited in claim 1 wherein water is removed by azeotropic distillation.
4. The process as recited in claim 1 or 3 wherein said second compound is a primary aryl amine or a substituted aryl primary amine.
- 20 5. The process as recited in claim 1 or 3 wherein said transition metal is nickel.
6. The process as recited in claim 1 or 3 wherein said transition metal compound is a chloride, bromide, or carboxylate.
- 25 7. The process as recited in claim 1 wherein a temperature is about 0°C to about 250°C.
8. The process as recited in claim 1 wherein said aprotic solvent is a hydrocarbon.
9. The process as recited in claim 1 or 3
30 additionally comprising contacting said complex with one or more polymerizable olefins and optionally cocatalysts to polymerize said polymerizable olefins.
10. The process as recited in claim 9 wherein said complex is not isolated before said contacting with one
35 or more polymerizable olefins.
11. The process as recited in claim 5 wherein said second compound is a primary amine or a substituted aryl primary amine.





12. The process as recited in claim 6 wherein said second compound is a primary amine or a substituted aryl primary amine.

13. The process as recited in claim 9 wherein said
5 second compound is a primary amine or a substituted aryl primary amine.

14. The process as recited in claim 6 wherein transition metal is nickel.

15. The process as recited in claim 9 wherein
10 transition metal is nickel.

16. The process as recited in claim 9 wherein transition metal compound is a chloride, bromide or carbonate.

17. The process as recited in claim 15 wherein
15 transition metal compound is a chloride, bromide or carbonate.