Editor-in-Chief

GEORGE W. PARSHALL

Central Research Department
E. I. du Pont de Nemours & Company
Wilmington, Delaware

INORGANIC SYNTHESES

Volume XV

McGRAW-HILL BOOK COMPANY
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INORGANIC SYNTHESES

Volume XV

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To Ronald S. Nyholm
1917–1971

CONTENTS

PREFACE

Almost inevitably the content of a volume of INORGANIC SYNTHESES reflects the interests of the Editor-in-Chief to a considerable extent. Thus Volume XIII had a strong flavor of metal-metal bonded compounds and Volume XIV contains a remarkably fine collection of solid-state syntheses. The present volume is no exception. It contains syntheses of many transition-metal compounds important in homogeneous catalysis, especially complexes of olefins, hydrogen, and nitrogen, which have interested me and my colleagues. However, I hope and believe that this volume also has general interest and that the techniques described will have broad application in inorganic chemistry. One of the strengths of INORGANIC SYNTHESES is the diversity of interests among the members of the Editorial Board. Their help in assembling preparations of all sorts of inorganic compounds prevents a volume from ever becoming a collection for just the practitioners of one narrow specialty.

Perhaps the greatest strength of INORGANIC SYNTHESES is the support that it has received from inorganic chemists generally. Assembling this volume has done much to restore my faith in human nature. People have been immensely helpful in soliciting, contributing, checking, and editing syntheses. At the risk of slighting individuals by omission, I am especially indebted to Charles Van Dyke for his initiative in assembling the chapter on germanium hydride derivatives and to George Ryschkewitsch and Roland Köster for contributing the two groups of syntheses that make up most of the chapter on boron compounds. Similarly S. D. Robinson contributed and E. R. Wonchoba checked most of the chapter on triphenylphosphine complexes of the transition metals.

Finally it is a pleasure to thank Mrs. Kathy Jones, Mrs. Kathy Schloegel, and Mrs. Suzanne Grandel for the typing of this volume and the members of the Editorial Board for repeated editing and proofreading of it.

G. W. Parshall

NOTICE TO CONTRIBUTORS

The INORGANIC SYNTHESES series is published to provide all users of inorganic substances with detailed and foolproof procedures for the preparation of important and timely compounds. Thus the series is the concern of the entire scientific community. The Editorial Board hopes that all chemists will share in the responsibility of producing INORGANIC SYNTHESES by offering their advice and assistance in both the formulation of and the laboratory evaluation of outstanding syntheses. Help of this kind will be invaluable in achieving excellence and pertinence to current scientific interests.

There is no rigid definition of what constitutes a suitable synthesis. The major criterion by which syntheses are judged is the potential value to the scientific community. An ideal synthesis is one which presents a new or revised experimental procedure applicable to a variety of related compounds, at least one of which is critically important in current research. However, syntheses of individual compounds that are of interest or importance are also acceptable.

The Editorial Board lists the following criteria of content for submitted manuscripts. Style should conform with that of previous volumes of INORGANIC SYNTHESES. The *Introduction* should include a concise and critical summary of the available procedures for synthesis of the product in question. It should also include an estimate of the time required for the synthesis, an indication of the importance and utility of the product, and an admonition if any potential hazards are associated with the procedure. The *Procedure* should present detailed and unambiguous laboratory directions and be written so that it anticipates possible mistakes and misunderstandings on the part of the person who attempts to duplicate the procedure. Any unusual equipment or procedure should be clearly described. Line drawings should be included when they can be helpful. All safety measures should be stated clearly. Sources of unusual starting materials must be given, and, if possible, minimal standards of purity of reagents and solvents should be stated. The scale should be reasonable for normal laboratory operation, and any problems involved in scaling the procedure either up or down should be discussed. The criteria for judging the purity of the final product should be delineated clearly. The section on *Properties* should list and discuss those physical and chemical characteristics that are relevant to judging the purity of the product and to permitting its handling and use in an intelligent manner. Under *References*, all pertinent literature citations should be listed in order.

The Editorial Board determines whether submitted syntheses meet the general specifications outlined above. Every synthesis must be satisfactorily reproduced in a different laboratory from that from which it was submitted.

Each manuscript should be submitted in duplicate to the Secretary of the Editorial Board, Professor Stanley Kirschner, Department of Chemistry, Wayne State University, Detroit, Michigan, 48202, U.S.A. The manuscript should be typewritten in English. Nomenclature should be consistent and should follow the recommendations presented in "The Definitive Rules for Nomenclature of Inorganic Chemistry," *J. Am. Chem. Soc.*, **82,** 5523 (1960). Abbreviations should conform to those used in publications of the American Chemical Society, particularly *Inorganic Chemistry.*

INORGANIC SYNTHESES

Volume XV

Chapter One

METAL COMPLEXES OF OLEFINS

Transition-metal complexes of olefins have been extensively studied as possible intermediates in homogeneous catalysis. However, in recent years, it has been recognized that olefin complexes are extremely useful intermediates for synthesis of many other transition-metal complexes. The olefin ligand is often labile and is easily replaced by a phosphine or by carbon monoxide.

The olefin complexes of iron, nickel, rhodium, and iridium described in this chapter have found broad application in the synthesis of phosphine, phosphite, and carbonyl derivatives of these metals. In Chapter Two, the synthesis of another labile olefin complex, (ethylene)bis(tricyclohexylphosphine)nickel, is described as an initial step in synthesis of a complex of dinitrogen.

The utility of the olefin complexes in synthesis has been judged sufficient to warrant their inclusion in this volume despite the hazards and difficulties involved in their preparation.

Several of the syntheses involve the reduction of a metal salt by an alkylaluminum compound. Since these reducing agents are extremely air-sensitive, even pyrophoric, extreme care is needed, and the preparation should not be undertaken without adequate facilities for handling these compounds. However, all these syntheses have been reproduced many times and give consistently good yields when conducted *exactly as described.*

1. BIS(1,3,5,7-CYCLOOCTATETRAENE)IRON(0)

$$\mathrm{Fe(C_5H_7O_2)_3 + 2C_8H_8 + 3Al(C_2H_5)_3 \longrightarrow Fe(C_8H_8)_2 + 3Al(C_2H_5)_2(C_5H_7O_2) + \tfrac{3}{2}C_2H_4 + \tfrac{3}{2}C_2H_6}$$

Submitted by D. H. GERLACH* and R. A. SCHUNN†
Checked by M. A. BENNETT,‡ I. B. TOMKINS,‡ and T. W. TURNEY‡

The synthesis of bis(1,3,5,7-cyclooctatetraene)iron(0) by reduction of anhydrous iron(III) chloride with the isopropyl Grignard reagent in the presence of cyclooctatetraene was reported recently.[1] This compound promotes oligo- and co-oligomerization of several unsaturated hydrocarbons[1] and is useful as a precursor in the preparation of a number of dihydridoiron complexes.[2] The procedure described here is simpler than the original method[1] and gives significantly higher yields.

Materials

1,3,5,7-Cyclooctatetraene§ is purified by passage through 1–2 cm. of activated alumina supported on a coarse sintered-glass filter. Anhydrous tris(2,4-pentanedionato)iron(III)¶ and triethylaluminum¶ are used without further purification.

■ **Caution.** *Triethylaluminum is a pyrophoric liquid that reacts violently with water or alcohols. It should be handled only in a rigorously oxygen- and moisture-free atmosphere, using face shield and gloves.* The solution of triethylaluminum in diethyl ether is prepared by slowly adding 50 ml. of triethylaluminum to 150 ml. of ether in a nitrogen-filled flask cooled to *ca.* 0° and is transferred to the addition funnel with a 100-ml. hypodermic syringe.

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§Aldrich Chemical Co., 2371 North 30th St., Milwaukee, Wis. 53210.

¶Alfa Inorganics, P.O. Box 159, Beverly, Mass. 01915.

Procedure

The entire procedure is performed in an anhydrous, oxygen-free atmosphere using anhydrous, deoxygenated solvents. Standard techniques[3,4] for bench-top inert-atmosphere reactions are used in this procedure. A 1-l. three-necked flask is equipped with a magnetic stirring bar, a thermometer, a 250-ml. pressure-equalizing addition funnel with a Teflon stopcock, and a condenser topped with a nitrogen inlet connected in parallel with a mineral-oil bubbler. The flask is charged with 36 g. (0.10 mole) of tris(2,4-pentanedionato)-iron(III), 80 g. (0.77 mole) of 1,3,5,7-cyclooctatetraene, and 400 ml. of dry diethyl ether and is purged thoroughly with nitrogen. While the mixture is being cooled to − 15°*, the previously prepared solution of triethylaluminum in ether is syringed into the addition funnel. The triethylaluminum solution is added dropwise over 1.5 hours while the temperature is maintained at about − 10°. [If the temperature during the addition is allowed to rise above 0°, tris(2,4-pentanedionato)aluminum(III) forms and interferes with the purification of the product.] During the addition the red color of the mixture changes to dark brown. The mixture is stirred at − 10° for 2 hours, warmed slowly to room temperature, and gently boiled for 0.5 hour. Gas evolves during this process. The flask is cooled to − 78° for 16 hours, and the resulting black crystalline solid is collected by filtration in an inert atmosphere at low temperature.†,‡ It is washed with 100 ml. of cold (− 78°) ether and dried *in vacuo* at room temperature for several hours. The purity of the product is sufficiently high for use in the preparation of FeH_2L_4 complexes.[2] Analytically pure samples in the form of shiny black needles can be obtained by recrystallization from ether, *n*-pentane, or petroleum ether (b.p. 38–51°). The yield of the unrecrystallized product is 20 g.

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*Dry Ice is added to a toluene bath as necessary to obtain the desired temperature. A wet ice-methanol bath may also be used but is somewhat more hazardous because of the violent reaction of triethylaluminum with water and methanol.

†Figure 1 (p.7) illustrates an apparatus which is useful for the filtration of large-scale preparations of air-sensitive compounds at temperatures down to − 78°. For smaller-scale reactions, Schlenk-tube techniques[3,4] may be used.

‡The filtrate contains highly reactive ethylaluminum compounds which react violently with water or alcohols and is most conveniently disposed of by incineration. Alternatively, the mixture may be decomposed by the careful, dropwise addition of 200 ml. of ethanol to the cooled, stirred solution (much gas is evolved), followed by the cautious addition of water.

(74%). *Anal.* Calcd. for $C_{16}H_{16}Fe$: C, 72.75; H, 6.11; Fe, 21.14. Found: C, 72.38, 72.36; H, 6.14, 6.15; Fe, 21.38, 21.33.

Properties

Bis(1,3,5,7-cyclooctatetraene)iron(0) is a black crystalline solid which is unstable toward atmospheric oxygen. It can be stored for several weeks in an inert atmosphere at room temperature without significant decomposition. Temperatures of − 40° or lower should be maintained if the compound is to be stored for several months.

The complex is soluble in diethyl ether and common aliphatic and aromatic solvents. It is less stable in solution and decomposes at room temperature within a few days even when a rigorously inert atmosphere is maintained. Chlorinated hydrocarbons rapidly decompose $Fe(C_8H_8)_2$, with the formation of precipitates.

The solid- and solution-state structures of $Fe(C_8H_8)_2$ have been established by x-ray crystallography[5] and infrared and proton-magnetic-resonance spectroscopy.[6] In the solid the iron atom is five-coordinate and achieves a noble-gas configuration by π bonding to six carbon atoms of one ring and four of the other.[5] In solution, $Fe(C_8H_8)_2$ is stereochemically nonrigid on the proton n.m.r. time scale. Near room temperature all ring protons are equivalent, but at low temperatures the tricoordinate and bicoordinate C_8 rings can be "frozen" out.[6]

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2. BIS(1,5-CYCLOOCTADIENE)NICKEL(0)

$$Ni(C_5H_7O_2)_2 + 2C_8H_{12} + 2Al(C_2H_5)_3 \longrightarrow Ni(C_8H_{12})_2 + 2Al(C_2H_5)_2(C_5H_7O_2) + C_2H_4 + C_2H_6$$

Submitted by R. A SCHUNN*
Checked by R. BAKER,† R. J. COLE,† J. D. GILBERT,† and D. P. MADDEN†

Bis(1,5-cyclooctadiene)nickel(0) is useful for the synthesis of a variety of novel nickel complexes,[1-5] since the cyclooctadiene ligands are easily displaced. The procedure given here is based on that described by Wilke;[6] butadiene is used to prevent the formation of nickel metal.[6]

Materials

Anhydrous bis(2,4-pentanedionato)nickel(II) is obtained from $Ni(C_5H_7O_2)_2 \cdot 2H_2O$ (Alfa Inorganics) by azeotropic distillation of the water with toluene. The hot, dark-green slurry is filtered through Celite under nitrogen, and the filtrate is evaporated to dryness on a rotary evaporator. The green, solid residue is crushed in a mortar and dried at 80°/0.1μm./16 hours to give the anhydrous complex. Peroxide impurities are removed from 1,5-cyclooctadiene (Aldrich Chemicals) by filtration through grade 1 neutral alumina; the filtration is repeated until the alumina is no longer colored yellow. Further purification is not necessary, but the liquid should be used immediately. Butadiene is dried by passing it through a U trap containing Type 3A molecular sieves, condensing the gas at − 78°, and storing it in a small stainless-steel cylinder.

■ **Caution.** *Triethylaluminum is a pyrophoric liquid that reacts violently with water or alcohols. It should be handled only in a rigorously oxygen- and moisture-free atmosphere, using face shield and gloves.* The solution of triethylaluminum in toluene is most conveniently

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prepared in an inert-atmosphere box[7] and transferred to the addition funnel with a 100-ml. hypodermic syringe.

Procedure

The entire procedure is performed in an anhydrous, oxygen-free atmosphere using anhydrous, deoxygenated solvents. Standard techniques[7,8] for bench-top inert-atmosphere reactions are used in this procedure. A 1-l., four-necked, round-bottomed flask is equipped with a stopcock adapter having a hose end, a thermometer, and a Dry Ice condenser topped with a T tube which is connected to a mineral-oil bubbler and a source of dry nitrogen. The center neck of the flask is left open. The flask is flushed thoroughly with nitrogen and charged through the center neck with 102.8 g. (0.4 mole) of anhydrous bis(2,4-pentanedionato)nickel(II), 250 ml. of toluene, and 216 g. (2.0 moles) of 1,5-cyclooctadiene. The center neck is then equipped with a mechanical stirrer, and the mixture is stirred and cooled to − 10°;* the condenser is filled with a mixture of Dry Ice and acetone. Approximately 18 g. (0.33 mole) of anhydrous 1,3-butadiene is admitted to the flask through the stopcock adapter;† the gas dissolves in the cold mixture. The stopcock adapter is then replaced with a nitrogen-flushed 250-ml. pressure-equalizing dropping funnel having a Teflon stopcock, and the system is flushed with nitrogen by removing the stopper from the top of the addition funnel. A solution of 103 g. (0.9 mole) of triethylaluminum in 100 ml. of toluene is placed in the addition funnel and added dropwise to the cold, stirred mixture. The temperature is maintained at − 10 to 0°; the addition requires *ca.* 45–90 minutes. During the addition, the green slurry becomes yellow-brown and a yellow crystalline solid is formed. After being stirred at 0° for 0.5 hour, the mixture is allowed to warm to room temperature and is stirred overnight.‡

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*Dry Ice is added to a toluene bath as necessary to obtain the desired temperature. A wet ice-methanol bath may also be used but is somewhat more hazardous because of the violent reaction of triethylaluminum with water and methanol.

†The weight transferred to the reaction flask is determined by supporting the cylinder on a balance while conducting the gas into the reaction flask through rubber tubing attached to the hose end of the stopcock adapter.

‡Several hours of stirring are probably sufficient. Since the product is often light-sensitive, the reaction flask should be covered during this period.

The Dry Ice condenser is also allowed to warm. Gas (predominantly ethylene and ethane) is evolved.

The yellow slurry is stirred for 2–3 hours at − 15°. With rapid nitrogen flushing, the addition funnel is replaced with an adapter attached to a nitrogen line, the thermometer and mechanical stirrer are replaced with stoppers, and all joints are secured with standard-taper-joint clips (A. H. Thomas Co.). The apparatus shown in Fig. 1* is assembled and filled with nitrogen. The joints *B* and *C* are secured with standard-taper-joint clips. With nitrogen flushing through stopcock 1 and the reaction flask, the Dry Ice condenser is removed from the reaction flask and replaced by joint *A*; the joint is secured with a joint clip. Care must be taken to support the reaction flask suitably, and it must be replaced in the cold bath. The filter is im-

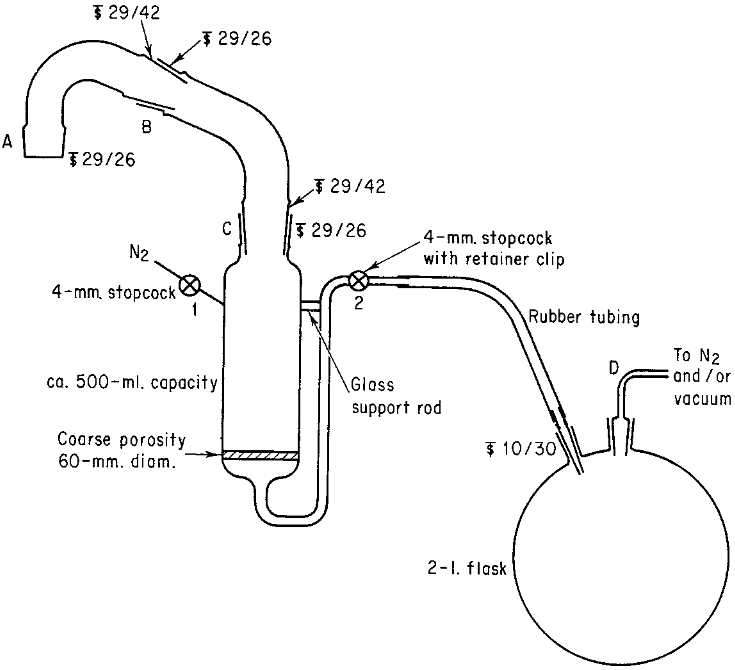

Fig. 1. Apparatus for low-temperature filtration.

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*This apparatus is useful for the filtration of large-scale preparations of air-sensitive compounds at temperatures down to − 78°. The glass adapters (joints *A*, *B*, *C*) may be replaced with a suitably adapted Flexi-joint (Cole-Parmer, Inc.). For smaller-scale reactions, Schlenk-tube techniques[7] may be used. The reaction mixture may also be filtered at room temperature, with a corresponding decrease in yield due to the increased solubility of the product.

mersed in a cold bath (− 15°), the reaction solution is transferred to the filter in portions by rotating at joint *B*, and the mixture is filtered by opening stopcock 2 and pressuring with nitrogen; the mineral-oil bubbler may be replaced by a mercury bubbler for this purpose.[7] Care must be taken to use sufficient pressure for filtering but avoid popping joints or stoppers. Alternatively, suction may be applied at *D*, but care must be taken to avoid introducing air into the system. When the entire reaction mixture has been filtered, the product is washed by adding 100 ml. of toluene to the reaction flask (via hypodermic needle through the thermometer joint), cooling it to − 15°, and pouring it onto the filter. After three washes, the filtrate is pale yellow. A final wash with 100 ml. of cold anhydrous ether facilitates drying. With nitrogen flushing rapidly through stopcock 1, the adapter at joint *C* is replaced with a stopper and stopcock 2 is closed.* A vacuum line is attacked to stopcock 2, stopcock 1 is closed, and the filter is evacuated. After 0.5 hour the filter is warmed to 25°, and after 0.5 hour the product is transferred to a vacuum-line flask and dried further (protect from light) at 25°/0.1 μm./16 hours to give 97.0 g. (89%) of $Ni(1,5\text{-}C_8H_{12})_2$; decomposes *ca.* 135–140°. *Anal.* Calcd. for $C_{16}H_{32}Ni$: C, 69.9; H, 8.8; Ni, 21.3. Found: C, 69.1; H, 8.7; Ni, 21.2.

Properties

The solid complex is decomposed after several minutes in air; solutions are more rapidly decomposed. It is moderately soluble in benzene and tetrahydrofuran, but heating these solutions above *ca.* 60° causes decomposition. It is nearly insoluble in diethyl ether and saturated hydrocarbons. The complex may be purified by extraction with benzene at 45–50°, addition of *n*-heptane to the yellow filtrate, and concentration of the mixture on a rotary evaporator.

^1H n.m.r. (C_6D_6, ext. $(CH_3)_4Si$): δ 1.38 (s, 8, CH_2); δ 3.64 (s, bd, 4, CH).

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*The filtrate contains highly reactive ethylaluminum compounds which react violently with water or alcohols and is most conveniently disposed of by incineration. Alternatively, the mixture may be decomposed by the careful, dropwise addition of 200 ml. of ethanol to the cooled, stirred solution (much gas is evolved), followed by the cautious addition of water.

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3. ETHYLENEBIS(TRI-*o*-TOLYL PHOSPHITE)NICKEL(0) AND TRIS(TRI-*o*-TOLYL PHOSPHITE)NICKEL(0)

Submitted by W. C. SEIDEL* and L. W. GOSSER†
Checked by H. BÖNNEMANN‡ (Secs. A and B) and L. VANDE GRIEND§ and J. G. VERKADE§ (Sec. C)

Ethylenebis(tri-*o*-tolyl phosphite)nickel(0)[1,2] is a useful catalyst for many reactions of dienes.[3] It can be prepared by reduction of bis(2,4-pentanedionato)nickel(II) with triethylaluminum in the presence of excess phosphite ligand. However, much better yields are obtained by the procedure described in Sec. A, in which a stoichiometric quantity of phosphite is used in conjunction with excess ethylene.[1]

Tris(tri-*o*-tolyl phosphite)nickel(0),[4] likewise a useful catalyst,[5] is conveniently prepared by displacement of ethylene from the olefin complex by a mole of phosphite ligand as described in Sec. B. Alternatively, it can be prepared directly by reduction of hydrated nickel nitrate with sodium tetrahydroborate in acetonitrile (Sec. C). This method avoids the need to handle spontaneously flammable triethylaluminum.

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§Department of Chemistry, Iowa State University, Ames, Iowa 50010.

A. ETHYLENEBIS(TRI-*o*-TOLYL PHOSPHITE)NICKEL(0)

$$Ni(C_5H_7O)_2 + C_2H_4 + 2P(OC_6H_4CH_3)_3 + (C_2H_5)_3Al \longrightarrow Ni(C_2H_4)[P(OC_6H_4CH_3)_3]_2$$

Materials

This procedure can be greatly simplified if the appropriate starting materials are available. Handling of the triethylaluminum is facilitated by use of the nonpyrophoric 25% solution in hexane available from Texas Alkyls Division of the Stauffer Chemical Co., Deer Park, Tex. 77536. (■ **Caution.** *Neat triethylaluminum is spontaneously flammable in air.*) Dehydration of the bis(2,4-pentanedionato)nickel(II) dihydrate can be avoided by purchase of the anhydrous complex from Königswarter and Ebell, Postfach 2020, 58 Hagen/Westfalen, Germany. Tri-*o*-tolyl phosphite is available from DAP, 6140 Marienberg, Post Bensheim, Germany, or it may be prepared by the procedure of Walsh.[6]

Procedure

■ **Caution.** *The ligand, reducing agent, and product are oxygen-sensitive and must be handled under an inert atmosphere at all times.*

The synthesis is conducted in a 500-ml. two-necked flask equipped with magnetic stirrer and a gas inlet. If hydrated bis(2,4-pentanedionato)nickel(II) (ROC/RIC, 11686 Sheldon St., Sun Valley, Calif. 91352) is to be used, 5.88 g. (20 mmoles) of the dihydrate and 125 ml. of toluene are placed in the flask, and it is fitted with a Dean-Stark trap.* The mixture is boiled under reflux under nitrogen until 0.72 ml. of water collects in the trap.

The solution of 20 mmoles of anhydrous bis(2,4-pentanedionato)nickel in *ca.* 100 ml. of toluene obtained as above or prepared from anhydrous reagents is cooled to 0°. The Dean-Stark trap is replaced with a rubber septum, and 14.08 g. (12.4 ml., 40 mmoles) of tri-*o*-tolyl

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*A device for separating water from an azeotropic distillate while returning toluene to the flask is available from A. H. Thomas Co., Philadelphia, Pa.

phosphite is added. The solution is bubbled with ethylene gas for 5 minutes. Then, with the ethylene stream off, 27 ml. of 25% triethylaluminum in hexane (0.04 mole) is added by syringe through the septum over a period of 20 minutes. The originally green solution becomes yellow. The color deepens to orange as the solution is stirred at *ca.* 0° for 3 hours.

The product is precipitated by addition of oxygen-free methanol (200 ml.) by syringe through the septum. (■ **Caution.** *The addition of methanol is accompanied by vigorous gas evolution.*) It should be added 1 ml. every 5 minutes for the first 5 ml.

The reaction mixture is transferred to an inert-atmosphere "drybox" and cooled to − 25°. The bright yellow crystals are collected on a filter pad and recrystallized by dissolving in 35 ml. of warm (60°C.) toluene, filtering through a medium-porosity-filter frit, and precipitating by the addition of 100 ml. of cold methanol. The product is dried under high vacuum; yield 10.4 g. (66%). *Anal.* Calcd. for $C_{44}H_{46}NiO_6P_2$: C, 66.8; H, 5.8; Ni, 7.4; P, 7.8. Found: C, 66.6; H, 5.7; Ni, 7.3; P, 7.8.

Properties

The ethylene complex is a yellow, air-sensitive, crystalline solid which melts with decomposition at 118–120°.

B. TRIS(TRI-*o*-TOLYL PHOSPHITE)NICKEL(0)

$$Ni(C_2H_4)[P(OC_6H_4CH_3)_3]_2 + P(OC_6H_4CH_3)_3 \longrightarrow Ni[P(OC_6H_4CH_3)_3]_3 + C_2H_4$$

Procedure

A solution of 10.0 g. (12.6 mmoles) of ethylenebis(tri-*o*-tolyl phosphite)nickel(0) and 4.4 g. (3.9 ml.) of tri-*o*-tolyl phosphite in 50 ml. of benzene is evaporated to dryness under vacuum. Nitrogen is admitted to the flask, and the resulting red foam is dissolved in 75 ml. of toluene. The tris(tri-*o*-tolyl phosphite)nickel is precipitated as red crystals by addition of 150 ml. of methanol and cooling; yield 12 g. (85%). The checker obtained an 88% yield of product, which gave the following analysis. *Anal.* Calcd. for $C_{63}H_{63}NiO_9P_3$: Ni, 5.3. Found: Ni, 5.3.

C. TRIS(TRI-*o*-TOLYL PHOSPHITE)NICKEL(0)

$$Ni(NO_3)_2 \cdot 6H_2O + 2NaBH_4 + 3P(OC_6H_4CH_3)_3 \longrightarrow Ni[P(OC_6H_4CH_3)_3]_3 + 2NaNO_3 + 7H_2 + 2B(OH)_3$$

Materials

Sodium tetrahydroborate, nickel nitrate hexahydrate, and nominally anhydrous acetonitrile are commercially available. Tri-*o*-tolyl phosphite is prepared by the method of Walsh.[6]

Procedure

A solution* of 6.0 g. (20 mmoles) of nickel nitrate hexahydrate in 150 ml. of acetonitrile is prepared in a 1-l., three-necked, round-bottomed flask equipped with a nitrogen inlet, gas vent (oil bubbler), and magnetic stirrer. Tri-*o*-tolyl phosphite (30 g., 85 mmoles) is added to the stirred nickel nitrate solution. Sodium tetrahydroborate (10 g., 260 mmoles) is placed in a 125-ml. Erlenmeyer flask which is attached to one of the necks of the reaction flask with Gooch tubing as described by Fieser.[7] The flask is flushed briefly with nitrogen and surrounded with a bath of room-temperature water. The sodium tetrahydroborate is added in portions to the stirred solution. (■ **Caution.** *Vigorous gas evolution.*) The gas evolution is allowed to subside before addition of the next portion. After the addition of the sodium tetrahydroborate is complete, the pale gray-green mixture is stirred at room temperature for 2 hours. The reaction vessel is transferred to a nitrogen-filled glove box, and the reaction mixture is filtered through a medium glass frit.† The acetonitrile is

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*Ideally the solution of nickel nitrate and tri-*o*-tolyl phosphite in acetonitrile should be prepared in a nitrogen atmosphere. In practice satisfactory results are obtained if the materials are handled in air briefly for measurement before closing and nitrogen-flushing the reaction vessel. After the addition of sodium tetrahydroborate, no oxygen can be allowed to contact the reaction mixture or the solutions containing the product. Solvents must be nitrogen-purged or degassed, with the exception of the acetonitrile for the initial reaction mixture.

†The excess sodium tetrahydroborate is collected at this point and should be handled with appropriate caution.