

of sodium hydroxide in 10 ml. of water was added. After 20–30 minutes of gentle refluxing, filtration and dilution with water, 650 mg. (80%) of complex II and a small amount of complex V were isolated. Complex II was identified by m.p. and infrared analysis.

Conversion of Complex III to Complex V by Base.—Complex III (72.5 mg.) was dissolved in 10 ml. of methanol, and 0.5 ml. of 7 *N* sodium hydroxide solution was added. This solution was heated in an evacuated tube for three hours at 70–80° bath temperature. At the end of the reaction, a small amount of uncondensable gas (carbon monoxide) was detected. The contents of the tube were acidified with 5 ml. of hydrochloric acid (1:1) upon which carbon dioxide and a small amount of iron hydrocarbonyl could be detected, the latter by odor. Iron which split off from complex III in form of ferrous hydroxide was determined, and amounted to 0.16 mole (83% of the theoretical amount). Complex V was isolated as described above under "Base Reaction of Complex II" yielding 22.4 mg., 47%. A small amount of tetraphenylbutadiene (m.p.) and of complex II could be detected as by-products of the saponification.

Isolation of Complex IV.—Diphenylacetylene (2 g.) and 3 g. of iron pentacarbonyl were refluxed/irradiated in 50 ml. of benzene for one to two hours. The deep-red solution was evaporated *in vacuo*, the residue was redissolved in 20 ml. of methanol, and filtered. To the filtrate, *n*-hexane (50–100 ml.), 5 ml. of diluted hydrochloric acid and 50 ml. of water were added. The hexane layer was washed (methanol-water, 1:1) and dried over calcium chloride. Complex IV (100–200 mg.) crystallized from the hexane solution. (The yield can be increased, however, if the temperature of irradiation is lowered by using a lower boiling solvent (diethyl ether).) Molecular weight determinations were initially performed by the isopiestic method; they are, however, unreliable due to the low stability of solutions of complex IV. Cryoscopic measurements with gram quantities of complex IV gave a molecular weight of 600 and 602 in benzene (calcd. 664).

Anal. Calcd. for $\text{Fe}_2\text{C}_{30}\text{H}_{20}\text{O}_7$: C, 63.29; H, 3.03; O, 16.85; Fe, 16.83. Found: C, 63.40; H, 3.07; O, 16.80; Fe, 16.79; m.p. 158°, dec.

Conversion of Complex IV into Complex I.—Complex IV (400 mg.) was heated in a sealed tube in toluene solution for three hours at 130° bath temperature. The volatile fraction contained, besides the toluene, 0.30 mmole of iron pentacarbonyl. Upon filtration of the redissolved residue, metallic iron (0.28 mmole) was found. From the filtrate, 250 mg. (82%) of complex I and 30 mg. (13%) of crude tetracyclone were isolated. The same conversion of complex IV into I can be accomplished by refluxing a benzene solution for some time.

Bromination and Saponification of Complex IV.—Bromination of complex IV, performed under the conditions described above for complex II, yielded tetracyclone. Saponification of IV with dilute sodium hydroxide in aqueous methanol also yielded tetracyclone and, upon acidification of the solution, iron carbonylhydride.

Infrared spectra were recorded on a Beckman IR 4 and a Baird instrument in Nujol suspension: complex I, 2055, 2005, 1990 cm^{-1} , Fe-CO; 1638, ketonic carbonyl; 1600, 1580, 1550, C=C phenyl; 773, 763, 750, 728, 712, 695 cm^{-1} , phenyl monosubstitution; complex II, 2070, 2010, 2000, 1970, 1925, Fe-CO; 755, 730, 712, 700, 695 cm^{-1} , phenyl monosubstitution; complex III, 2070, 2025, 1975, Fe-CO; 1850, 1800, Fe-CO-Fe; 755, 725, 700 cm^{-1} , phenyl monosubstitution; complex IV, 2070, 2050, 2020, Fe-CO; 1665, ketonic carbonyl; 1600, 1580, 1500, C=C phenyl; 748, 730, 710 cm^{-1} , phenyl monosubstitution; complex V, 2030, 1970, 1950, Fe-CO; 760, 755, 730, 710, 700, 695 cm^{-1} , phenyl monosubstitution.

Magnetic measurements were performed by the Gouy method at 16° at various field strengths to eliminate the influence of traces of ferromagnetic impurities. Under these conditions, Complexes I–IV were found to be diamagnetic.

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[CONTRIBUTION FROM THE RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

Bisacrylonitrile Nickel and Related Complexes from the Reaction of Nickel Tetracarbonyl with Compounds Containing Activated Double Bonds (I)

BY G. N. SCHRAUZER¹

RECEIVED FEBRUARY 14, 1959

Acrylonitrile reacts with nickel tetracarbonyl to produce a new and highly reactive complex of composition $\text{Ni}(\text{CH}_2=\text{CH}-\text{CN})_2$. Infrared analysis and chemical reactions suggest that this compound represents a new type of transition metal π -complex capable of promoting the reaction of acrylonitrile with acetylene to heptatrienenitrile and polymerizing acetylene to cyclooctatetraene. Some of the requirements and limitations for the formation of structural analogs are reported.

Introduction

The carbonyl groups in metal carbonyls are known to be partly or completely replaceable by a number of compounds capable of donating electrons to the d-orbitals of the metals.

In the search for other ligands with similar properties it was discovered that certain compounds with double bonds activated by one or more strongly electronegative groups replace carbon monoxide in nickel tetracarbonyl to form a new class of highly reactive nickel complexes. The preparation, properties and suggested structure of these complexes are exemplified for the parent compound, bisacrylonitrile nickel.

Preparation, Properties and Structure of Bisacrylonitrile Nickel.—If nickel tetracarbonyl is refluxed with acrylonitrile in an inert atmosphere, all four CO groups are evolved in a smooth reaction

and a red, crystalline substance precipitates. This material was found to have the composition of a bisacrylonitrile nickel (I), $\text{Ni}(\text{CH}_2=\text{CH}-\text{CN})_2$. Compound I, which is sparingly soluble in most solvents, is pyrophoric and must be handled under complete exclusion of oxygen. On heating in a closed tube it begins to decompose into nickel and acrylonitrile at about 100°. The proposed structure is based on its infrared spectrum and is supported by chemical reactions. The absence of the intense vinyl absorption of acrylonitrile in the 900–1000 cm^{-1} region in the complex indicates that the π -electrons of the double bond in acrylonitrile are involved in the bonding. The nitrile absorption, however, is still present and has shifted only slightly (from 2245 cm^{-1} in liquid acrylonitrile to 2220 cm^{-1} in I).

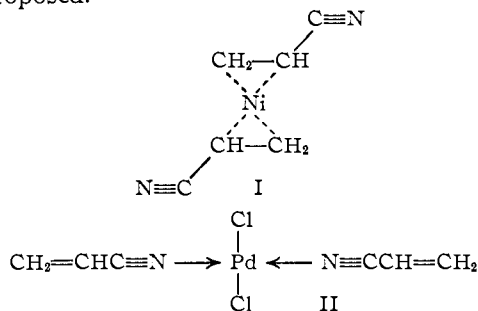
From the infrared analysis it follows that I is evidently a new type of transition metal π -complex. The previously-known complexes of nitriles all in-

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volve a coördinative type of bonding on the free electron pair of nitrogen. In complexes of this kind an increase in the CN stretching frequency is observed.²

To illustrate the new type of structure in I, the palladium dichloride complex of acrylonitrile (II) was prepared as a model substance. Its infrared spectrum showed all characteristics of the vinyl group and the nitrile stretching frequency had shifted, as expected, to the higher frequency of 2290 cm^{-1} . If for bisacrylonitrile nickel structure Ia is assumed, this would indicate that the metal has a half-filled inert N orbital which might account for its reactivity. For such a structure, some electron-deficient character is to be expected. This electron deficiency was demonstrated by formation of a 1:1 adduct of triphenylphosphine and I. This adduct, $\text{Ni}(\text{CH}_2=\text{CH}-\text{CN})_2\text{P}(\text{C}_6\text{H}_5)_3$ (III), is a yellow, pyrophoric material which starts to decompose at 185°. Its infrared spectrum shows the nitrile stretching frequency at 2180 cm^{-1} (Nujol) and absence of the vinyl absorption in the 900–1000 cm^{-1} range.

The evidence thus excludes the presence of a metal-nitrile group interaction of the conventional coördinative type in I and does not give sufficient indication of any other interaction of the nitrile group with the metal. Therefore, structure I is proposed.

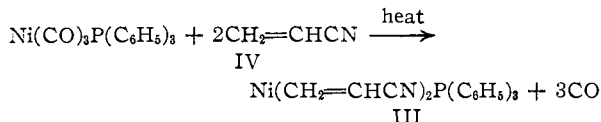


Catalytic Applications of Bisacrylonitrile Nickel.

—Further indication for the electron deficient nature of I and its interesting structure is its catalytic activity in the reaction of acetylene with acrylonitrile. Cairns, *et al.*,³ found that acetylene reacts with acrylonitrile and Reppe's nickeltriacarbonyl triphenylphosphine (IV) catalyst⁴ to produce 2,4,6-heptatrienenitrile. This reaction is of considerable interest in regard to the cyclobutadiene hypothesis of Longuet-Higgins and Orgel.^{5,6}

Little is known about the changes IV undergoes during its catalytic applications. In most cases an "induction period" is required to initiate the reaction, indicating that IV itself is not the reacting species. Since IV has to be heated in acrylonitrile under acetylene pressure for about 30 minutes at 75° before exothermic formation of heptatrienenitrile occurs,³ it is presumed that IV is converted into the new compound III during the in-

duction period according to the equation



Thus, bisacrylonitrile nickel or its triphenylphosphine adduct should be able to promote the reaction of acrylonitrile with acetylene without an induction period. This was found to be the case. Moreover, the above conversion of IV into III was verified by refluxing IV in acrylonitrile.

Since it is now established that bisacrylonitrile nickel and its triphenylphosphine adduct are the catalytically active intermediates in the heptatrienenitrile formation, one can assume that these complexes react with acetylene to form transitory intermediates of composition $\text{Ni}(\text{CH}_2=\text{CHCN})_2(\text{C}_2\text{H}_2)_2$ or $\text{Ni}(\text{CH}_2=\text{CHCN})(\text{C}_2\text{H}_2)_2\text{P}(\text{C}_6\text{H}_5)_3$ which could, under the conditions of the reaction, rearrange to form heptatrienenitrile. The fact that heptatrienenitrile is the only reaction product³ strongly suggests the presence of such intermediates which might contain cyclobutadiene and in which the nickel atom would have krypton configuration.

The formation of heptatrienenitrile and the condensation of acetylene to benzene and cyclooctatetraene with nickel compounds as catalysts are considered to be related processes and seem to involve similar reactive nickel complexes with acetylene. That this is so could be demonstrated also for the new catalyst bisacrylonitrile nickel (I). While in the presence of acrylonitrile heptatrienenitrile is obtained, it was found that when (I) was used to catalyze the polymerization of acetylene, cyclooctatetraene is formed.

Preparation of Structural Analogs.—Structural analogs of I have been, so far, only obtained if the prospective ligands contained a double bond activated by one or more strongly electronegative and inert substituents in α -position. A sufficient activation of the double bond is provided by the CN and CHO group. Bisfumaronitrile nickel, bis-cinnamonitrile nickel and bisacrolein nickel have been prepared. Whereas the nitrile complexes indicate a structure similar to I, the infrared spectrum of bisacrolein nickel shows a decrease of the carbonyl frequency from 1680 to 1540 cm^{-1} which indicates that the carbonyl group is polarized. Attempts to isolate a nickel complex of methylacrylate were unsuccessful. It is, however, conceivable that the reported synthesis of methylheptatrienoate with IV as catalyst⁸ involves similar complexes of nickel with the acrylic ester. No complexes would be isolated with acrylamide vinyl methyl ketone and 1,1,1-trifluoropropene as prospective ligands but further work is in progress.

Experimental

Preparation of Bis-acrylonitrile Nickel.—Nickel tetracarbonyl (2.6 g.) was refluxed (CO_2 condenser) in 25 ml. of freshly distilled acrylonitrile (stabilized with hydroquinone). The evolved gas (CO) was collected. After 4 hours of refluxing a total of 1290 ml. of CO corresponding to 57.5 mmoles was obtained, indicating that the reaction was practically quantitative. The first red crystals appeared after a transitory yellow color when about one-fourth of the

(2) H. J. Coerver and C. Curran, *THIS JOURNAL*, **80**, 3522 (1958).

(3) T. L. Cairns, V. A. Engelhardt, H. L. Jackson, G. H. Kalb and J. C. Sauer, *ibid.*, **74**, 5636 (1952).

(4) W. Reppe and W. J. Schweckendieck, *Ann.*, **560**, 104 (1948).

(5) J. C. Sauer and T. L. Cairns, *THIS JOURNAL*, **79**, 2659 (1957); Th. I. Bieber, *Chemistry & Industry*, 1126 (1957).

(6) L. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

total amount of gas was liberated. The solid was collected under nitrogen, washed with methanol and ether, and dried.

Anal. Calcd. for $\text{Ni}(\text{CH}_2=\text{CHCN})_2$: Ni, 35.62; acrylonitrile, 64.38.

Acrylonitrile was determined by careful thermal decomposition of the nickel complex in a high vacuum apparatus. The volatile fraction was weighed and identified by infrared analysis as pure acrylonitrile.

Found: Ni, 35.3, 35.6; acrylonitrile, 63.3, 60.2.

Preparation of the Complex of PdCl_2 with Acrylonitrile.—Palladium dichloride (1 g.) was dissolved in hot acrylonitrile, and the solution was filtered. Diethyl ether was added, and the solution was cooled to about -40° , whereby yellow crystals appeared. The complex is not very stable and loses acrylonitrile slowly at room temperature.

Anal. Calcd. for $\text{PdCl}_2(\text{NC}-\text{CH}=\text{CH}_2)_2$: Pd, 37.5; Cl, 25.0. Found: Pd, 37.5; Cl, 26.3.

Preparation of Bis-acrylonitrile Nickel Triphenylphosphine.—Freshly prepared bis-acrylonitrile nickel (2.5 g.) was suspended under nitrogen in a solution of 4 g. of triphenylphosphine in 40 ml. of ether and was refluxed for 3 hours. The red starting material was slowly converted into a yellow powder. This was filtered, washed with ether, and dried under exclusion of oxygen. When heated in a sealed tube, it decomposed into acrylonitrile, triphenylphosphine and nickel at 185° .

Anal. Calcd. for $\text{Ni}(\text{CH}_2=\text{CHCH})_2\text{P}(\text{C}_6\text{H}_5)_3$: Ni, 13.75; P, 7.3; N, 6.3. Found: Ni, 13.8, 13.9; P, 7.3; N (Kjeldahl), 6.1.

Preparation of Heptatrienenitrile with Bisacrylonitrile Nickel as Catalyst.—The conditions were essentially the same as described by Cairns, *et al.*,¹ except that the bis-

acrylonitrile nickel was employed as catalyst. The reaction was carried out at 75° and 13.5 atm. and required no induction period. The resulting heptatrienenitrile boiled at 53° (2–3 mm.). Its infrared and ultraviolet spectra were identical with those reported for heptatrienenitrile.³

Anal. Calcd. for $\text{C}_7\text{H}_7\text{N}$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.92; H, 6.72; N, 13.19.

Cyclooctatetraene from Acetylene and Bisacrylonitrile Nickel.—Freshly prepared bisacrylonitrile nickel (1 g.) was suspended in 50 ml. of dry tetrahydrofuran and was allowed to react under the usual precautions,⁷ in a stainless steel rocker bomb (500 ml.) at $80-85^\circ$ and 20.4 atm. acetylene pressure for 18 hours. The lowest boiling fractions (after filtration from a polymeric resin-like material (polyacetylene) and removal of the solvent) consisted mainly of cyclooctatetraene as evidenced by comparison of the infrared spectra with an authentic sample and vapor-phase chromatography. A small amount of a higher-boiling fraction was found to consist of a complicated mixture (vapor-phase chromatography) and was not examined further.

Infrared analysis was performed on a Beckman IR 4 Instrument.

Compound	State	$-\text{C}\equiv\text{N},$ cm. ⁻¹	Vinyl absorption (900– 1000 cm. ⁻¹)
Acrylonitrile	Liquid	2245	Present
$\text{Ni}(\text{CH}_2=\text{CHCN})_2$	Solid (in Nujol)	2220	Absent
$\text{Ni}(\text{CH}_2=\text{CHCN})_2\text{P}(\text{C}_6\text{H}_5)_3$	Solid (in Nujol)	2180	Absent
$\text{PdCl}_2(\text{NCCH}=\text{CH}_2)_2$	Solid (in Nujol)	2290	Present

(7) W. Reppe, "Neue Entwicklungen auf dem Gebiet der Chemie des Acetylens und Kohlenoxyds," Springer, 1949, pp. 137–138.

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[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO.]

Complexes of Aluminum Chloride and Methylaluminum Dichloride with Bis-(cyclopentadienyl)-titanium Dichloride as Catalysts for the Polymerization of Ethylene¹

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RECEIVED MAY 4, 1959

The interactions of bis-(cyclopentadienyl)-titanium dichloride, $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$, with aluminum chloride and with methylaluminum dichloride have been followed spectrophotometrically. In each case two complexes are formed, the first at a ratio of one Al per Ti and the second at a higher ratio. Only acid-catalyzed polymerization was observed with $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ and aluminum chloride, whereas linear polyethylene was obtained with methylaluminum dichloride. The initial rate of polymerization paralleled the spectroscopic concentration of the first complex. The active catalyst is discussed.

A few years ago Ziegler² gave great impetus to the field of low-pressure, ordinary temperature polymerization of 1-olefins. Since his release of information there has been a heavy concentration of effort to commercialize such polymerizations; considerable effort also has been made to explain the mechanism of this type of reaction.

As ordinarily used, the Ziegler process involves activated catalyst particles dispersed in an inert medium. Activity is subject to many factors: the metals used, their valence states and ligands; the catalyst history; the temperature and pressure; and the monomer. For mechanism studies, the most difficult variable is the solid surface of the catalyst. For the present study, this problem has been avoided by the choice of a completely soluble catalyst based on bis-(cyclopentadienyl)-titanium dichloride (I), $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$.

(1) Presented in part before the Delaware Science Symposium, Newark, Del., February 14, 1959, and at the Symposium on Stereospecific Polymerization at the 135th National Meeting of the American Chemical Society, Boston, Mass., April 5–10, 1959.

(2) K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.* **67**, 541 (1955).

The catalyst based on I was first reported by Breslow.³ Natta⁴ and his co-workers have used the compound and some of its derivatives in their mechanism studies. In the presence of triethylaluminum or diethylaluminum chloride, I is reduced rapidly to complexes of trivalent titanium. The high degree of catalytic activity for ethylene polymerization associated with the compound is dependent on the presence of a transitory complex of tetravalent titanium^{3a}; the trivalent state is very much less active.

Complexes of I with methylaluminum compounds are much more stable than the corresponding ethyl derivatives. For this reason, the methyl derivatives have been used for the study reported here. Information has been obtained which correlates catalyst structure with catalytic activity.

(3) (a) D. S. Breslow, Belgian Patent 551,283 (1957), U. S. Patent 2,827,446 (1958); (b) D. S. Breslow and N. R. Newburg, *This Journal*, **79**, 5072 (1957); **81**, 81 (1959).

(4) G. Natta, P. Pino, G. Mazzanti, U. Giannini, E. Mantica and M. Peraldo, *Chim. e ind. (Milan)*, **39**, 19 (1957); *J. Polymer Sci.*, **26**, 120 (1957).