ORGANOMETALLIC COMPOUNDS
RUTHENIUM AND IRON DERIVATIVES OF INDENE*

JEANNE H. OSIECKI, CHARLES J. HOFFMAN
Lockheed Missiles & Space Company, Palo Alto, California (U.S.A.)
and
D. P. HOLLIS
Varian Associates, Palo Alto, California (U.S.A.)
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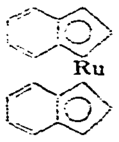
As part of an investigation to obtain a fundamental understanding of the electronic distribution in certain organometallic compounds, the indenyl and the tetrahydroindenyl derivatives of ruthenium and of iron were synthesized and the compounds further characterized. Although the synthesis and properties of the iron compounds, diindenyliron and bis(tetrahydroindenyl)iron have been fairly well described, a similar situation for the ruthenium analogues does not exist. The existence of the two ruthenium compounds has been mentioned[1,2,3], but no data other than their magnetic susceptibilities have been reported[1,2].

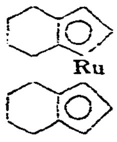
RESULTS AND DISCUSSION

Ruthenium compounds

Diindenylruthenium (I) was prepared by the reaction of indenylsodium with anhydrous ruthenium(III) chloride and ruthenium sponge in tetrahydrofuran. Indenylsodium was prepared by the interaction of sodamide with indene in benzene. The final product, pure diindenylruthenium (I), obtained by sublimation of the crude reaction product, is an orange crystalline solid, stable in air and melting at 200–201° and can be obtained in yields up to 12%. Treatment of an ethanolic solution of diindenylruthenium (I) with hydrogen at atmospheric pressure and room temperature in the presence of platinum dioxide resulted in a rapid uptake of hydrogen. This ease of hydrogenation together with the volume of hydrogen absorbed, four moles per mole of diindenylruthenium (I), thus demonstrated the olefinic character of the two double bonds in each six-membered ring of compound (I). The product, bis(tetrahydroindenyl)ruthenium (II) was isolated as a white crystalline material melting at 66–67°;



(I)



(II)

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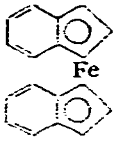
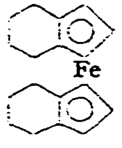
it was stable in air and easily sublimed. Magnetic measurements, using the Gouy method, of diindenylruthenium (I) and bis(tetrahydroindenyl)ruthenium (II) confirmed their previously reported[1,2] diamagnetic character.

Iron compounds

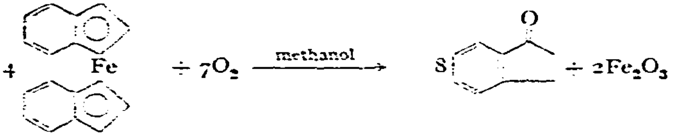
Diindenyliron (III) has been previously synthesized[4,5] by routes which differ from the reaction of indenylsodium with iron(II) chloride[6]. The present route, similar to one recently reported[7], gave remarkably high yields, 90 % and 94.5 %, of diindenyliron (III) provided all traces of oxygen were excluded during the synthesis. Since diindenyliron (III) is readily oxidized in solution, this precaution is one of the key factors for obtaining such yields. Complete decomposition of diindenyliron (III) dissolved in organic solvents has been reported[4,5], however, no prior attempts have been made to study the oxidation and to identify the decomposition products. Detailed decomposition studies of diindenyliron (III) in methanol indicated the decomposition proceeds as follows:



(III)



(IV)



with the "sandwich type" structure undergoing complete destruction with the elimination of iron as the oxide and the formation of indenone. Isolation of the decomposition products was carried out in methanol at 0° and also at room temperature with exclusion of light as much as possible to minimize polymerization of the indenone. This product, a yellow liquid, was identified by the boiling point, the refractive index, the infrared spectrum[8], which displayed a strong carbonyl band at 1715 cm^{-1} and by the dibromide derivative.

In decomposition runs where extreme care was exercised, yields of indenone close to the theoretical amounts were obtained.

Solutions of diindenyliron (III) exposed to air decompose at rates varying with the polarity of the solvent. The decomposition rate in benzene is slow, whereas decomposition in methanol or acetonitrile is rapid (Table 1).

Hydrogenation[9] of diindenyliron (III) was not quantitative unless all traces of oxygen were removed from the solvent. Removal of dissolved oxygen from ethanol by passing purified nitrogen through the solvent prior to dissolving the diindenyliron (III) is necessary to insure the desired quantitative hydrogenation. By using this modification, compound (III) was smoothly hydrogenated within thirty minutes to the bis(tetrahydroindenyl)iron (IV) which was fairly stable in air; less than 5 % decomposition was detected after a four-day exposure to air.

TABLE 1

RELATIVE DECOMPOSITION RATES OF DIINDENYLIRON (III)

Solvent	*Solvent dielectric constant ε*	*Relative decomposition rate*
benzene	2.27	slow
diethyl ether	4.34	medium
methanol	32.63	rapid
acetonitrile	37.5	rapid

Spectra

The infrared, visible, and ultraviolet data on the four metallocenes studied are summarized in Table 2.

NMR

The NMR data on the four metallocenes studied are given in Table 3. The spectra were taken on approximately 10 % solutions of the compounds in deuterochloroform. The chemical shifts of the cyclopentadienyl ring protons move toward lower field in going from Fe to Ru as found for other metallocenes[10]. The benzene ring protons in the indenyl compounds, however, are shifted in the opposite direction as the metal is changed. The benzene ring protons in both compounds resonate at somewhat higher field than those of benzene itself (7.37 δ). The apparent divergence in shielding of

TABLE 2

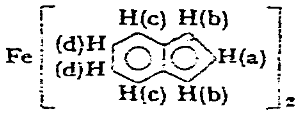
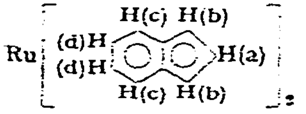
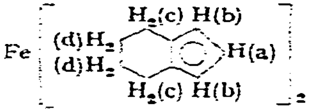
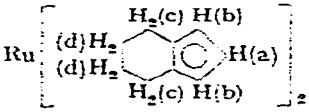
ABSORPTION BANDS IN THE UV, VISIBLE, AND IR REGIONS

	$FeC_{18}H_{14}$		$RuC_{18}H_{14}$		$FeC_{18}H_{22}$		$RuC_{18}H_{22}$	
A.					3100 (m)		3100 (m)	
	2900 (s)		2900 (s)		2900 (s)		2900 (s)	
	2850 (s)		2850 (s)		2850 (s)		2850 (s)	
					1240 (m)		1240 (m)	
	1025 (m)		1025 (m)		1030 (s)		1030 (s)	
			990 (w)		950 (m)		950 (m)	
					910 (m)		910 (m)	
					870 (m)			
					845 (m)		835 (m)	
					815 (s)			
	808 (s)		808 (s)		805 (s)		805 (s)	
	742 (s)		740 (s)					
	727 (s)		725 (s)					
B.	*mμ*	*log ε*	*mμ*	*log ε*	*mμ*	*log ε*	*mμ*	*log ε*
	563	2.49	420	2.87	435	2.09	315	2.40
	415	2.77	340	3.21	325	1.96	215	3.60
	260	4.33	292	3.73	215	4.04		
			230	4.29				

(s) strong; (m) medium; (w) weak.
A. Infrared spectra in cm^{-1}. (The compounds were run as Nujol mulls and KBr pellets).
B. Ultraviolet and visible spectra in hexane.

TABLE 3

NMR DATA

	$\delta(H_a)$	$\delta(H_b)$	$\delta(H_c)$	$\delta(H_d)$	$J(H_a\text{–}H_b)$ cps
	4.05 (triplet)	4.61 (doublet)	6.91	6.91	2.5
	4.59 (triplet)	4.89 (doublet)	6.61	6.66	2.5
	3.70 (triplet)	3.80 (doublet)	1.75	2.42	2.5
	4.25	4.25	1.62	2.35	—
Ferrocene[10]	4.14	—	—	—	—
Ruthenocene[10]	4.55	—	—	—	—

the cyclopentadienyl and the benzene ring protons is in excellent agreement with the results reported recently concerning NMR shifts in the series: ferrocene, ruthenocene, osmocene[11].

EXPERIMENTAL PART

All temperatures reported here are uncorrected. Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. The infrared spectra were recorded on a Perkin-Elmer Infracord spectrophotometer.

The thiophene free benzene was dried over anhydrous calcium chloride and distilled from sodium wire. Tetrahydrofuran was refluxed over lithium aluminum hydride and distilled, this procedure being repeated three times. Indene (Aldrich Chemical Co., Inc.) was purified by fractional distillation under vacuum. The sodamide, free flowing powder, was obtained from Farchan Research Laboratories, Wickliffe, Ohio; the ruthenium(III) chloride from Englehard, Newark, N.J.; the anhydrous ferric chloride from Matheson Coleman & Bell; the iron powder (hydrogen reduced, 325 mesh) from Rascher & Betzold Inc., Chicago, Ill.; and the ruthenium sponge from Baker & Co., Inc., Newark, N.J.

Diindenylruthenium

A solution of 110 ml of benzene and 8 g of indene was refluxed, dried by azeotropically distilling off 20 ml of benzene and then cooled to room temperature. During cooling, a stream of purified dry nitrogen was passed through the solution. The sodamide, 2.5 g, was then added while stirring vigorously and the reaction mixture heated to reflux temperature for 7$^1/_2$ h. After cooling, the benzene was decanted, 200 ml of dried tetrahydrofuran was added and the solution cooled to 0°. A suspension of 4.34 g of ruthenium(III) chloride, specially dried[12] and 1.06 g of ruthenium sponge in 30 ml of tetrahydrofuran was first heated to reflux for 6$^1/_2$ h under nitrogen while stirring vigorously, then cooled to room temperature and diluted to 60 ml before being added dropwise to the tetrahydrofuran solution of indenylsodium. The addition was completed within 10 min. The reaction mixture was stirred vigorously at 0° for an additional 50-min period, then for 2 h at room temperature. The solvent was removed *in vacuo* and the black powdery residue high vacuum sublimed to yield a dark orange product which was further purified by a second sublimation at about 140° (0.05 mm). A 12 % yield of orange colored crystals of diindenylruthenium was obtained: m.p. 200–201° (sealed tube); soluble in cyclohexane, benzene, ether, ethanol, methanol; d_{20} 1.5121 (determined by flotation in potassium iodide solution). (Found: C, 65.15; H, 4.50; Ru, 30.80. $C_{18}H_{14}Ru$ calcd.: C, 65.23; H, 4.26; Ru, 30.51 %.)

Bis(tetrahydroindenyl)ruthenium

The starting material, 100 mg of diindenylruthenium, dissolved in 60 ml of 95 % ethanol was hydrogenated at 25° using 10 mg of PtO_2 catalyst which had been previously treated by hydrogen for 20 min at room temperature. The hydrogenation was stopped after 30 min in which time 30 ml of hydrogen was absorbed, the solution filtered and the ethanol evaporated *in vacuo*. The white crystalline residue weighed 99 mg. The product was purified by sublimation at 65–70° (0.05 mm). The crystalline white bis(tetrahydroindenyl)ruthenium is very soluble in ether, cyclohexane, and in methanol and melts at 66–67°. (Found: C, 63.70; H, 6.80; Ru, 29.64. $C_{18}H_{22}Ru$ calcd.: C, 63.68; H, 6.53; Ru, 29.79 %.)

Diindenyliron

The synthesis for this compound was essentially that for diindenylruthenium with the following differences. Ferrous chloride was prepared as described in the literature[6]; after being added to the indenylsodium, the reaction mixture was stirred at 0° for 20 min and at room temperature for one hour. The solvent was removed *in vacuo*. The residue was maintained under nitrogen and extracted with benzene previously purged with nitrogen. The benzene extracts were concentrated until precipitation took place. Yields of 90 and 94.5 % of diindenyliron were thus obtained. The product was further purified by sublimation.

Decomposition of diindenyliron – Indenone and its derivative, 2,3-dibromoindanone (typical run out of 12)

The diindenyliron, 0.3 g, was dissolved in 25 ml of ether at room temperature and 25 ml of methanol was added. A stream of air was passed through the solution while the solution was stirred. The reaction was stopped after 20 min, the solution filtered through Celite and the filtrate concentrated to almost dryness at 0° and *in vacuo* keeping the reaction flask in the dark. The residue was immediately distilled under high vacuum (0.05 mm) at room temperature. The yellow distillate, a strong lachrymator, was diluted with cold anhydrous ether and stored in the freezer over

CaCl$_2$. After 2 h, the ether was removed *in vacuo*. The IR spectrum (film) of the yellow liquid shows a strong band at 1715 cm^{-1} and the UV spectrum displays a band at 316 mμ; the index of refraction is n_D^{25} 1.5892; these properties are in agreement with those of the compound synthesized by Marvel and Hinman[8]. Indenone is described[13] as a yellow liquid (b.p. 69–70°/0.35 mm) with a sharp lachrymatory odor. The indenone, 130 mg, diluted with 10 ml of CCl$_4$ was treated with one mole of bromine in CCl$_4$ at 0°. The solvent was removed *in vacuo* and the oily residue diluted with a small portion of ligroin. A crop of yellow crystals of the dibromide of indenone was obtained, m.p. reported[8] 60–62°.

Bis(tetrahydroindenyl)iron

The hydrogenation of diindenyliron was run in a similar way as that of diindenylruthenium, the only modification, important in the present case, was that the solvent was freed from oxygen by purging it with purified nitrogen and the diindenyliron was dissolved under a nitrogen atmosphere. The hydrogenation was complete within 30 min and after removal of the ethanol *in vacuo*, the orange-brown liquid residue was chromatographed on Woelm alumina, neutral grade I, with benzene. The product was then distilled *in vacuo*: b.p. 110–115° (0.5 mm); n_D^{25} 1.6143. (Found: C, 73.29; H, 7.39; Fe, 18.82. C$_{18}$H$_{22}$Fe calcd.: C, 73.47; H, 7.54; Fe, 18.99%.)

SUMMARY

A synthetic preparation of diindenylruthenium is described together with the hydrogenation of this compound to the bis(tetrahydroindenyl)ruthenium. The physical properties of these compounds are listed as well as their IR, UV and NMR spectra. It is also shown that traces of oxygen in solutions of diindenyliron are responsible for the complete destruction of the organometallic compound, the products being iron oxide and indenone. Through a complete exclusion of oxygen in the preparation of diindenyliron, almost quantitative yields are obtained. The hydrogenation of the latter compound is accomplished smoothly provided oxygen is completely excluded.

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