ORGANIC AND BIOLOGICAL CHEMISTRY

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

Diphenylacetylene Derivatives of Iron Carbonyl[1,2]

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RECEIVED DECEMBER 19, 1958

A study of the reaction of diphenylacetylene with iron pentacarbonyl under ultraviolet irradiation has led to the isolation of four new types of transition metal π-complexes. Properties, reactions and chemical evidence for their structures are presented.

Introduction

Reppe and Vetter[4] have described a number of iron carbonyl complexes of acetylenes whose exact nature is not yet known. Other authors[5-7] have prepared similar compounds, the structures of which were subject to several proposals. Thus far, the structures of comparatively few complexes of this kind are known.[6,8,11]

A study of the reactions of acetylenes with iron carbonyls together with structural evaluations of the reaction products seemed, therefore, important, especially since some of the proposed structures of known complexes include cyclobutadiene ring systems for which, however, direct chemical evidence has not been obtained.[6,9]

For the present study, diphenylacetylene was chosen as the acetylenic component. As to the iron carbonyl employed, it was found that both $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$ reacted when heated with the acetylene in benzene solution yielding identical products. Iron pentacarbonyl did not react under the same conditions but gave results similar to those obtained with the above carbonyls when simultaneously irradiated with ultraviolet light. Since the latter method gave better yields and is experimentally the most simple, it was generally used in this work. Because of the fact that upon ultraviolet irradiation of iron pentacarbonyl $Fe_2(CO)_9$ is formed which, when heated, decomposes into $Fe(CO)_5$ and $Fe_3(CO)_{12}$ it may be concluded that iron tetracarbonyl is the actually reacting species.

Results

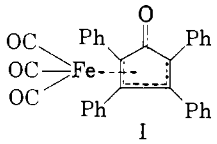
The products formed under the stated conditions from iron carbonyl and diphenylacetylene are all well crystallized, diamagnetic and stable, under normal conditions. Altogether four different complexes could be isolated and are listed with their general properties in Table I.

TABLE I

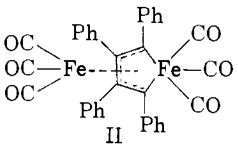
Complex no.	Composition	Color	M.p., °C.
I	$FeC_{32}H_{20}O_4$	Yellow	174 d.
II	$Fe_2C_{34}H_{20}O_6$	Orange	174–178 d.
III	$Fe_3C_{36}H_{20}O_8$	Black	208 d.
IV	$Fe_2C_{35}H_{20}O_7$	Ruby-red	158 d.

Also, small amounts of hexaphenylbenzene (a trimerization product of tolane[10]) and tetracyclone were isolated from the reaction mixture. All complexes were found to be moderately soluble in methanol, hexane and acetic acid and well soluble in benzene and toluene. The solutions of all materials showed signs of decomposition after prolonged standing in air.

Structure and Reactions of the Complexes.—The structure of complex I was determined by thermal decomposition and direct synthesis. Thermal decomposition yielded tetraphenylcyclopentadienone quantitatively, suggesting a structure I. Proof of this structure was obtained by direct synthesis of the complex from tetracyclone and iron tetracarbonyl. This compound represents the first member of a complex in which a cyclopentadienone is bonded *via* π-electrons to a transition metal. An analogous compound is obtained from the reaction of phenylacetylene, iron pentacarbonyl and nickel tetracarbonyl in aqueous acetic acid and was initially formulated as tetracarbonyliron bisphenylacetylide.[7] Its true structure has recently[11] been established as 2,5-diphenylcyclopentadienone iron tricarbonyl.



I



II

Complex II, a binuclear iron carbonyl complex, is isolated in about 42% yield. Structure II is proposed, on the basis of chemical reactions performed with this material and infrared analysis. If complex II is treated with sodium hydroxide in aqueous methanol, ferrous hydroxide precipitates and a yellow complex, m.p. 228–231° dec., is isolated in up to 75% yield. This material ("complex V"), was found to have the composition $FeC_{31}H_{22}O_3$. Upon thermal decomposition 1,2,3,4-tetraphenyl-1,3-butadiene could be isolated which indicates that complex V is a structural analog of the

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[1] Paper IX; π-Complexes of the Transition Metals"; Paper VIII, W. Herwig and H. Zeiss, THIS JOURNAL, **81**, 4798 (1959).

[2] A preliminary communication on a part of this work has appeared in *Chemistry & Industry*, 1403 (1958).

[3] Monsanto Research Fellow, 1957–1958. Now: Department of Inorganic Chemistry, University of Munich, Germany.

[4] W. Reppe and H. Vetter, *Ann.*, **582**, 133 (1953).

[5] I. Wender, R. A. Friedel, R. Markby, H. W. Sternberg, THIS JOURNAL, **77**, 4946 (1955); **78**, 3621 (1956); R. Clarkson, E. R. H. Jones, P. C. Wailes and M. C. Whiting, *ibid.*, **78**, 6206 (1956).

[6] H. W. Sternberg, R. Markby and I. Wender, *ibid.*, **80**, 1009 (1958).

[7] E. R. H. Jones, P. C. Wailes and M. C. Whiting, *J. Chem. Soc.*, 4021 (1955).

[8] A. A. Hick and O. S. Mills, *Proc. Chem. Soc.*, 233 (1958).

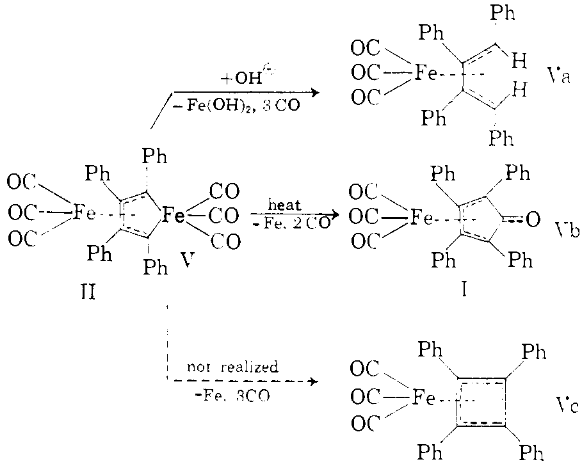
[9] H. C. Longuet-Higgins and I. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

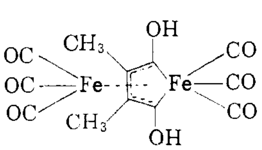
[10] G. Büchi, 71st Conference on Organic Reaction Mechanisms, Chicago, Ill., September 30 to October 6, 1958.

[11] G. N. Schrauzer, *Chemistry & Industry*, 1404 (1958).

long-known butadiene iron-tricarbonyl, first prepared by Rheilen, *et al.*[12,13] The same material (V) is obtained if tetraphenylbutadiene is heated with iron pentacarbonyl under ultraviolet irradiation.

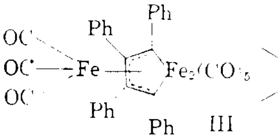
The isolation of complex V from reaction (Va) of complex II with base can be considered as a proof of structure II and indicates that the most reactive bonds in the molecule are doubtless the somewhat unusual iron–carbon σ-bonds. Equally compatible with the suggested structure (II) is the fact that complex II undergoes thermal decomposition to complex I according to scheme Vb. It is interesting for future attempts to prepare π-complexes of cyclobutadiene from acetylenes that a ring closure according to step Vc could not yet be realized. Decomposition under mild conditions (stoichiometric bromination in acetic acid) similarly yielded only tetracyclone. The infrared spectrum of complex II is in accord with the proposed structure, since it shows only metal carbonyl absorptions in the 2000 cm.$^{-1}$ region besides the usual vibrations typical of aromatic character and monosubstitution; a ketonic carbonyl absorption is clearly absent. A complex prepared from iron hydrocarbonyl and 2-butyne by Reppe and Vetter[4] and further studied by several workers[1] was assigned structure VI on the basis of X-ray analysis,[1] and obviously represents a structural analog to complex II.



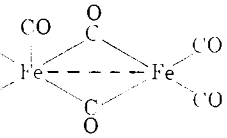


VI

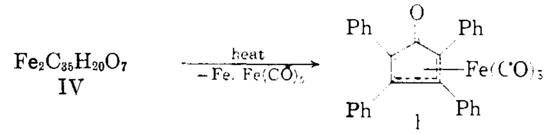
In order to acquire an atomic number of 36 for both iron atoms in VI, Hock and Mills[8] assume a dative bond between the two iron atoms in the molecule. Similar reasoning could also be applied to complexes II and III (see below), which would furthermore explain the observed diamagnetism. These bonds, however, have not been specifically indicated in this paper. Complex III, a black material, is isolated in about 14% yield. Structure III is proposed on the basis of infrared analysis and chemical reactions. The infrared spectrum shows a carbonyl frequency of strong intensity at 1850 cm.$^{-1}$, which can be assigned a "bridged" carbonyl type structure.[14] Bromination of III yields tetracyclone, and thermal decomposition of III at 170–185° gives iron, CO and complex II. The same conversion of complex III into complex II can be accomplished by gentle saponification with sodium hydroxide in aqueous methanol. If, however, concentrated alkali is used, complex III can be directly converted into complex V. A close relationship of complex III and II is clearly indicated. There is, however, some uncertainty as to the structure of the binuclear metal carbonyl unit in III, for which structure IIIa is possible.



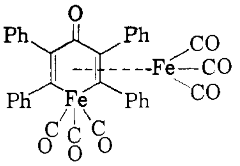
III



IIIa



In the search for possible intermediates prior to the formation of the above mentioned complexes, a ruby-red material could be isolated in low yield, if the reaction of diphenylacetylene with iron carbonyl was interrupted soon after the beginning of the irradiation. This complex (complex IV) is evidently an intermediate in the formation of complex I and does not appear with the end products. It was initially formulated[2] as a monomer of composition $FeC_{18}H_{10}O_4$; further experiments, however, indicated that it is a dimer of composition $Fe_2C_{35}H_{20}O_7 = Fe_2(CO)_7(C_6H_5C_2C_6H_5)_2$. If complex IV is heated in benzene or toluene solution, it readily converts into complex I, iron and iron pentacarbonyl. Bromination in cold acetic acid yields tetracyclone and saponification in aqueous methanol gives, besides tetracyclone, also the anion of iron carbonylhydride. These results permit the conclusion that complex IV contains tetracyclone. The presence of a ketonic ring in the molecule would well explain the observed carbonyl frequency at 1665 cm.$^{-1}$. NOTE ADDED IN PROOF.—In the meantime it was found that if complex IV is degraded with dilute nitric acid in aectic acid small amounts of tetraphenyl-*p*-quinone (m.p. 321°) could be isolated. This is compatible with structure VII for complex IV, which is similar to the proposed structure of complex II.



VII

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(12) H. Rheilen, A. Gruhl, G. v. Hessling and O. Pfrengle, *Ann.*, **482**, 161 (1930).

(13) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

(14) R. K. Sheline and K. S. Pitzer, THIS JOURNAL, **72**, 1107 (1950).

Complex no.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Iron, % Calcd.	Iron, % Found	Oxygen, % Calcd.	Oxygen, % Found	Mol. wt. Calcd.	Mol. wt. Found
I	73.31	73.35	3.84	3.97	10.65	10.57	12.21	12.50	524	508[a]
II	64.17	64.29	3.17	3.15	17.55	17.51	15.09	15.33	636	694[b]
III	57.79	57.81	2.70	2.83	22.40	22.49	17.11	17.06	748	760[b]

[a] Isopiestic method. [b] Cryoscopic in benzene.

Summary.—The most important reactions found in the system under study are summarized in Chart I. Due to the complexity of this field no generalizations are as yet permissible until our empirical knowledge is better. Further work with other acetylenes is necessary and in progress.

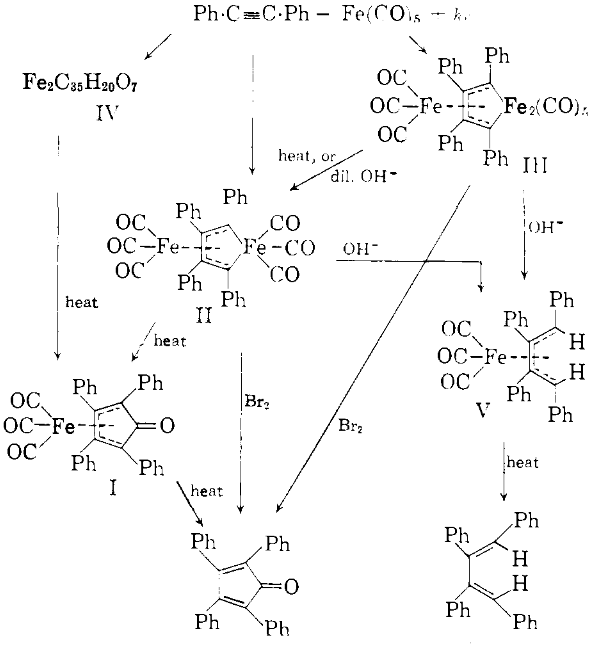

CHART I

Experimental

Analyses were made by Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. Melting points are corrected.

Reaction of Diphenylacetylene with Iron Pentacarbonyl.—Diphenylacetylene (5 g.) and iron pentacarbonyl (7 g.) were dissolved in 75 ml. of benzene in a quartz flask (250 ml.) equipped with reflux condenser. This flask was placed over a General Electric 100-watt projector spot mercury lamp, and the solution was irradiated for 20 hours under reflux (due to the heat generated by the lamp). After this time, the dark-colored solution was evaporated *in vacuo*, and the residue was dissolved in 75 ml. of hot acetic acid. Upon cooling, complex III ($Fe_3C_{36}H_{20}O_8$, 1.5 g., 14%) precipitated out and was conveniently recrystallized from acetic acid, m.p. 208° dec. Complex III forms black needles; solutions of it are dark green.

To the filtrate of complex III, water was added dropwise until a precipitate formed, consisting of complex II ($Fe_2C_{34}H_{20}O_6$, 3.8 g., 42%), which on recrystallization from methanol or methanol–benzene yielded orange crystals, m.p. 174–178° dec.

After removal of complexes III and II, the filtrate now contained mainly complex I, small amounts of tetracyclone, and perhaps some unreacted diphenylacetylene. Complex I ($FeC_{32}H_{20}O_4$) was isolated upon addition of 100 ml. of *n*-hexane and dilution with 100–200 ml. of water. It appeared between the layers of the solvents upon cooling (3.4 g., 45%) and was recrystallized from methanol, m.p. 174° dec. Solutions of complex I are unstable in air, depositing iron oxide and tetracyclone.

Direct Synthesis of Complex I.—Commercial tetracyclone (0.5 g.) was refluxed/irradiated with 2.95 g. of iron pentacarbonyl in 50 ml. of benzene for two hours. The solution was evaporated *in vacuo*, the solid residue redissolved in 50 ml. of acetic acid and worked up as described above, yielding 0.58 g. (85%) of complex I.

Base Reaction of Complex II.—Complex II (500 mg.) was dissolved in 25 ml. of benzene in a one-liter round-bottomed flask. Methanol (200 ml., warmed to 50°) was added, the yellow solution was stirred, and then 50 ml. of a 7 *N* aqueous sodium hydroxide solution was added quickly. A vigorous reaction occurred, evidenced by iron hydroxide precipitation. The suspension was stirred for another 30 minutes, filtered, and diluted with water. A yellow material precipitated out and was collected. Further amounts of this substance were obtained from the filtrate upon extraction with *n*-hexane and from the iron hydroxide fraction, which was dissolved in dilute hydrochloric acid. The yield totaled 298 mg. (75%) of crude complex V, m.p. 228–231°, dec., after several recrystallizations from methanol and acetone. The by-product of this reaction was a small amount of tetracyclone.

Anal. Calcd. for $FeC_{31}H_{22}O_3$: C, 74.71; H, 4.45; Fe, 11.21; O, 9.63; mol. wt., 498. Found: C, 75.00; H, 4.24; Fe, 11.32; O, 9.96; mol. wt. (Rast), 485.

Thermal Decomposition of Complex V.—Complex V (265 mg.) was heated in 15 ml. of toluene in a sealed tube at 220° bath temperature for 50 hours, during which an iron mirror appeared on the walls of the tube, and the formerly yellow solution decolorized. From the reaction solution, a white, crystalline solid was isolated and was repeatedly recrystallized from methanol and *n*-hexane until it melted at 181–183°. This material gave no melting point depression with a sample of 1,2,3,4-tetraphenyl-1,3-butadiene, m.p. 183–184°, prepared from diphenylacetylene and lithium in ether according to Smith and Hoehn.[15] The identity of both substances was further confirmed by comparison of the infrared spectra in KBr.

Synthesis of Complex V.—Tetraphenylbutadiene, m.p. 183–184°,[15] (1 g.) was refluxed/irradiated with 1.5 g. of iron pentacarbonyl in 40 ml. of benzene for 15 hours. Recrystallizations of the reaction product from methanol and acetone gave a yellow substance melting at 227–231° dec., which did not depress the melting point of complex V and had an identical infrared spectrum.

Thermal Decomposition of Complex II.—Complex II (1.0 g.) was heated in toluene in a sealed tube for 68 hours at 180–195° bath temperature. Isolated products were 401 mg. (50%) of complex I, identified by m.p. and infrared analysis, and 252 mg. of crude tetracyclone (42%).

Bromination of Complex II.—Complex II (116.1 mg.) was dissolved in 5 ml. of warm acetic acid, and 1 ml. of an 0.60 *N* solution of bromine in acetic acid was added. The solution turns red. Upon dilution with water, tetracyclone (31 mg., 47%) and some unchanged complex II were isolated. If the recovered complex II was again brominated, more tetracyclone was isolated, giving a total yield of 85% of theoretical. If, however, an excess of bromine was employed, only the decomposition products of tetracyclone were obtained.

Bromination of Complex III.—Complex III (60.5 mg.) was brominated in similar fashion as described above with 1 ml. of an 0.6 *N* solution of bromine in acetic acid; yield 15 mg. of tetracyclone (46.5%).

Thermal Conversion of Complex III into Complex II.—Complex III (89 mg.) was heated with 10 ml. of toluene for 84 hours at 170–185° bath temperature in a sealed tube. After that time, the solution was clear yellow, and an iron mirror had appeared on the walls of the tube. From this solution, complex II was isolated in better than 70% yield.

Conversion of Complex III into Complex II by Base.—Complex III (1 g.) was dissolved in 50 ml. of benzene. The solution was diluted with 400 ml. of methanol, and 5 g.

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(15) L. I. Smith and H. H. Hoehn, THIS JOURNAL, **63**, 1184 (1941).

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 $Fe_2C_{35}H_{20}O_7$: 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.

DAYTON 7, OHIO

[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. SCHRAUZER[1]

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Acrylonitrile reacts with nickel tetracarbonyl to produce a new and highly reactive complex of composition $Ni(CH_2{=}CH{-}CN)_2$. 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 cycloöctatetraene. 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), $Ni(CH_2{=}CH{-}CN)_2$. 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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