produced when the yellow complex is irreversibly transformed into the lavender complex. If the appearance of additional bands in this region is due to cyanide bridging, then it would follow that an increase in extent of bridging should be mirrored by changes in relative intensities. Whether or not such is the case here remains to be substantiated.

Additional studies which might reveal more about the structural features of the lavender complex were unfortunately precluded by failure to find a solvent which would dissolve sufficient amounts to enable measurement of molecular weight, dipole moment or conductivity.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Structure of the Reaction Product of Phenylacetylene with Iron Pentacarbonyl

BY J. R. LETO AND F. A. COTTON

RECEIVED SEPTEMBER 8, 1958

A compound first prepared by Jones, Wailes and Whiting in 1955 has been further studied. It is concluded from analytical data that its formula is $C_{20}H_{12}O_4Fe$ and not $C_{20}H_{10}O_4Fe$. Detailed study of the infrared spectrum and the fact that it has a dipole moment of $\sim$3 Debye units lead to the proposal of a structure in which a diphenylcyclopentadienone is bonded by π electrons to an $Fe(CO)_3$ group.

Introduction

In 1955 Jones, Wailes and Whiting[1] reported the isolation of a compound with the formula $C_{20}H_{10\text{ or }12}O_4Fe$(I), their analytical accuracy being insufficient to distinguish between 10 or 12 hydrogen atoms. This compound was obtained in very small quantities by adding $Ni(CO)_4$ to a mixture of $Fe(CO)_5$ and phenylacetylene in aqueous ethanol and acetic acid. Without the $Ni(CO)_4$ no reaction occurred, but upon addition of $Ni(CO)_4$ the usual carbonylation reaction producing $C_6H_5C(COOC_2H_5){=}CH_2$ proceeded essentially quantitatively and traces of I were found among the products. Jones, *et al.*, proposed that I is actually $C_{20}H_{10}O_4Fe$ with structure a, Fig. 1. Since, however, transition metal acetylides are commonly unstable, whereas I is extremely stable, we have considered that I might have the structure b (Fig. 1)[2] and thus be $C_{20}H_{12}O_4Fe$. With this in mind, we felt that the compound merited further study. We have confirmed its existence, preparing it by the same irrational procedure used by Jones, *et al.*, with slight modifications and have determined a number of its properties which bear on its constitution and structure. It appears to us that the evidence now available is inconsistent with structure a, but consistent with structure b.

Experimental

Preparation.—This was carried out in essentially the manner described by Jones, Wailes and Whiting.[1] The yield is increased somewhat (from 3.3 to 6.0%) by employing longer reaction times, and especially if the material is allowed to crystallize overnight from the cooled solution. In a typical run 2.2 g. of I was obtained from a reaction mixture consisting of 19.4 g. of $Fe(CO)_5$, 4.9 g. of $Ni(CO)_4$ and 25 g. of phenylacetylene, which had been held at 70° for 3 hr. Altogether a stock of 6.5 g. of I was accumulated from 4 runs. The product was purified as described by Jones, *et al.*, and had a melting point of 221–222° (222° reported[1]).

Purification by Chromatography.—A column of 200 g. of alumina was thoroughly washed with benzene and a solution of 0.2 g. of I in benzene was put on the column. Elution was carried out slowly by using a benzene–chloroform mixture, gradually increasing the proportion of chloroform. No separation of the band occurred. Elution was continued using benzene–acetone mixtures and again no separation was observable. Elution was then completed with pure acetone from which I was crystallized and found to have the same melting point as before.

Magnetic Susceptibility.—The bulk susceptibility was measured on the solid material using a Gouy balance. Material which was *not* rigorously purified shortly before measurement and carefully protected from light was found to be far less diamagnetic than would be expected and on some occasions slightly paramagnetic. The molar susceptibility obtained on the most highly purified and carefully handled sample was -40.0×10^{-6} c.g.s.μ which is still less than would be expected from Pascal's constants.

Nuclear Magnetic Resonance.—The proton resonance spectrum of a saturated solution of the iron compound in acetone-d_6 was taken in an effort to decide the number and kinds of protons in the molecule. The highest power level of a Varian 4300B high resolution spectrometer was used, and the spectrum was scanned at various speeds; only one weak resonance was observed at +1.68 p.p.m. from water and is without any doubt due to the phenyl protons. In our experience compounds containing acetylenic or olefinic protons have a resonance in the region +0.7 to +1.0 p.p.m. from water, but a careful search in this region (and all regions) yielded nothing. The phenyl resonance peak height (or area) in the saturated solution of the iron compound and the peak height (or area) of the cyclopentadienyl protons of ferrocene (added in mole for mole amount to the solution) were the same within experimental error—that is 10 protons per mole in ferrocene gave the same area under resonance peak as all the observable protons per mole (phenyl) in the iron compound. Although this indicates that the 2 other protons are not "masked" by the phenyl resonance, it does not positively disprove their existence. The observed peak is sufficiently weak that in our judgment another peak $^1/_5$ its intensity could escape detection.

Infrared Spectra.—Infrared spectra were taken on saturated solutions in CS_2, $CHCl_3$ and CCl_4 and on the solid mulled in Nujol and hexachlorobutadiene and pressed in KBr. Using 0.1 mm. cells, the solutions were all too dilute to reveal any but the strongest bands. The spectrum of pure liquid phenylacetylene was also run for comparison. All of the observed bands are listed in Table III. A Perkin–Elmer model 21 double beam spectrometer equipped with a rocksalt prism was used, employing both scanning cams to obtain the best possible resolution around 2000 cm.$^{-1}$.

Measurement of Dipole Moment.—The dipole moment of the iron compound in benzene solution was calculated in the usual way[3] from measurements of the total polarization and the electronic polarization of the molecule. The di-

---

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

(2) We cannot tell from our experiments which isomer of diphenylcyclopentadienone is present and so we write structure b in a generic way. Our concern has been with the general structure and not with this detail.

(3) See, for example, R. J. W. LeFevre, "Dipole Moments," Methuen and Co., London, 1953.

TABLE I

EXPERIMENTAL DATA AND RESULTS OF DIPOLE MOMENT MEASUREMENT[a]

Solution	N_1	N_2	ϵ_{12}	d	$_T$P	n^D	$_E$P	μ
Benzene	1.0000	0.0000	2.274$_1$	0.8734	......	1.4975	......	....
I (satd. in benz.)	0.99818	.00182	2.301$_1$	0.8742	326 ± 17	1.4982	130 ± 13	3.1 ± 0.2
I (satd. in $CHCl_3$)	0.99432	.00568	....	1.4678	......	1.4453	116 ± 2	....
Chloroform	1.0000	.0000	....	1.4717	......	1.4400	......	....

[a] N_1 = mole fraction solute, N_2 = mole fraction compound; ϵ_{12} = dielectric constant of solutions (to ±0.0003); d = density of solutions (to 0.0002 g./cc.); $_T$P = calculated total molar polarization of solute; n^D = refractive index of solution; $_E$P = electronic polarization of solute calculated from n^D; μ = dipole moment (Debyes) = $0.0128\sqrt{(_TP - {}_EP)T}$.

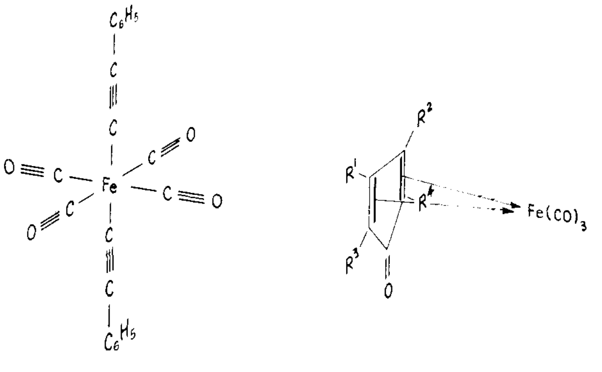
electric constants of pure benzene and a saturated solution of I in benzene were measured on a high-frequency capacitance bridge designed in the Laboratory for Insulation Research at M. I. T., employing a self-filling, thermostated cell with cylindrical electrodes. Densities were determined by means of a calibrated 10-cc. pycnometer and a Mettler balance accurate to 0.02 mg. The densities given are in error by no more than 0.0002 g./cc. Indices of refraction were measured on an Abbé Refractometer, using the sodium-D lines. All measurements were carefully thermostated to 25.0 ± 0.5°. The mole fraction of the solution was determined by weighing the residue after evaporation of the saturated solution. Data are collected in Table I. Also included are data checking the electronic polarization in chloroform which is a better solvent for the compound. An attempted series of measurements in dioxane was not successful because of slow decomposition of I in even carefully purified dioxane.

Discussion

The principal lines of evidence bearing on the composition and structure of I are: (1) analytical data, (2) its dipole moment and (3) its infrared spectrum. Before proceeding to discuss these in detail a few other observations may be noted. We have confirmed in general all of the chemical and physical properties of the compound which were reported by Jones, Wailes and Whiting. The chromatographic homogeneity study confirms the fact that I is a single compound and that it is pure as obtained by the procedure of Jones, *et al.* The compound is doubtless diamagnetic. It might be expected to have a negative susceptibility of the order of several hundred × 10^{-6} c.g.s.u. whereas we obtain only -40×10^{-6} c.g.s.u. on the purest samples. This might be due to the presence of a low-lying paramagnetic state of the molecule, but it is more likely due to photochemical or possibly oxidative decomposition producing traces of paramagnetic substances such as iron oxides. Jones, *et al.*, observed the photochemical instability of I, and we have noted that on standing in strong light a greenish cast develops and that such visibly greenish specimens are appreciably paramagnetic.

The infrared spectrum of phenylacetylene shows a very strong band at 3350 cm.$^{-1}$ due to the ≡C—H stretching mode. Jones, *et al.*, reported that there was no such band in their infrared spectrum of I. We have confirmed this on spectra under a variety of conditions and thus are in agreement that a structure having two $C_6H_5C{\equiv}C{-}H$ groups coordinated *via* the C≡C bonds to an $Fe(CO)_4$ moiety is not admissible. Such a structure would also require the iron atom to have an effective atomic number of 20. The n.m.r. spectrum does not provide any firm evidence for or against either structure in Fig. 1. The peak due to the phenyl protons is weak even in $(CD_3)_2CO$, the best solvent we have found, and it is impossible to say whether another peak one-fifth its intensity is truly absent or simply undetected.

1. **Analytical Data.**—If we consider the theoretical analyses to be expected for $C_{20}H_{10}O_4Fe$ and $C_{20}H_{12}O_4Fe$, Table I, we see that differences in the carbon, oxygen and iron percentages are too small to be of any use in reaching a decision between the two structures. However, the hydrogen percentages differ appreciably. Table I records the results of numerous analyses performed independently by several different laboratories. It is clear that these results argue strongly for the formula $C_{20}H_{12}O_4Fe$ and hence against structure a.



(a) (b)

Fig. 1.—Possible structures for $C_{20}H_{10}$ or $_{12}O_4Fe$: (a) the structure proposed by Jones, Wailes and Whiting assuming the formula $C_{20}H_{10}O_4Fe$; (b) the structure proposed in this work for the formula $C_{20}H_{12}O_4Fe$. R^1, R^2, R^3 and R^4 represent two hydrogen atoms and two phenyl groups the distribution of which we cannot specify.

2. **Dipole Moment.**—The dipole moment of the compound was found to be 3.1 ± 0.2 Debye units. The significance of this datum is clear without much comment. The relatively low accuracy is unavoidable because of the low solubility. The concentration of the saturated solution in benzene was so low that no attempt was made to measure more dilute solutions for the purpose of extrapolating to zero concentration as is usually done. Since it is generally found that apparent moments increase with decreasing concentration of the solutions measured, the result obtained can be regarded as a lower limit. The moment found may be compared with the moment of 3.3 Debye units found for $(\pi\text{-}C_5H_5)Mn(CO)_3$ by Weiss[4] which suggests that it is reasonable if the compound has structure b. It appears quite impossible to reconcile it with structure a since this is centrosymmetric and uncorrected-for atomic polarization could scarcely

---

[4] E. Weiss, *Z. anorg. allgem. Chem.*, **287**, 223 (1957).

TABLE II

ANALYTICAL RESULTS FOR THE COMPOUND

	Source	Mol. wt.[a]	Analyses, %			Computed empirical formula
			C	Fe	H	
1.	Calcd.	370.13	64.90	15.09	2.723	$C_{20}H_{10}O_4Fe$
2.	Calcd.	372.15	64.54	15.01	3.250	$C_{20}H_{12}O_4Fe$
3.	Jones, Wailes, Whiting	....	64.4	15.5	3.0	$C_{19.4}H_{10.4}O_{3.8}Fe$[b]
			64.5		3.1	
4.	S. M. Nagy, M. I. T.	....	61.2	...	3.34	
5.	Schwarzkopf Labs., N. Y.	....	61.2[c]	16.7[c]	3.33	$C_{17.1}H_{11.0}O_{3.7}Fe$[d]
6.	Present authors	....	...	15.2[e]	...	$C_{19.1}H_{12.1}O_{4.0}Fe$[f]
7.	W. Manser	....	60.80	...	3.63	$C_{19.8}H_{13.3}O_{4.1}Fe$[g]

[a] The compound is not sufficiently soluble in camphor to make possible a determination by the Rast method and its low solubility in benzene and other solvents discouraged attempts to determine an approximate molecular weight cryoscopically or ebullioscopically. We are thus assuming that the molecule is not a dimer or other polymeric form of the basic unit which contains only one iron atom. [b] Oxygen obtained by difference. [c] The high iron and low carbon analyses suggest an incomplete decomposition of the sample, leaving some type of iron carbide in the residue, from which the iron percentage was calculated. In one analysis performed by Mr. D. L. Guernsey of the Metallurgy Dept. of M. I. T., a sample was decomposed at 1250°, giving a percentage of 62.5 ± 0.5%. [d] Oxygen 17.59% by *direct* analysis; total 98.8%. [e] Iron by direct titration. Result of five determinations, four by titration of the iron(III) thiocyanate complex with 0.1 *N* disodium ethylenediaminetetraacetate, one sample by a Zimmerman–Reinhardt permanganate titration. Care must be taken to decompose the samples *completely* in concd. HCl–HNO$_3$, and then to adjust the *p*H to a proper range for titration. [f] Calculated using C = 62.5, Fe = 15.2, O = 17.6, H = 3.3. Total 98.6%. [g] Direct oxygen determination gave 18.05 %; formula calculated using C, 64.5; Fe, 15.2.

TABLE III

INFRARED SPECTRA OF PHENYLACETYLENE AND ITS ADDUCT WITH IRON CARBONYL[a]

Phenylacetylene	Adduct in:					
	KBr	Nujol	C_4Cl_6	CS_2	$CHCl_3$	CCl_4
3350(vs)						
3120sh(m)	~3155(w)		~3140(w)			
3105(m)	3090(w)		~3080(vw)			
3075sh(m)			~3040?(vw)			
2104(m)						
1970B(w)						
1890B(w)	1885(vw)					
	2090(vs)	2085(vs)	2083(vs)	2090(sv)	2093(vs)	2091(vs)
	2026(vs)	2024(vs)	2022(vs)	2034(vs)	2036(vs)[b]	2036(vs)
	2008(vs)	2002(vs)	2000(vs)	2017(vs)		2020(vs)
1810B(w)	1800(vw)					
1760B(w)	1740(vw)					
1675B(w)	1700(w)	1700(w)	1700(w)			
1604(m)	1620(vs)	1618(vs)	1615(vs)	1647(s)	1640(vs)	1624(vs)
1581(m)						
1496(s)	1507(w)	1506(w)	1506(w)			
1451(s)	1457(m)		1453(m)		1460(s)	
	1445(m)		1442(m)		1440(s)	
1395(w)						
1335(w)	1340(w)		1335(vw)			
1285(w)						
1250B(m)	1213(m)	1212(w)	1210(w)			
1180(w)	1188(w)	1187(vw)				
1160(w)	1156(vw)	1156(vw)				
1100(w)	1103(vw)	1103(vw)	1103(vw)			
1073(ms)	1088(w)	1084(w)	1082(w)			
1028(ms)	1030(w)	1030(w)	1027(w)			
918(ms)						
883(w)	884(w)	886(w)				
840(w)	855(w)	852(w)				
	776(s)	772(m)	770(w)			
758(vs)	753(s)	749(s)	747(m)			
690(vs)	697(s)	693(s)	692(m)			
655(vs)	652(m)	648(m)				

[a] B, broad; s, strong; m, medium; w, weak; v, very; ms, medium strong. [b] Shows pronounced broadening on the low-frequency side.

be so large as to account for all of the measured $_TP - {}_EP$.

3. Infrared Spectrum.—Various features of the infrared spectrum appear to be inconsistent with structure a but consistent with structure b. Let us consider first the region between 1900 and 2100 cm.$^{-1}$. In all cases (with the possible exception of the CHCl$_3$ solution) three strong bands are observed. This is perfectly consistent with structure b since the symmetry of the molecule cannot be higher than C_s and the $Fe(CO)_3$ grouping would therefore produce three infrared-active CO stretching modes. In structure a it seems unlikely that the D_{4h} symmetry of the $Fe(CO)_4$ grouping would be significantly disturbed by the remote phenyl groups. If this assumption be correct, the $Fe(CO)_4$ grouping would produce only one infrared-active CO stretching mode. The linear $C_6H_5C{\equiv}C{-}Fe{-}C{\equiv}CC_6H_5$ would produce only one infrared-active $C{\equiv}C$ stretching mode which could occur as low as ~2000 cm.$^{-1}$.[5] Thus one would expect structure a to produce only two bands in this region contrary to observation.

Another critical feature of the spectrum of I is the strong band appearing in the range 1618–1647 cm.$^{-1}$ depending on sample state. Phenylacetylene has two bands of medium intensity near this region, at 1581 and 1604 cm.$^{-1}$ which can probably be assigned as phenyl ring deformation modes. It does not seem reasonable that changes occurring at the carbon atom second removed from the ring should drastically alter the number, position and intensity of such bands and this is supported by the fact that the phenyl hydrogen wagging bands between 600 and 800 cm.$^{-1}$ are virtually identical in phenylacetylene and the complex. This reasoning thus makes structure a implausible. However, the appearance of a very strong band in the ketone CO stretching region is only to be expected for a compound with structure b.

The structure b and the bonding which we are proposing for I are not without some precedent. The most direct analog is the duroquinone–$Fe(CO)_3$ compound of Sternberg, Markby and Wender.[6] Also, the (1,3-butadiene)–$Fe(CO)_3$ compound of Reihlen, *et al.*,[7] and the similar (1,3-cyclohexadiene)–$Fe(CO)_3$ compound prepared by Hallam and Pauson[8] and the structures proposed for these by Hallam and Pauson are quite analogous to structure b for $C_{20}H_{12}O_4Fe$. Finally, we learned recently[9] that Sternberg, Markby and Wender have isolated a compound in which a π-C_5H_5Co grouping is bonded to tetrasubstituted cyclopentadienone, for which they independently assumed a geometry similar to what we are proposing for $C_{20}H_{12}O_4Fe$.

If I is actually $C_{20}H_{12}O_4Fe$ with structure b as seems reasonable from the preceding discussion, then the failure of Jones, Wailes and Whiting to obtain it by several "rational" syntheses is easily understandable. Their "rational "syntheses were both intended to produce structure a and started with either $C_6H_5C{\equiv}CMgBr$ or $C_6H_5C{\equiv}C{-}I$ so that a compound containing twelve hydrogen atoms could not normally be expected to result from their reactions with $Fe(CO)_5$ or $Na_2Fe(CO)_4$, respectively. Confirmation of the structure proposed here might be obtained by syntheses of the compound by reaction of one of the iron carbonyls with the appropriate diphenylcyclopentadienone (whichever one that may be) except that none of the three isomeric forms has been isolated and unsubstituted or partially substituted cyclopentadienones are generally thought to be unstable. We do not consider it unlikely, however, that a diphenylcyclopentadienone system could be stabilized by combination with the $Fe(CO)_3$ group. For example, Wilkinson[10] has recently shown that cyclopentadiene (C_5H_6) can coördinate to metals *via* its two double bonds, whereas free C_5H_6 itself is unstable in the sense that it readily dimerizes. Perhaps the best possibility for rational synthesis of a compound similar to $C_{20}H_{12}O_4Fe$ would be by the reaction of the well-known tetraphenylcyclopentadienone (tetracyclone) with one of the iron carbonyls, although the stability of tetracyclone against polymerization may also mean that it will be unable to form the required pair of μ bonds. The matter is under study in these Laboratories.

Acknowledgments.—We thank Dr. R. W. Fessenden for assistance with the proton resonance measurements and Mr. William Westphal for the use of his dipole moment apparatus. This work was supported by the United States Atomic Energy Commission under Contract AT(30-1)-1965.

Cambridge, Massachusetts

---

(5) The $C{\equiv}C$ stretches in silver acetylides occur at ~2000 cm.$^{-1}$; L. Luttinger, private communication.

(6) H. W. Sternberg, R. Markby and I. Wender, This Journal, **80**, 1009 (1958).

(7) H. Reihlen, A. Gruhl, G. Hessling and O. Pfrengle, *Ann.*, **482**, 161 (1930).

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

(9) H. W. Sternberg and I. Wender, private communication, in course of publication.

(10) G. Wilkinson, Presented at 133rd National Meeting of The American Chemical Society, San Francisco, April, 1958.