[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Bis-cyclopentadienyl Compounds of Nickel and Cobalt

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The preparation and properties of bis-cyclopentadienylnickel(II) and bis-cyclopentadienylnickel(III) salts are described. The heat of formation of bis-cyclopentadienylnickel(II) from the elements is 62.8 ± 0.5 kcal. New preparations of bis-cyclopentadienylcobalt(II) and -iron(II) are reported. The electronic structures of bis-cyclopentadienyl compounds are discussed.

The structure suggested[2] for bis-cyclopentadienyliron(II),[3] in which the iron atom is symmetrically placed between two cyclopentadienyl rings has been confirmed by X-ray crystal structure measurements.[2b,4]

The formation of bis-cyclopentadienyl compounds having this "sandwich" structure appears to be a general property of transitional elements which have two vacant or singly occupied *d* orbitals that can be used in bonding, and various derivatives of titanium,[5] vanadium,[5] cobalt,[6,8] nickel,[5,7] zirconium,[5] ruthenium,[9] rhodium[10] and iridium[10] have been noted.

Bis-cyclopentadienylcobalt(II), which was briefly described[8] in a preliminary communication whilst the present work was in progress, is here made by the direct vapor phase reaction of cyclopentadiene with cobalt octacarbonyl, a method previously used in the preparation of bis-cyclopentadienylchromium(II).[11] The preparation of bis-cyclopentadienylnickel(II), first reported in a preliminary communication,[5] involves a method analogous to that employed for the preparation of bis-cyclopentadienylruthenium(II).[9] Fischer and Jira[7] have subsequently described the preparation by a different method.

Bis-cyclopentadienylnickel(II) has the same structure as bis-cyclopentadienyliron(II) and may be represented as a molecular "sandwich." This is clearly evident from a comparison of the infrared absorption spectra shown in Fig. 1; the differences between the two compounds in the region near 1700 cm.$^{-1}$ are better illustrated in Fig. 2. The similarity of the structure of $(C_5H_5)_2Co$ and of $(C_5H_5)_2Ni$ to that of $(C_5H_5)_2Fe$ has been confirmed by X-ray diffraction studies.[7,8,12]

The ultraviolet spectra of $(C_5H_5)_2Ni$ in cyclohexane and in carbon tetrachloride are shown in Fig. 3 and should be compared with the corresponding curves for $(C_5H_5)_2Fe$.[13]

The heat of combustion of $(C_5H_5)_2Ni$ has been measured. The heat of formation calculated therefrom, and the chemical equation to which it applies are

$$10C(s) + 5H_2(g) + Ni(s) = (C_5H_5)_2Ni(s) \qquad \Delta H^\circ_{298^\circ} = +62.8 \pm 0.5 \text{ kcal.}$$

For the standard enthalpy of formation of bis-cyclopentadienyliron(II), a value of +33.8 kcal. has been obtained.[14] It thus appears that the thermodynamic stability of $(C_5H_5)_2Ni$ is considerably less than that of $(C_5H_5)_2Fe$. Values for the gaseous reactions provide a more significant comparison, however; these may be obtained as follows. The estimate[14] of the heat of formation of cyclopentadienyl radicals and the heats of formation of gaseous iron and nickel atoms[15] are used. It is assumed that the heat of sublimation of $(C_5H_5)_2Ni$ is the same as the measured value of 16.8 kcal. for $(C_5H_5)_2Fe$[13]; this assumption is supported by the facts that the two substances have analogous structures, almost the same molecular dimensions, and have identical melting point. It is further assumed that the heat of vaporization of cyclopentadiene can be estimated by Trouton's rule. We then have

$$2C_5H_5^*(g) + Fe(g) = (C_5H_5)_2Fe(g) \qquad \Delta H_{298^\circ} = -147 \text{ kcal.}$$
$$2C_5H_5^*(g) + Ni(g) = (C_5H_5)_2Ni(g) \qquad \Delta H_{298^\circ} = -123 \text{ kcal.}$$

From these values it can be seen that although there is a difference of 24 kcal. in favor of the $(C_5H_5)_2Fe$ binding, the metal–ring bond energies are in both cases quite high and of comparable magnitude. Bis-cyclopentadienylnickel(II) is stable in vacuum at 150°, but in contrast to the behavior of $(C_5H_5)_2Fe$, the liquid at the melting point (173°) decomposes almost instantaneously. Although $(C_5H_5)_2Fe$ is thermodynamically more stable than $(C_5H_5)_2Ni$, the main source of the great difference in their stabilities, *e.g.*, in the failure of $(C_5H_5)_2Ni$ to survive a Friedel–Crafts acylation and its rather rapid decomposition in air, is the presence of two unpaired electrons in the nickel compound which render it chemically vulnerable.

Oxidation of $(C_5H_5)_2Ni$ to the bis-cyclopentadienylnickel(III) ion occurs with great ease, and in a 90% ethanolic electrolyte solution, a reversible polarographic wave can be observed at −0.08 v. *vs.* S.C.E. Further oxidation to a dipositive ion isoelectronic with $(C_5H_5)_2Fe$ and with the $(C_5H_5)_2Co^+$

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(2) (a) G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, THIS JOURNAL, **74**, 2125 (1952); (b) E. O. Fisher and W. Pfab, *Z. Naturforschung*, **7B**, 377 (1952).

(3) (a) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951); (b) S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).

(4) (a) P. F. Eiland and R. Pepinsky, THIS JOURNAL, **74**, 4971 (1952); (b) J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953).

(5) G. Wilkinson, P. L. Pauson, J. M. Birmingham and F. A. Cotton, THIS JOURNAL, **75**, 1011 (1953).

(6) (a) G. Wilkinson, *ibid.*, **74**, 6148 (1952); (b) E. O. Fischer and R. Jira, *Z. Naturforschung*, **8B**, 1 (1953).

(7) E. O. Fischer and R. Jira, *ibid.*, **8B**, 217 (1953).

(8) *Ibid.*, **8B**, 327 (1953).

(9) G. Wilkinson, THIS JOURNAL, **74**, 6146 (1952).

(10) F. A. Cotton, R. O. Whipple and G. Wilkinson, *ibid.*, **75**, 3586 (1953).

(11) G. Wilkinson, *ibid.*, **76**, 209 (1954).

(12) R. Pepinsky, private communication, January, 1953.

(13) L. Kaplan, W. J. Kester and J. J. Katz, THIS JOURNAL, **74**, 5764 (1952).

(14) F. A. Cotton and G. Wilkinson, *ibid.*, **74**, 5764 (1952).

(15) "Tables of Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1947.

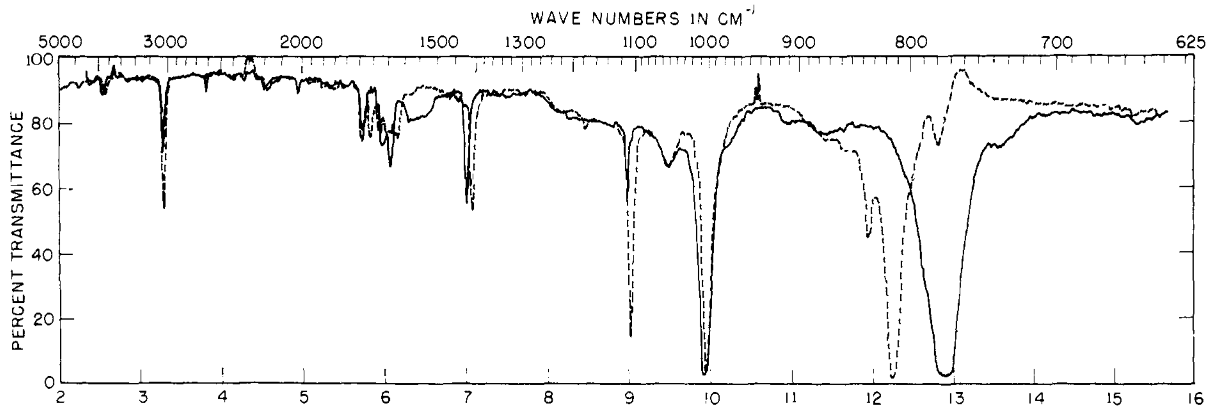

Fig. 1.—Infrared absorption spectra of $(C_5H_5)_2Fe$ (——) and $(C_5H_5)_2Ni$ (- - - -); 30 mg./ml. 2-8 μ in CCl_4, 8-16 μ in CS_2; Baird double beam spectrophotometer.

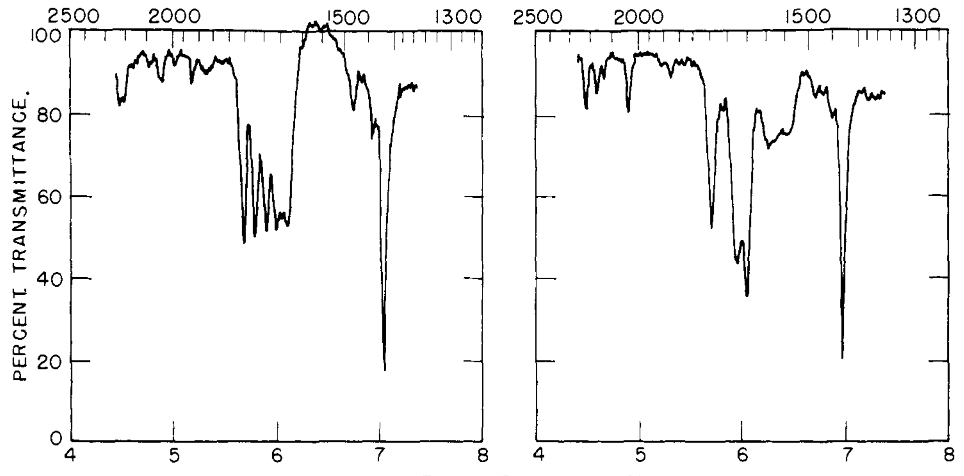

Fig. 2.—Infrared spectra of $(C_5H_5)_2Fe$ (left) and $(C_5H_5)_2Ni$ (right) 100 mg./ml. in CCl_4; Baird double beam spectrophotometer.

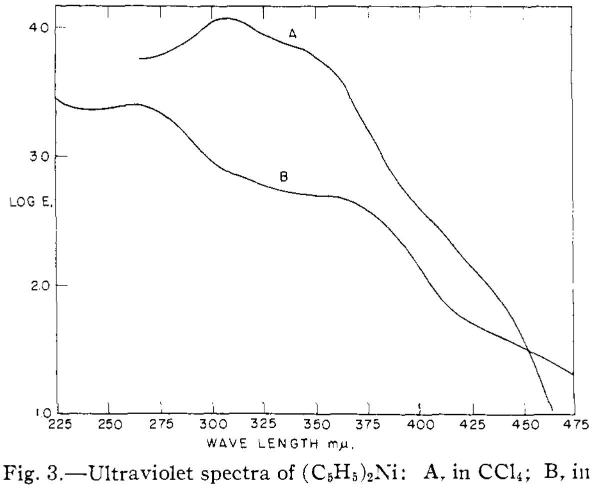

Fig. 3.—Ultraviolet spectra of $(C_5H_5)_2Ni$: A, in CCl_4; B, in cyclohexane.

ion cannot be achieved, and only complete disruption of the molecule results. This may possibly be due to the fact that the nickel(IV) atom would be so small that the metal orbitals responsible for the ring to metal bonding could no longer sufficiently overlap the π-orbitals of the rings.

Measurements of the magnetic susceptibilities of $(C_5H_5)_2Ni$ and of biscyclopentadienylnickel(III) picrate have been made; in both cases, Curie's law is followed between 77° and 298°K. and the mean effective magnetic moments obtained are, respectively, 2.88 ± 0.02 BM. and 1.75 ± 0.1 BM., in close agreement with the values for two and one unpaired electron spins, respectively. Measurement of the susceptibility of $(C_5H_5)_2Co$ confirms the conclusion[8] that the molecule has a single unpaired electron; Fischer and Jira[7] have also measured the susceptibilities of $(C_5H_5)_2Ni$ and the $(C_5H_5)_2Ni^+$ ion, but only at a single temperature.

The magnetic data now available on bis-cyclopentadienyl compounds of chromium[11] and nickel provide an experimental test of theoretical discussions of the bonding in bis-cyclopentadienyl compounds which have been given by Jaffé[16] and by Dunitz and Orgel.[4b] The experimental facts which these treatments (which were formulated on the basis of data for bis-cyclopentadienyliron(II) only) should predict, or should at least accommodate, are: the chromium(II) and nickel(II)

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(16) H. H. Jaffé, *J. Chem. Phys.*, **21**, 156 (1953).

compounds are in triplet states, while the iron(II) compound is diamagnetic.

Jaffé's treatment correctly predicts the triplet state of bis-cyclopentadienylnickel(II) and the diamagnetism of bis-cyclopentadienyliron(II), but predicts diamagnetic bis-cyclopentadienylchromium(II). Jaffé also concluded that in bis-cyclopentadienyliron(II) each ring is bonded to the metal atom by four covalent bonds and that the iron atom attains a krypton structure as a result of what may be considered as the filling of all the vacant *d* and *p* orbitals by π-electrons from the rings. The complete filling of vacant metal atom orbitals with π-electrons from the rings was suggested when the "sandwich" structure was first proposed,[2a] but must now be regarded as unlikely in view of the aromatic character[17] of bis-cyclopentadienyliron(II) which strongly indicates that the π-electrons are not appreciably withdrawn from the rings. The stability of bis-cyclopentadienyltitanium(IV) dihalides,[5] which may be considered to be $[(C_5H_5)_2Ti]^{++}X_2^-$, where the metal atom has no more than two electrons available for bonding to the rings, indicates that it is necessary to postulate only one two-electron bond to each ring. It would seem that Jaffé's treatment suffers less from any error in principle than from a somewhat unsuccessful estimate of the relative energies of the various orbitals involved.

The treatment of Dunitz and Orgel, which is formulated on the results and in the notation of group theory, provides for one primary bond between each ring and the metal atom, the remaining π-electrons being, to a first approximation, undisturbed. They postulate the following electronic configurations: for the system comprising the two rings—$(A_{1g})^2(A_{1u})^2(E_{1g})^2(E_{1u})^4(E_{2g})^0(E_{2u})^0$; for the iron atom—$(A_{1g})^2(E_{1g})^2(E_{2g})^4$. The two bonds are formed between the E_{1g} orbitals of the ring system and the iron atom. Since they specify that the metal orbital denoted A_{1g} is to be regarded as the d_{z^2} orbital, there is still the 4s orbital, also of symmetry A_{1g}, to be dealt with. This, however, is not mentioned, although it is precisely this omission which makes it impossible to attribute to their theory any definite prediction about the magnetic properties of the bis-cyclopentadienyl compounds of chromium and nickel, or indeed of iron. If this second A_{1g} orbital is included in their formulation of the electronic structure of the iron atom, one obtains $(A_{1g})^2(E_{1g})^2(E_{2g})^4(A_{1g})^0$, where it is most natural to assume that the filled A_{1g} orbital is the 4s orbital. This arrangement makes bis-cyclopentadienyliron(II) diamagnetic. However, without any further statement regarding possible perturbations of this "free-atom" structure, it is more reasonable to assume that the electrons would be distributed either $(A_{1g})^2(E_{1g})^2(E_{2g})^3(A_{1g})^1$ or $(A_{1g})^2(E_{1g})^2(E_{2g})^2(A_{1g})^2$ since the E_{2g} and A_{1g} orbitals would be degenerate. Thus the diamagnetism of the iron(II) compound is not predicted; in fact, a triplet state seems the most logical consequence. Since chromium has two less electrons than iron, its structure might logically be $(A_{1g})^2(E_{1g})^2(E_{2g})^2(A_{1g})^0$. Remembering that the E_{1g} orbital is involved in the bonding we have, invoking Hund's rule, two unpaired electrons in the doubly degenerate E_{2g} level. We may thus say that with only a slight and straightforward amendment, the Dunitz and Orgel formulation correctly predicts the triplet state of the chromium compound. However, if we now add two electrons to the amended iron configuration, obtaining that of the nickel atom, difficulties arise. It is, of course, certain that the *p* orbitals of the metal atom will lie well above the remaining A_{1g} level, and it seems very likely that the strongly anti-bonding E_2 orbitals of the ring system are also well above this A_{1g} level. We then have no choice but to place the two additional electrons in this level and thus incorrectly predict a singlet state for bis-cyclopentadienylnickel(II).

Professor W. Moffitt has carried out a more thorough treatment of the bonding in bis-cyclopentadienyl compounds in which he invokes a mixing and splitting of the two A_{1g} orbitals of the metal atom, as the result of an electrostatic perturbation by the π-electrons of the rings. One of the resulting orbitals lies somewhat lower than the E_{1g} and E_{2g} orbitals of the metal, while the other falls at about the same level as the *p* orbitals. The two electrons which are added to the iron configuration thus go unpaired into two of the four orbitals now in the energy range of the *p* orbitals, giving, correctly, a triplet state for bis-cyclopentadienylnickel(II). In bis-cyclopentadienyliron(II) the configuration of the iron atom is then unambiguously $(A_{1g})^2(E_{1g})^2(E_{2g})^4$, leading to diamagnetism. The analysis of the chromium case remains the same as that given above.

Experimental

Bis-cyclopentadienylnickel(II).—Nickel(II) acetylacetonate is prepared according to Gach.[18] It is conveniently dehydrated by azeotropic distillation with toluene and the crystalline compound may be isolated by concentration of the filtered toluene solution. Benzene (500 cc.) is added to the Grignard reagent prepared from magnesium (10 g.) and ethyl bromide (46 g.) and the ether removed by distillation. Cyclopentadiene (30 g.) is now added dropwise and after complete addition, the mixture is warmed until evolution of ethane ceases. The mixture is then cooled in ice and a benzene or toluene solution of nickel(II) acetylacetonate (16 g.) is added dropwise. Finally the mixture is maintained at room temperature for one hour to ensure complete reaction. The reaction must be carried out in an atmosphere of nitrogen and efficient stirring should be maintained throughout. The product is poured on ice and extracted with ether. Evaporation *in vacuo* leaves the product which is most conveniently purified by rapid crystallization from light petroleum with use of a solid carbon dioxide–acetone cooling bath. Bis-cyclopentadienylnickel(II) is thus obtained in 60% yield as dark green needles, m.p. 171–173° (in an evacuated tube). Slightly better yields, about 70%, may be secured if the product is isolated by vacuum sublimation of the crude product. The substitution of cyclopentadienylpotassium for the Grignard reagent lowered the yield to about 50%.

Bis-cyclopentadienyliron(II).—This compound has been previously prepared by the reaction of cyclopentadienylmagnesium bromide with ferric chloride.[3a] The reaction of a large excess of the Grignard reagent with a ferrous acetylacetonate–pyridine complex[19] in benzene solution has been found to give an almost quantitative yield of bis-cyclopentadienyliron(II). This preparation from an iron(II) com-

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[17] R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 3458 (1952).

[18] F. Gach, *Monatsh.*, **21**, 98 (1900).

[19] B. Emmert and R. Jarczynski, *Ber.*, **64**, 1072 (1931).

pound provides additional evidence that in bis-cyclopentadienyliron(II) the iron is in the II oxidation state.

The Reaction of Cyclopentadiene with Iron, Cobalt and Nickel Carbonyls.—The reaction of cyclopentadiene with metal carbonyls at elevated temperatures has been found[11] to produce metal cyclopentadienyl compounds of chromium, molybdenum and tungsten. The method is further extended for iron, cobalt and nickel carbonyls.

Pure nitrogen was bubbled through iron pentacarbonyl and cyclopentadiene separately at room temperature, and the mixed vapors were led through a Pyrex tube held in a furnace at 250°. Bis-cyclopentadienyliron(II) was condensed from the gas stream by a water-cooled probe. The carbonyl decomposed partly, giving metal, and no search has been made for conditions giving maximum conversion to bis-cyclopentadienyliron(II). The yield of the compound was about 15%, based on the carbonyl, after recovery by sublimation.

Cyclopentadiene was passed in a stream of pure nitrogen over cobalt octacarbonyl. Ten grams of the carbonyl in a porcelain boat was held at 50° in a tube furnace. The mixed vapors then passed through a reaction zone at 300° from which the **bis-cyclopentadienylcobalt(II)** was collected on a water-cooled probe. The crude material was purified by sublimation above 40° at about 0.1 μ and was obtained in about 10% yield based on the carbonyl. The $(C_5H_5)_2Co$ is an almost black crystalline solid, m.p. 171–173° [*Anal.* Calcd. Co, 31.15. Found: Co, 31.20]. It is soluble in deoxygenated organic solvents, giving purple solutions. The compound is exceedingly rapidly oxidized in air, and as is to be expected from the oxidation potential,[20] liberates hydrogen from water and dilute acids, being oxidized to the bis-cyclopentadienylcobalt(III) ion.[6] In carbon disulfide, bis-cyclopentadienylcobalt(II) shows strong infrared absorption bands at 9.98 and 12.78 μ and a band of medium strength at 9 μ, the spectrum in this region being very similar to that of bis-cyclopentadienylnickel(II). We were unable to obtain a spectrum in carbon tetrachloride owing to too rapid decomposition.

The preparation of $(C_5H_5)_2Ni$ by the reaction of cyclopentadiene with nickel carbonyl has been attempted. The reaction was studied from 100° to 300°, but in no case was more than a few milligrams of $(C_5H_5)_2Ni$ isolated from several grams of carbonyl; extensive decomposition of the carbonyl to the metal always occurred.

Magnetic Susceptibilities.—The magnetic susceptibilities of $(C_5H_5)_2Ni$ and bis-cyclopentadienylnickel(III) picrate were determined using a Gouy balance designed to operate down to the temperature of liquid nitrogen.[21] The molar susceptibility values of $(C_5H_5)_2Ni$, uncorrected for the diamagnetic contribution, were at 296°K., $+3414 \times 10^{-6}$ c.g.s. unit; at 201°K., $+5015 \times 10^{-6}$ c.g.s. unit; and at 77°K., $+13{,}490 \times 10^{-6}$ c.g.s. unit. The corresponding values for the picrate were 295°K., $+1293 \times 10^{-6}$ c.g.s. unit; 204°K., $+1747 \times 10^{-6}$ c.g.s. unit; and 77°K., $+4670 \times 10^{-6}$ c.g.s. unit. The susceptibility of $(C_5H_5)_2Ni$ was also measured in 0.07 *M* solution in ligroin, and a value of $\chi_{\text{mol}}^{298°}$ + 3348×10^{-6} c.g.s. unit was obtained. Results quoted for measurements on the solids are averaged values for several packings of the tube; the sample weights were about 1 g. Results from the several packings agreed well, and there was no observable dependence of the susceptibilities on field strength. The following values were used for the susceptibilities of the standard substances: water, $\mathcal{X} = -0.72 \times 10^{-6}$ c.g.s. unit at 25°; $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, $\chi = +32.0 \times 10^{-6}$ c.g.s. unit at 22°. The diamagnetic correction for the two rings, computed from Pascal constants was taken to be -92×10^{-6} c.g.s. unit; the diamagnetic correction for the picrate ion, taken as -78×10^{-6} c.g.s. unit was computed by combining the experimental values for benzene, phenol and trinitrobenzene.

After correcting for diamagnetism of the rings, the mean effective magnetic moments of $(C_5H_5)_2Ni$ and $(C_5H_5)_2Ni^+$ picrate were, respectively, 2.88 ± 0.2 BM. 1.75 ± 0.1 BM. Measurements on $(C_5H_5)_2Co$ in ligroin solution led to a value of 1.83 BM.

Heat of Combustion of Bis-cyclopentadienylnickel(II).—Bis-cyclopentadienylnickel(II) is spontaneously inflammable in oxygen at a pressure of 30 atmospheres. In order to determine the heat of combustion, it was necessary to protect the compound from attack by oxygen until the preliminary cooling rate of the calorimeter and bomb could be determined. Confining the sample either in a gelatin capsule or a glass bulb failed; the sample could not be packed tightly enough into the capsule to prevent cracking of the capsule under pressure and repeated experiments with samples of both $(C_5H_5)_2Ni$ and $(C_5H_5)_2Fe$ in glass bulbs (the bulb being shattered by ignition of a small pellet of benzoic acid placed under it) proved that under these conditions combustion of the sample is incomplete. The method finally adopted was to coat the pellet of $(C_5H_5)_2Ni$ with ordinary paraffin wax (Gulfwax, Gulf Oil Corp., Pittsburgh, Pa.).

Samples of $(C_5H_5)_2Ni$ were freshly recrystallized from petroleum ether (30–60°) and were dried in high vacuum at room temperature for several hours. The thread used for ignition was tied around a pellet of the compound. The pellet was cooled by suspending it in a tube immersed in a Dry Ice–acetone-bath, and then dipped into wax which was just warm enough to be liquid. The dipping procedure was repeated four or five times, heavy deposits resulting from drippage being trimmed off when necessary, until a uniform coating several millimeters thick was built up.

The apparatus and method used for computing results were the same as those used for the determination of the heat of combustion of bis-cyclopentadienyliron(II).[14] Because of minor structural changes, the bomb and calorimeter were recalibrated using U. S. Bureau of Standards benzoic acid (sample 39f). The average of ten calibration runs gave a water equivalent for the bomb and calorimeter of 415.2 g. with a mean deviation of ±0.6 g. and an estimated maximum error of ±0.5 g.

Data and results of the determination of the heat of combustion of the wax are presented in Table I.

TABLE I

HEAT OF COMBUSTION OF WAX AT 25°

1905.0 g. of water was used in the calorimeter in each case

Sample wt. in air, g.	Corrected temperature rise, °C.	Calories from thread and *Eit*[a]	Heat of combustion, cal./g.	Deviation from mean, %
0.81914	3.9747	50.4	11171.0	0.06
.68867	3.3438	54.8	11160.4	.03
.81160	3.9379	52.8	11166.8	.02
.86970	4.2133	49.7	11157.5	.06
.72880	3.5362	50.4	11162.9	.01
.61935	3.0169	65.7	11169.9	.05
.80203	3.8975	75.0	11155.8	.07
.83546	4.0583	64.1	11168.1	.04
		Mean	11164.1	0.04

[a] Input of electrical energy during ignition.

The combustion of $(C_5H_5)_2Ni$ converted 25 to 50% of the nickel to nickel oxide NiO and the remainder to metal. This is in accord with the observations of Roth[22] on the combustion of nickel carbide. The nickel metal usually remained entirely within the cup in the form of small round globules. The nickel oxide blanketed the inside of the bomb

TABLE II

HEAT OF COMBUSTION OF BIS-CYCLOPENTADIENYLNICKEL(II) AT 25°

1905.0 g. of water was used in the calorimeter in each case

True mass, g.	Corr. temp. rise, °C.	Cal. from thread and *Eit*[a]	Wt. of wax in air, g.	Mole % NiO	ΔH_{comb}, kcal. mole^{-1}	$\Delta H f^{\circ}_{298}$, kcal. mole^{-1}
0.66132	6.8494	57.9	0.98868	0.259	1359.5	62.3
.53631	6.2930	51.1	.95477	.244	1358.5	62.2
.50543	5.9755	52.0	.90855	.242	1359.3	63.1
.60630	6.8356	58.6	1.01821	.420	1370.0	63.4
					Mean	62.8 ± 0.5

[a] Input of electrical energy during ignition.

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(20) J. A. Page and G. Wilkinson, THIS JOURNAL, **74**, 6149 (1952).

(21) We are indebted to Dr. Norman Elliot of the Brookhaven National Laboratory for allowing us to use his apparatus.

(22) W. A. Roth, *Z. angew. Chem.*, **42**, 981 (1929).

in the form of a fluffy green powder. It was possible to recover the oxide, together with a few small, non-adherent globules of metal, almost quantitatively by washing it out with water. This mixture of metal and oxide was then weighed and dissolved in hydrochloric acid, analyzed for nickel and the oxide-to-metal ratio computed. The metal remaining in the cup was determined from the weight gain of the cup. The nickel determined always agreed within 2 mg. with the nickel content of the sample. The data and results for the heat of formation of $(C_5H_5)_2Ni$ are presented in Table II.

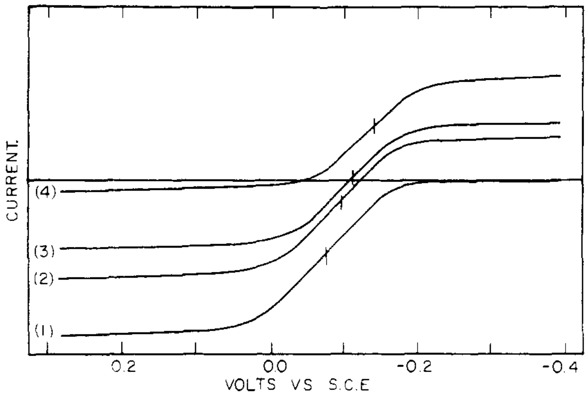

Fig. 4.—Polarographic curves of $(C_5H_5)_2Ni$ and $(C_5H_5)_2Ni^+$. Curve for 7 mg. $(C_5H_5)_2Ni$ in 10 ml. of absolute ethanol (1); curves after addition of 0.1 ml. (2), 0.2 ml. (3) and 3.3 ml. (4) of 0.1 *N* ceric sulfate solution.

Bis-cyclopentadienylnickel(III) Salts.—Bis-cyclopentadienylnickel(II) can be oxidized to the bis-cyclopentadienylnickel(III) cation by many reagents. On mixing ethereal solutions of $(C_5H_5)_2Ni$ and picric acid and bubbling air through the mixture, a black precipitate of bis-cyclopentadienylnickel(III) **picrate** is formed. This salt may be purified by rapid recrystallization from water followed by drying in vacuum at room temperature. (*Anal.* Calcd. for $C_{16}H_{12}N_3O_7Ni$: Ni, 14.07; N, 10.18. Found: Ni, 14.06; N, 9.9.) On mixing ethereal solutions of $(C_5H_5)_2Ni$ and benzoquinone, and passing into these dry hydrogen chloride or hydrogen bromide, brownish-black precipitates are obtained. They contain the salts, since they dissolve to give yellow solutions, but were non-stoichiometric and could not be further characterized. Aqueous solutions of the ion can be obtained by extracting ether solutions of $(C_5H_5)_2Ni$ with 2 *N* nitric acid, 0.01 *N* silver nitrate solution (slightly acidified) or 0.01 *N* ceric sulfate solution. Upon treatment of the compound with an excess of the latter two reagents and also with acid potassium dichromate, complete degradation of the molecule results. Aqueous solutions of the $(C_5H_5)_2Ni^+$ ion are yellow-orange in color; they decompose within an hour on standing, and immediately upon the addition of base. The aqueous solutions give precipitates with triiodide ion, silicotungstic acid, mercuriiodide ion and Reinecke's salt.

Anal. Calcd. for $[(C_5H_5)_2Ni][Cr(NH_3)_2(CNS)_4 \cdot H_2O$: Ni, 11.17; Cr, 9.90; C, 32.0; H, 3.5. Found: Ni, 11.14; Cr, 9.87; C, 31.9; H, 3.5.

Stannous ion fails to effect reduction of the $(C_5H_5)_2Ni^+$ ion. However, it can be reduced to $(C_5H_5)_2Ni$, which can be re-extracted into ether, with a solution of titanous sulfate. This would indicate that the reduction potential lies in the range −0.05 to −0.15 v. *vs.* N.H.E.

Solutions of $(C_5H_5)_2Ni$ in a 90% ethanolic 0.1 *M* sodium perchlorate supporting electrolyte show an oxidation wave at −0.08 v. *vs.* S.C.E. Calculation using the values for the wave height and concentration, and utilizing the polarographic constant for $(C_5H_5)_2Fe$[20] shows that the oxidation is a one-electron process. The appearance of the wave suggests that the oxidation is reversible in the alcoholic medium. This conclusion was established by treating the solution of $(C_5H_5)_2Ni$ with successive portions of nitric acid or ceric sulfate solution. The results of the experiment with ceric sulfate are shown in Fig. 4. The heavy horizontal line is the line of zero current, waves below it representing oxidation and waves above it reduction. Curve 1 shows the oxidation wave obtained from pure $(C_5H_5)_2Ni$ at −0.08 v. Curves 2, 3 and 4 show the waves obtained after successive additions of ceric sulfate solution; curve 4 was obtained on a solution to which sufficient ceric ion had been added to oxidize about 95% of the $(C_5H_5)_2Ni$ originally present. The progressive decrease in wave height is due to some decomposition and the shift of potential is due to the increasing water content of the alcoholic supporting electrolyte as a result of the additions of aqueous ceric sulfate. Aqueous supporting electrolyte solutions of $(C_5H_5)_2Ni^+$ ion obtained by one of the above oxidation–extraction procedures show reduction waves at −0.21 v. *vs.* S.C.E. (equivalent to −0.05 v. *vs.* N.H.E., in agreement with the chemical study of this reduction, described above). The best reduction waves are obtained with the nitric acid solutions. The appearance of the reduction wave in aqueous solution indicates that it is irreversible, as would be expected.

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