boron preparations. It is noteworthy that this multiplication of structural variants seems practically to be concentrated within a temperature band (*ca.* 1000–1500°) below which the relatively very simple α-rhombohedral structure is consistently obtained, above which the highly complex β-rhombohedral framework is reliably produced. However, the integrated effect of the empirical observations is to suggest thermodynamic stability for the β-rhombohedral polymorph at all temperatures above approximately 1100°. The multiplication of structural variants and the only occasional production of the β-rhombohedral phase within the cited temperature band would then be attributable to restrictions on the growth kinetics.[24]

Acknowledgment.—We wish to express our appreciation to Dr. J. S. Kasper for his helpful comments.

---

[24] Readers of this paper may find useful two reviews, (1) Arthur E. Newkirk, "Preparation and Chemistry of Elementary Boron," and (2) J. L. Hoard, "Structure and Polymorphism in Elemental Boron," both to appear in the forthcoming volume "From Borax to Boranes" in "Advances in Chemistry Series," Amer. Chem. Soc., Washington, D. C. An extensive bibliography of publications dealing with elementary boron is given in (1).

ITHACA, NEW YORK
SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE INSTITUTE FOR INORGANIC CHEMISTRY, UNIVERSITY OF MUNICH]

The Aromatic Reactivity of Ferrocene, Ruthenocene and Osmocene[1,2]

BY MARVIN D. RAUSCH,[3] ERNST O. FISCHER AND HEINRICH GRUBERT

RECEIVED JUNE 15, 1959

Both ruthenocene and osmocene, like ferrocene, exhibit substitution reactions that are characteristic of aromatic systems. The electrophilic reactivity of these metallocenes decreases in the order: ferrocene > ruthenocene > osmocene. Ruthenocene undergoes hydrogen–metal interchange with *n*-butyllithium to a greater degree than does ferrocene. The gradation in reactivity of ferrocene, ruthenocene and osmocene, together with acid dissociation constant and infrared measurements, indicate a tighter ring-to-metal bonding in the higher molecular weight derivatives.

The discovery of ferrocene (I)[4,5] in 1951 has been followed by numerous chemical confirmations that the compound possesses an aromatic system.[6] In this respect, ferrocene undergoes Friedel–Crafts acylation[7] and alkylation,[8] can be formylated,[9] sulfonated,[10] metalated with *n*-butyllithium,[11,12] phenylsodium[13] and mercuric acetate,[11] arylated with diazonium salts,[11,14] and treated with isocyanates to produce N-substituted amides.[15,16] On the other hand, typical aromatic-type reactions such as nitration and direct halogenation lead to destruction of the molecule, presumably through oxidation of the iron atom.

Although cyclopentadienyl derivatives of most of the transition metals have now been prepared, no direct chemical evidence regarding the aromatic reactivity of these compounds (metallocenes) has yet been reported other than for ferrocene itself.[17] As already has been pointed out,[17c] many metallocenes may possess aromatic character and still not exhibit typical aromatic reactions as does ferrocene, because of the instability of the metallocene under the reaction conditions involved. Thus, attempts to prepare acyl derivatives of nickelocene under Friedel–Crafts conditions have been unsuccessful,[17c] and attempts to metalate cyclopentadienylmanganese tricarbonyl with *n*-butyllithium result in collapse of the molecule, even though Friedel–Crafts reactions are successful.[17a] The most logical metallocenes for investigations of the type described for ferrocene should be the dicyclopentadienyl derivatives of ruthenium(II)[18] and osmium(III),[19] since both compounds possess rare gas configurations and should be similar in chemical reactivity and stability to ferrocene. The results of these investigations are discussed below.

Ruthenocene (II) has been prepared previously in 20% yield by the reaction of ruthenium acetyl-

---

[1] For a preliminary report of this work, see: M. D. Rausch, E. O. Fischer and H. Grubert, *Chemistry and Industry*, 756 (1958).

[2] The name "osmocene" is assigned for dicyclopentadienylosmium (II), in accordance with earlier suggestions of "ferrocene" for dicyclopentadienyliron(II) [R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 5531 (1952)], and "ruthenocene" for dicyclopentadienylruthenium(II) [G. Wilkinson, *ibid.*, **74**, 6146 (1952)].

[3] Monsanto Chemical Co., Dayton, Ohio.

[4] T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

[5] S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).

[6] For a review of the aromatic reactions of ferrocene, see: (a) P. Pauson, *Quart. Revs.* (*London*), **9**, 409 (1955); (b) M. D. Rausch, M. Vogel and H. Rosenberg, *J. Chem. Educ.*, **34**, 268 (1957); (c) K. Schlögl, *Österr. Chem. Ztg.*, **59**, 93 (1958).

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

[8] A. N. Nesmeyanov and N. S. Kotschetkova, *Doklady Akad. Nauk S.S.S.R.*, **109**, 543 (1956).

[9] G. D. Broadhead, J. M. Osgerby and P. L. Pauson, *Chemistry and Industry*, 209 (1957).

[10] V. Weinmayr, THIS JOURNAL, **77**, 3009 (1955).

[11] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. S. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 459 (1954).

[12] R. A. Benkeser, D. Goggin and G. Schroll, THIS JOURNAL, **76**, 4025 (1954).

[13] A. N. Nesmeyanov, E. G. Perevalova and S. A. Beinoravitschute, *Doklady Akad. Nauk S.S.S.R.*, **112**, 439 (1957).

[14] G. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 367 (1955).

[15] M. D. Rausch, P. Shaw, D. Mayo and A. M. Lovelace, *J. Org. Chem.*, **23**, 505 (1957).

[16] N. Weliky and E. S. Gould, THIS JOURNAL, **79**, 2741 (1957).

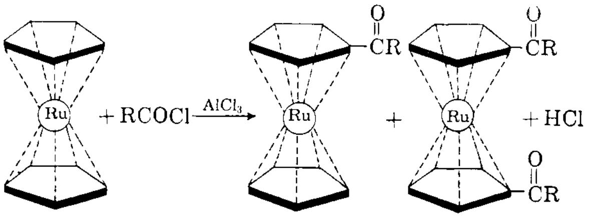
[17] It has been reported recently by several groups of investigators [(a) E. O. Fischer, Division of Inorganic Chemistry, 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 13–18, 1958 (not in abstract); see also E. O. Fischer and K. Pletske, *Ber.*, **91**, 2719 (1958); (b) J. Kozikowski, R. E. Maginn and M. Klove, Division of Organic Chemistry, 134th Meeting of the American Chemical Society, Chicago, Ill., Sept. 7–12, 1958; see Abstracts of Papers, p. 58-P; (c) F. A. Cotton and J. R. Leto, *Chemistry and Industry*, 1368 (1958)] that cyclopentadienylmanganese tricarbonyl undergoes the Friedel–Crafts reaction.

[18] In contrast to the well established antiprismatic structure of ferrocene, the cyclopentadienyl rings of ruthenocene lie in an eclipsed configuration with respect to one another around the ruthenium atom (G. L. Hardgrove and D. H. Templeton, *Acta Cryst.*, **12**, 28 (1959)).

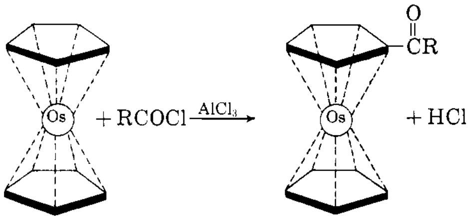
[19] Osmocene also probably possesses an eclipsed configuration (E. O. Fischer and H. Grubert, *Ber.*, in press)).

acetonate with cyclopentadienylmagnesium bromide.[2b] Substantially higher yields (43–52%) have been obtained by the reaction of ruthenium trichloride with cyclopentadienylsodium in either tetrahydrofuran or ethylene glycol dimethyl ether solution. Cyclopentadienylsodium also reacts with osmium tetrachloride in these solvents to produce 18–23% yields of osmocene (III).

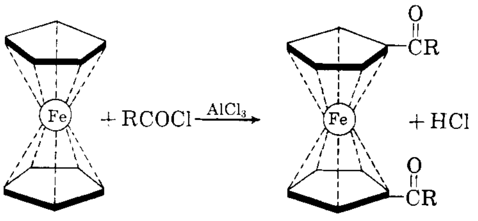
The reaction of 1 equivalent of ruthenocene with 3 equivalents each of benzoyl chloride and aluminum chloride in methylene chloride solution produced an orange-red reaction complex[20] with steady evolution of hydrogen chloride. After hydrolysis, chromatography of the organic residue resulted in 63–64% yields of monobenzoylruthenocene (IV) and 19–24% yields of dibenzoylruthenocene (V), respectively. The reaction of osmocene with the same molar ratio of benzoyl chloride–aluminum chloride and under exactly the same conditions produced only monobenzoylosmocene (VI) in 60% yield. As a basis for comparison, an identical reaction was carried out with ferrocene; 1,1'-dibenzoylferrocene (VII) was the only isolable product (70% yield). As has already been reported for the synthesis of monobenzoylferrocene,[21] the slow addition of approximately equimolar quantities of benzoyl chloride and aluminum chloride to ruthenocene produced solely the monobenzoyl derivative IV.



II
IV, R = C_6H_5
VIII, R = CH_3
V, R = C_6H_5
IX, R = CH_3



III
VI, R = C_6H_5
XI, R = CH_3



I
VII, R = C_6H_5
X, R = CH_3

Although the results were not as consistent as the benzoylation experiments, the Friedel–Crafts reaction of 1 equivalent of ruthenocene with 3 equivalents each of acetyl chloride and aluminum chloride produced, after hydrolysis and chromatography of the residue, monoacetylruthenocene (VIII) and diacetylruthenocene (IX) in yields of 4–37% and 19–21%, respectively. Under exactly the same conditions and reactant ratio, ferrocene produced only 1,1'-diacetylferrocene (X), while osmocene again yielded only a monosubstituted derivative, monoacetylosmocene (XI). Even under severe conditions, *viz.*, a large excess of acetylating agent and a high reaction temperature, no diacetylated osmocene could be isolated.

In a reaction between ruthenocene, acetyl chloride and aluminum chloride in which the catalyst was present in large excess, only diacetylruthenocene was isolated. These results are in accord with similar findings of Knox and Pauson,[22] in which excess quantities of aluminum chloride promote the diacetylation of ferrocene. Acetic anhydride also was found to be a successful acetylating agent for ruthenocene. The results of the Friedel–Crafts benzoylations and acetylations are summarized in Table I.

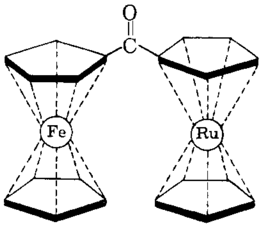
TABLE I

FRIEDEL–CRAFTS REACTIONS OF METALLOCENES ($MeC_{10}H_{10}$)[a]

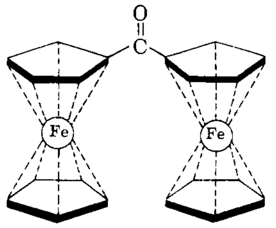
				% Yield		
$MeC_{10}H_{10}$	Acylating agent	Ratio of $MeC_{10}H_{10}$: Acylating agent: $AlCl_3$	Reaction time, hr.[b]	Mono-ketone	Di-ketone	Total ketone
$FeC_{10}H_{10}$	C_6H_5COCl	1:3:3	21	0	70	70
$RuC_{10}H_{10}$	C_6H_5COCl	1:3:3	21	64	19	83
$RuC_{10}H_{10}$	C_6H_5COCl	1:3:3	6	63	24	87
$RuC_{10}H_{10}$	C_6H_5COCl	1:1.05:1.05[c]	5	39	0	39
$OsC_{10}H_{10}$	C_6H_5COCl	1:3:3	21	60	0	60
$FeC_{10}H_{10}$	CH_3COCl	1:3:3	2.25	0	69	69
$RuC_{10}H_{10}$	CH_3COCl	1:3:3	2.75	37	21	58
$RuC_{10}H_{10}$	CH_3COCl	1:3:3	2.25	4	19	23
$RuC_{10}H_{10}$	$(CH_3CO)_2O$	1.25:1:2.24[d]	2	45	5	50
$RuC_{10}H_{10}$	CH_3COCl	1:3:6	2.25	0	22	22
$OsC_{10}H_{10}$	CH_3COCl	1:3:3	21	70	0	70
$OsC_{10}H_{10}$	CH_3COCl	1:6:6[e]	20	89[f]	0	89

[a] All reactions were carried out at reflux in CH_2Cl_2 solution (except as noted in "e"). [b] The time required for the $MeC_{10}H_{10}$ addition is included. [c] The addition was reversed, *viz.*, the C_6H_5COCl–$AlCl_3$ complex was added to the $RuC_{10}H_{10}$ solution. [d] The $(CH_3CO)_2O$ solution was added to the $RuC_{10}H_{10}$ solution containing $AlCl_3$. [e] The reaction was made in chlorobenzene (b.p. 132°) instead of CH_2Cl_2. [f] The monoketone was slightly contaminated with *p*-chloroacetophenone.

The fact that metallocenes other than ferrocene can undergo the Friedel–Crafts reaction has made possible the synthesis of other interesting new ketone derivatives. For example, ferrocenoyl chloride reacted smoothly with ruthenocene in the presence of aluminum chloride to yield ferrocenyl



XII



XIII

---

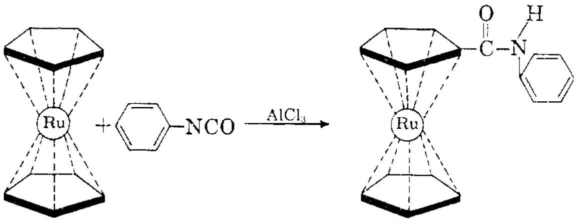
(20) Ferrocene reacts vigorously under the same conditions to form a violet complex [M. Rosenblum and R. B. Woodward, THIS JOURNAL, **80**, 5443 (1958)].

(21) M. D. Rausch, M. Vogel and M. Rosenberg, *J. Org. Chem.*, **22**, 903 (1957).

(22) G. R. Knox and P. L. Pauson, *J. Chem. Soc.*, 692 (1958).

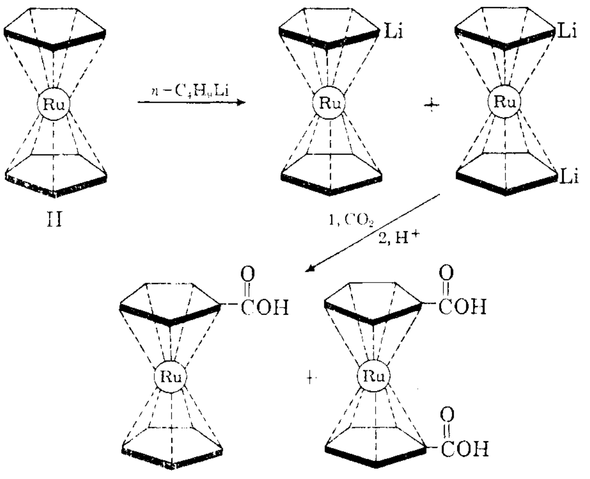
ruthenocenyl ketone (XII). This appears to be the first reported derivative in which more than one type of metallocene is incorporated into a neutral compound. A similar compound, diferrocenyl ketone (XIII), was also prepared by the Friedel–Crafts reaction of ferrocenoyl chloride and ferrocene.[23] A study of the reactions of these and related ketones is in progress.

The reaction of ruthenocene with an excess of both aluminum chloride and phenyl isocyanate produced a low yield of the anilide derivative, N-phenylruthenocenecarboxamide (XIV). This reaction, which is characteristic for various benzenoid aromatic systems,[24,25] has been shown recently to be successful for ferrocene.[15,16] As in the case of ferrocene, exclusive monosubstitution occurred, even in the presence of a large excess of phenyl isocyanate and aluminum chloride.



II XIV

The metalation of ruthenocene by means of *n*-butyllithium was likewise successful. In a series of comparative experiments, ruthenocene appeared to be even more reactive than ferrocene toward this metalating agent. For example, it has been reported that the reaction of 3 equivalents of *n*-butyllithium with 1 equivalent of ferrocene in diethyl ether solution produced, after carbonation and hydrolysis, about a 35% total yield of ferrocene acids, the major portion being the mono-derivative.[12] This procedure has been repeated under similar conditions to produce ferrocenemonocarboxylic acid and ferrocene 1,1′-dicarboxylic acid in yields of 24 and 9%, respectively. In comparison, an identical experiment with ruthenocene produced approximately equimolar amounts of ruthenocenemonocarboxylic acid (XV) and ruthenocenedicarboxylic acid (XVI), in yields of 24% for each acid.



II XV XVI

The use of a mixture of diethyl ether–tetrahydrofuran as a solvent system for the reaction of *n*-butyllithium and ferrocene has been reported to produce greatly enhanced yields of lithiated derivatives, particularly dilithioferrocene.[26] For example, the reaction of 6 equivalents of *n*-butyllithium with 1 equivalent of ferrocene over a period of 18 hr. produced ferrocenemonocarboxylic acid and ferrocene-1,1′-dicarboxylic acid in yields of 35 and 39%, respectively. A similar reaction in which ferrocene was replaced by ruthenocene resulted in an 86% yield of diacid XVI and only a 1% yield of monoacid XV. Osmocene also was metalated readily with *n*-butyllithium, and carbonation and hydrolysis produced a mixture of osmocene acids. The results of the lithiation experiments are summarized in Table II.

In analogy to ferrocene,[11,27] ruthenocene reacted with mercuric acetate in either methanol–ether solution or glacial acetic acid solution. Attempts to separate the resulting mixtures into pure mercurated derivatives as yet have not been successful.

Preliminary studies have also indicated that ruthenocene reacts with aryl-diazonium salts to produce arylated derivatives, although the reaction proceeds much less readily than in the case of ferrocene, and only trace amounts of arylated derivatives have been obtained. A study of the infrared spectra of these derivatives clearly indicates the presence of both ruthenocenyl and phenyl moieties.

Table III lists the important infrared absorption bands for the ferrocene, ruthenocene and osmocene derivatives reported above. Characteristic absorption bands for the carboxylic acids and amides are tabulated in column A. Column B lists the carbonyl absorption bands of all derivatives. The bands in column C are observed only in the case of acetylated metallocenes and are therefore undoubtedly associated with the acetyl group. These bands are mentioned here as they might be easily confused with the carbon–carbon ring-breathing bands listed in column D. Column E tabulates carbon–hydrogen bending bands.

It can be seen readily that all derivatives designated as "mono" in Table III possess absorption bands near 1000 and 1100 cm.$^{-1}$, indicative of an unsubstituted cyclopentadienyl ring. The two disubstituted ruthenocenyl ketones and ruthenocenedicarboxylic acid do not exhibit absorption in these regions[28] and in this respect are similar in

---

[23] It has been mentioned (ref. 6a) that the reaction of ferrocene with carbonyl dichloride and aluminum chloride produces mostly diferrocenyl ketone; further, a melting point of 206–208° is listed for this compound in the Appendix of Rosenblum's Ph.D. Thesis (Harvard University, 1953), although no experimental details have as yet been published.

[24] R. Leuckart, *Ber.*, **18**, 873 (1885).

[25] R. Leuckart and M. Schmidt, *ibid.*, **18**, 2338 (1885).

[26] D. W. Mayo, P. D. Shaw and M. Rausch, *Chemistry and Industry*, 1388 (1957).

[27] M. Rausch, M. Vogel and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957).

[28] It should be mentioned that both dibenzoylferrocene and dibenzoylruthenocene exhibit extremely weak absorption bands near 1000 cm.$^{-1}$. These bands may be due to the presence of very small amounts of unsymmetrical dibenzoylated isomers, whose presence could not be detected by chemical analysis.

TABLE II

REACTIONS OF METALLOCENES ($MeC_{10}H_{10}$) WITH *n*-BUTYLLITHIUM

$MeC_{10}H_{10}$	Ratio of n-C_4H_9Li: $MeC_{10}H_{10}$	Reaction time, hr.	Reaction temp., °C.	Solvent system	% Yield Mono-acid	Di-acid	Total acid
$FeC_{10}H_{10}$	3:1[a]	24	.......[b]	Et_2O[c]	..[d]	..[d]	35
$FeC_{10}H_{10}$	3:1	24	25	Et_2O	24	9	33 (62)[e]
$RuC_{10}H_{10}$	3:1	24	25	Et_2O	24	24	48 (81)
$FeC_{10}H_{10}$	6:1[f]	5	−50 to 25	Et_2O–THF 1:1	43	35	78 (91)
$FeC_{10}H_{10}$	6:1	18	−50 to 25	Et_2O–THF 1:1	35	39	74
$FeC_{10}H_{10}$	1.3:1	17	−50 to 25	Et_2O–THF 1:1	0	0	0
$RuC_{10}H_{10}$	6:1	18	−50 to 25	Et_2O–THF 1:1	1	86	87
$RuC_{10}H_{10}$	1.3:1	17	−50 to 25	Et_2O–THF 1:1	10	10	20
$OsC_{10}H_{10}$	6:1	18	−50 to 25	Et_2O–THF 1:1	..[g]	..[g]	..[g]

[a] Ref. 12. [b] The reaction temperature is not stated. [c] Et_2O = diethyl ether; THF = tetrahydrofuran. [d] Actual % yields are not given, but it is stated that the crude acids contained approximately 70% mono- and 30% diacid as indicated by elemental analysis. [e] Yields in parentheses are based on metallocene not recovered. [f] Ref. 26. [g] The mixed acids were not separated.

TABLE III

INFRARED SPECTRA OF METALLOCENE DERIVATIVES IN $CM.^{-1}$

Compound	A	B	C	D	E
Monoacetylferrocene		1658	1115	1101	1005
Monoacetylferrocene		1658	1116	1100	999
Monoacetylosmocene		1670	1116	1100	997
1,1′-Diacetylferrocene		1658	1115		
Diacetylruthenocene		1667	1114		
Monobenzoylferrocene		1626		1105	1002
Monobenzoylruthenocene		1631		1098	999
Monobenzoylosmocene		1627		1095	995
1,1′-Dibenzoylferrocene		1631			
Dibenzoylruthenocene		1634			
Diferrocenyl ketone		1612		1105	1008
Ferrocenyl ruthenocenyl ketone		1623		1105 1101	1000
N-Phenylferrocenecarboxamide	3247	1637		1105	999
N-Phenylruthenocenecarboxamide	3278	1639		1100	998
Ferrocenemonocarboxylic acid	2624 2551 939	1656–1661		1109	1005
Ruthenocenemonocarboxylic acid	2611 2538 940–948	1658–1664		1100	999
1,1′-Ferrocenedicarboxylic acid	2625 2544 919	1672–1692			
Ruthenocenedicarboxylic acid	2639 2558 916–924	1681–1695			
Monocarbomethoxyruthenocene		1709		1100	998

structure to corresponding ferrocene derivatives which already have been shown conclusively to possess symmetrical (1,1′) structures. These disubstituted ruthenocene derivatives may therefore be assigned the symmetrical structures shown in V, IX and XVI. The spectrum of ferrocenyl ruthenocenyl ketone exhibits two bands near 1100 cm.$^{-1}$; the band at 1101 cm.$^{-1}$ can be ascribed to the ruthenocene moiety and the band at 1105 cm.$^{-1}$ to the ferrocene moiety present in the molecule.

A comparison of the substitution reactions of ferrocene, ruthenocene and osmocene leads to the conclusion that while all three metallocenes indeed possess a certain degree of aromatic character, their degree of aromatic reactivity is markedly different. Thus, substitutions *via* Friedel–Crafts reactions, being of the electrophilic type, occur to a lesser degree with ruthenocene than with ferrocene, and to a still lesser extent with osmocene.[29] On the other hand, ruthenocene exhibits a marked increase in reactivity with *n*-butyllithium compared with ferrocene. This reaction is presumably of a nucleophilic type, if it is assumed that hydrogen–lithium interchange occurs by a nucleophilic attack of the butyl carbanion.[30]

Of considerable interest is a comparison of the dissociation constants of the respective carboxylic acids. Measured in 38 volume % ethanol at 20°, ferrocenemonocarboxylic acid exhibits a K_a of $(1.89 \pm 0.04) \times 10^{-6}$, while the K_a for ruthenocenemonocarboxylic acid under the same conditions is $(3.71 \pm 0.15) \times 10^{-6}$; the pK_a values are 5.72 ± 0.01 and 5.43 ± 0.02, respectively. The ruthenocene acid thus exhibits about a twofold increase in acidity compared with the ferrocene acid. Measurements of the dissociation constants of other related carboxylic acids are in progress and will be reported later.

The chemical reactivity of these metallocenes in substitution reactions and the acidity measurements of the carboxylic acids suggest that the cyclopentadienyl rings in ruthenocene and osmocene are bound more tightly to the central metal atom than in ferrocene. Tighter bonding would result in a lower π-electron density around the rings in the ruthenium and osmium complexes and account for the observed decreased electrophilic reactivity and increased acidity of the carboxylic acid derivatives. Tighter bonding could also conceivably result in increased resistance of the metal complex to oxidation. It has been experimentally observed that osmocene is much more resistant to oxidation than is ferrocene.[19] It is well known that similar effects are exhibited by ring substituents in ferrocene. Electron withdrawing substituents such as acyl and phenyl groups decrease the electrophilic reactivity of the cyclopentadienyl rings and increase the oxidative stability of the molecule.

Additional evidence for tighter bonding in ruthenocene and osmocene than in ferrocene can be

---

(29) Ferrocene exhibits a much greater reactivity than does ruthenocene in experiments in which equimolar quantities of these metallocenes are reacting competitively with benzoyl chloride–aluminum chloride complex in methylene chloride solution (M. D. Rausch, unpublished results).

(30) H. Gilman and J. W. Morton, Jr., "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954.

found in a careful examination of the infrared spectra of these metallocenes. The principal absorption bands of ferrocene, ruthenocene and osmocene are listed in Table IV. The slight but significant shift of the carbon–carbon stretching bands and carbon–carbon ring-breathing bands to longer wave lengths could indicate a weakening of the bonding between the ring carbon atoms proceeding from ferrocene to osmocene, as the result of stronger bonding between the cyclopentadienyl rings and the metal atom. Lippincott and Nelson[31–33] previously have interpreted the ring-ruthenium-ring symmetric stretching frequency at 332 cm.$^{-1}$ in ruthenocene compared to the corresponding frequency in ferrocene (303 cm.$^{-1}$) to indicate tighter bonding of the rings to the metal atom in the former complex.

TABLE IV

INFRARED SPECTRA OF GROUP VIII-A METALLOCENES IN CM.$^{-1}$

$FeC_{10}H_{10}$		$RuC_{10}H_{10}$		$OsC_{10}H_{10}$	Assignment
3083	(3085)^{a,b}	3078	(3100)^{a,b}	3095^{b}	Sym. CH stretching
1413	(1411)	1409	(1413)	1405	Anti-sym. CC stretching
1106	(1108)	1101	(1103)	1096	Anti-sym. CC ring-breathing
1002	(1002)	1001	(1002)	995	CH bending
814	(811)	806	(806)	819	CH bending

[a] Data in parentheses and assignments for $FeC_{10}H_{10}$ and $RuC_{10}H_{10}$ frequencies are by Lippincott and Nelson, refs. 31–33. [b] These values cannot be stated with exact certainty, due to the low degree of scale expansion in this region.

Mass spectra studies[34] as well as thermochemical measurements[19] further indicate greater stability in the case of the higher molecular weight complexes. The chemical evidence presented here is in agreement with these results.

A striking example of the high degree of aromatic reactivity of ferrocene is its ability to undergo the formylation reaction with phosphorus oxychloride and N-methylformanilide or dimethylformamide. It should be mentioned that attempts to produce a formyl derivative of ruthenocene using procedures reported for the formylation of ferrocene have as yet not been successful.

Additional studies concerning the aromatic reactivity of other metallocenes and related complexes are in progress.

Experimental

All melting points are uncorrected. In experiments in which nitrogen was used, the gas was thoroughly de-oxygenated and dried before use. Methylene chloride used in Friedel–Crafts reactions was dried over calcium chloride, distilled and stored over phosphorus pentachloride until use. Diethyl ether and tetrahydrofuran were dried over sodium, distilled and stored over sodium until use. Ruthenocene (II) and osmocene (III) were prepared in yields of 43–52% and 18–23%, respectively, by the reaction of the appropriate metal chloride with cyclopentadienylsodium in either tetrahydrofuran or ethylene glycol dimethyl ether. The reaction mixture was refluxed, the solvent was distilled under reduced pressure, and the residue was sublimed in high vacuum. Ruthenocene sublimed as light-yellow crystals, m.p. 199–200° (reported m.p. 195.5°)[2b]; osmocene was obtained as snow-white crystals, m.p. 229–230°.[35]

Infrared spectra of metallocene derivatives were obtained in potassium bromide pellets using sodium chloride optics and were recorded on a Perkin–Elmer Model 21 Infrared Spectrophotometer. Infrared spectra of ferrocene, ruthenocene and osmocene were obtained in carbon disulfide and carbon tetrachloride solutions using sodium chloride optics, and were recorded on a Beckman Model IR 4 Spectrophotometer. In order to ensure maximum accuracy in obtaining spectra of these three metallocenes, the instrument was calibrated immediately before and after use, using polystyrene as the standard. All frequency values have therefore been corrected for any calibration shifts, and the correction factors do not exceed ±1 cm.$^{-1}$. Duplicate measurements indicated high reproducibility. It should be noted that carbon tetrachloride solutions of all three metallocenes are appreciably unstable, necessitating prompt measurements in this solvent.

Monobenzoylruthenocene (IV) and Dibenzoylruthenocene (V).—In the usual Friedel–Crafts procedure, 0.928 g. (0.004 mole) of ruthenocene in 100 ml. of methylene chloride was added to a solution of 1.40 ml. (0.012 mole) of benzoyl chloride and 1.60 g. (0.012 mole) of aluminum chloride in 200 ml. of methylene chloride over a period of 1 hr. The reaction was carried out with stirring under an atmosphere of nitrogen. During the addition, steady evolution of hydrogen chloride and formation of an orange-red reaction complex were observed. After stirring at reflux for 20 hr., the reaction mixture was hydrolyzed with de-oxygenated water, the bright yellow organic phase was separated, washed and dried over anhydrous sodium sulfate. After filtration of the drying agent, the methylene chloride was evaporated, and the residue was transferred to an alumina chromatographic column (1.5 cm. × 45 cm.) in benzene solution.

Initial elution with petroleum ether (b.p. 60–80°)-benzene mixtures rapidly removed a light-yellow band which yielded a trace of ruthenocene. The column was developed further with benzene, producing two distinct bright yellow bands. The first band was eluted with benzene–ether mixtures to give 0.856 g. (64%) of monobenzoylruthenocene, m.p. 123–124°. An analytical sample was prepared by recrystallization from petroleum ether in the form of yellow needles, m.p. 124.5–125°.

Anal. Calcd. for $C_{17}H_{14}ORu$: C, 60.77; H, 4.20; O, 4.76; Ru, 30.27. Found: C, 60.70; H, 4.38; O, 4.60; Ru, 30.30.

Continued elution of the second band using benzene–chloroform mixtures yielded a yellow residue, m.p. 115–120°. The residue was rechromatographed on a smaller column; after removal of a trace of the monoketone, further elution produced 0.340 g. (19%) of golden yellow leaflets of dibenzoylruthenocene, m.p. 125–126°. One recrystallization from petroleum ether (b.p. 80–110°) raised the m.p. to 126–126.5°.

Anal. Calcd. for $C_{24}H_{18}O_2Ru$: C, 65.50; H, 4.12; O, 7.27; Ru, 23.11. Found: C, 65.79; H, 4.25; O, 7.35; Ru, 23.11.

Monobenzoylosmocene (VI) was prepared in a similar manner from 0.500 g. (0.00156 mole) of osmocene, 0.63 g. (0.00468 mole) of aluminum chloride and 0.6 ml. (0.0047 mole) of benzoyl chloride. The reaction mixture was refluxed for 20 hr., hydrolyzed with de-oxygenated water and the aqueous hydrolyzate was extracted well with chloroform. After standing for 3 days, yellow needles separated from the still yellow aqueous portion. The needles were filtered, dissolved in benzene, and the benzene solution was washed with dilute sodium carbonate solution and dried over anhydrous sodium sulfate. After filtration of the drying agent and distillation of the solvent, the residue was vacuum sublimed at 130–140°. Chromatography of the sublimate and resublimation yielded 0.400 g. (62% yield) of monobenzoylosmocene as light needles, m.p. 133.5°.

Anal. Calcd. for $C_{17}H_{14}OOs$: C, 48.10; H, 3.32; Os, 44.81; O, 3.77. Found: C, 48.18; H, 3.89; Os, 44.84; O, 3.40.

Osmocene (0.100 g.) was also recovered during chromatography of the reaction residue; however, no trace of disubstituted product could be detected. On the other hand,

---

(31) E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.*, **21**, 1307 (1953).

(32) E. R. Lippincott and R. D. Nelson, THIS JOURNAL, **77**, 4990 (1955).

(33) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1958).

(34) L. Friedman, A. P. Irsa and G. Wilkinson, THIS JOURNAL, **77**, 3689 (1955).

(35) A detailed description of the preparation of ruthenocene and osmocene can be found in ref. 19.

Friedel–Crafts benzoylation of ferrocene under identical conditions gave only 1,1′-dibenzoylferrocene (VII) in 70% yield.

Monoacetylruthenocene (VIII) was prepared by the slow addition of 0.39 ml. (0.004 mole) of redistilled acetic anhydride in 25 ml. of methylene chloride to a mixture of 1.49 g. (0.0112 mole) of aluminum chloride and 1.160 g. (0.005 mole) of ruthenocene in 100 ml. of methylene chloride. The addition was made at reflux temperature with stirring and under a nitrogen atmosphere. After refluxing for an additional hr., the orange-red reaction mixture was hydrolyzed with de-oxygenated water and worked up in the usual manner. Chromatography of the residue using benzene as the eluent produced 0.493 g. (45% yield) of monoacetylruthenocene as yellow needles, m.p. 111–112°. Further recrystallization from mixtures of benzene and petroleum ether did not raise the m.p.

Anal. Calcd. for $C_{12}H_{12}ORu$: D, 52.62; H, 4.42; O, 5.84; Ru, 37.13. Found: C, 52.67; H, 4.67; O, 5.60; Ru, 37.70.

Continued elution with benzene–chloroform mixtures removed a small trailing band. After evaporation of the solvent, recrystallization of the residue yielded 0.030 g. (5% yield) of crude diacetylruthenocene, m.p. 142–145°, identical with the product described below.

Diacetylruthenocene (IX) was best produced by Friedel–Crafts acetylation of ruthenocene using acetyl chloride. Thus, 0.464 g. (0.002 mole) of ruthenocene in 50 ml. of methylene chloride was added to a stirred mixture of 0.43 ml. (0.006 mole) of acetyl chloride, 1.60 g. (0.012 mole) of aluminum chloride and 75 ml. of methylene chloride under nitrogen. The reaction mixture was refluxed for 2 hr., then hydrolyzed with de-oxygenated water and worked up as described above. Chromatography of the organic residue after distillation of the solvent produced unreacted ruthenocene and resulted in the formation of a homogeneous yellow trailing band. Elution of this broad band and recrystallization of the product from either benzene–petroleum ether or methanol produced 0.137 g. (22% yield) of long yellow needles of diacetylruthenocene, m.p. 149–150°. The compound also could be purified readily by sublimation in high vacuum.

Anal. Calcd. for $C_{14}H_{14}O_2Ru$: C, 53.22; H, 4.47; O, 10.13. Found: C, 53.38; H, 4.46; O, 9.80.

Monoacetylosmocene (XI).—In a procedure similar to that described for the synthesis of VI, 0.500 g. (0.00156 mole) of osmocene in 40 ml. of methylene chloride was added dropwise over a period of 1 hr. to a solution of 0.63 g. (0.00468 mole) of aluminum chloride and 0.34 ml. (0.0047 mole) of acetyl chloride in 40 ml. of methylene chloride. After hydrolysis, separation of layers, and purification of the organic residue by means of chromatography and vacuum sublimation, 0.390 g. (69% yield) of monoacetylosmocene was obtained in the form of light yellow needles, m.p. 126°.

Anal. Calcd. for $C_{12}H_{12}OsO$: C, 39.76; H, 3.34; Os, 52.49; O, 4.42. Found: C, 40.18; H, 3.54; Os, 52.36; O, 4.75.

During chromatography of the reaction residue (in which 0.100 g. of osmocene was recovered), the appearance of a homogeneous light yellow band indicated that only one acetylated derivative was present. In an identical reaction carried out with ferrocene instead of ruthenocene, only 1,1′-diacetylferrocene (X) was isolated.

In a similar reaction with ruthenocene in which chlorobenzene (b.p. 132°) was used as the reaction solvent, refluxing for 20 hr. using a 6 molar excess of acetylating agent failed to produce any disubstituted derivative. Purification of the product gave only monoacetylosmocene, contaminated with a small amount of *p*-chloroacetophenone.

Ferrocenyl Ruthenocenyl Ketone (XII).—To a suspension of 1.38 g. (0.006 mole) of ferrocenemonocarboxylic acid in 15 ml. of benzene under nitrogen was added slowly 1.38 g. of phosphorus pentachloride. The reaction mixture was shaken at room temperature for 15 min. and the solvent was removed by agitation on a steam-bath under reduced pressure. The remaining orange oil was dissolved in 75 ml. of methylene chloride containing 1.62 g. (0.007 mole) of ruthenocene and the solution was transferred to an addition funnel under nitrogen. This solution was then added dropwise over a period of 30 min. to a mixture of 0.80 g. (0.006 mole) of aluminum chloride and 75 ml. of methylene chloride contained in a 250-ml., 3-necked flask. The violet colored reaction mixture was refluxed for 1 hr. and was hydrolyzed with de-oxygenated water. The organic phase was separated, washed with dilute sodium carbonate solution, dried over anhydrous sodium sulfate, the solvent removed and the residue transferred to an alumina column. Elution with petroleum ether–benzene 1:1 rapidly removed the unreacted ruthenocene, while slowly developing a broad, homogeneous, dark red band. Elution of this band with benzene–ether mixtures produced 1.226 g. (45% yield) of ferrocenyl ruthenocenyl ketone as beautiful orange-red needles, m.p. 216° with decomp. Recrystallization from 1-propanol did not raise the m.p.

Anal. Calcd. for $C_{21}H_{18}FeORu$: C, 56.82; H, 4.09; Fe, 12.58; O, 3.60; Ru, 22.91. Found: C, 57.38; H, 4.06; Fe, 12.3; O, 3.4; Ru, 22.5.

Diferrocenyl ketone (XIII) was prepared in an analogous manner as described above starting with 1.30 g. of ferrocene in place of ruthenocene. Chromatography of the reaction product gave 0.700 g. of unreacted ferrocene and 0.622 g. of crude ketone, m.p. 200–203°. One recrystallization from 1-propanol produced long, red-violet needles of diferrocenyl ketone, 0.585 g. (25% yield), m.p. 204° with decomp.

Anal. Calcd. for $C_{21}H_{18}Fe_2O$: C, 63.35; H, 4.56. Found: C, 63.30; H, 4.46.

N-Phenylruthenocenecarboxamide (XIV) was synthesized by the addition of a solution of 0.665 g. (0.005 mole) of aluminum chloride and 0.61 ml. (0.005 mole) of phenyl isocyanate in 40 ml. of methylene chloride to a solution of 0.464 g. (0.002 mole) of ruthenocene in 25 ml. of methylene chloride. After refluxing for 2 hr., the reaction mixture was poured into 100 ml. of 10% hydrochloric acid solution, the organic phase was washed twice with water, dried over anhydrous sodium sulfate, and the solvent was distilled. Chromatography of the residue on an alumina column yielded 0.196 g. of ruthenocene and 0.141 g. (20% yield) of *N*-phenylruthenocenecarboxamide, m.p. 208–209°. One recrystallization from ethanol gave an analytical sample in the form of fine light yellow crystals, m.p. 210°.

Anal. Calcd. for $C_{17}H_{15}NORu$: C, 58.16; H, 4.31; N, 3.99; O, 4.56; Ru, 28.97. Found: C, 58.16; H, 4.36; N, 4.4; O, 4.9; Ru, 28.2.

Mercuration of ruthenocene was accomplished readily as in the case of ferrocene in either methanol–ether[11,27] or glacial acetic acid solution.[27] Thus, a warm solution of 0.797 g. (0.0025 mole) of mercuric acetate in 25 ml. of glacial acetic acid was added slowly to a solution of 0.580 g. (0.0025 mole) of ruthenocene in the same solvent. The clear yellow solution was stirred at reflux for 3 hr. and then 0.23 g. (0.003 mole) of potassium chloride dissolved in 20 ml. of glacial acetic acid containing a little water was added. The voluminous light yellow precipitate which resulted was washed with water and with warm benzene, and the residue was recrystallized twice from 1-butanol, forming 0.358 g. of long yellow needles, m.p. 217–218° with decomp.

Anal. Calcd. for $C_{10}H_9ClHgRu$: C, 25.72; Ru, 21.87. Calcd. for $C_{10}H_8Cl_2Hg_2Ru$: C, 17.11; Ru, 14.49. Found: C, 18.87; Ru, 16.30. On this basis, the product consisted of about 21–25% mono- and 75–79% dimercurated derivative, assuming these are the only products present.

Ruthenocenemonocarboxylic acid (XV) was best produced by a procedure similar to that described by Benkeser, *et al.*,[12] for the synthesis of ferrocenemonocarboxylic acid. To 1.83 g. (0.0079 mole) of ruthenocene dissolved in 100 ml. of diethyl ether was added, under nitrogen, 63 ml. of a diethyl ether solution containing 0.0237 mole of *n*-butyllithium. After stirring at room temperature for 24 hr., the reaction mixture was cooled, carbonated and hydrolyzed in the usual manner. From the ether portion, 0.668 g. of ruthenocene was recovered. Acidification of the aqueous portion produced a voluminous yellow-white precipitate which was filtered and dried at 140–150° until a constant weight (1.110 g.) was attained. The crude acid was extracted for 3 hr. with ether in a Soxhlet extractor. The insoluble residue consisted of 0.588 g. (24% yield) of ruthenocenedicarboxylic acid, identical with the product described below. From the yellow ether extracts, 0.515 g. (24% yield) of ruthenocenemonocarboxylic acid was isolated, m.p. 233–235° (neut. equiv. calcd., 275.8; neut. equiv. found, 276.6). An analytical sample was prepared by recrystallization from benzene in the form of fine yellow crystals, m.p. 237–238° dec.

Anal. Calcd. for $C_{11}H_{10}O_2Ru$: C, 47.88; H, 3.65; O, 11.60; Ru, 36.86. Found: C, 48.21; H, 3.89; O, 11.21; Ru, 37.0.

In a similar experiment in which ruthenocene was replaced with an equimolar quantity of ferrocene, the yields of ferrocenemonocarboxylic acid and ferrocene-1,1′-dicarboxylic acid were 24 and 9%, respectively.

A methyl ester was prepared readily from a solution of the mono-acid in methanol containing a trace of sulfuric acid. Recrystallization from methanol and water gave monocarbomethoxyruthenocene as white leaflets, m.p. 107–107.5°.

Anal. Calcd. for $C_{12}H_{12}O_2Ru$: C, 49.71; H, 4.18. Found: C, 49.64; H, 4.31.

Ruthenocenedicarboxylic acid (XVI) was best prepared by the procedure described by Mayo, *et al.*,[26] for the synthesis of ferrocene-1,1′-dicarboxylic acid. A cold solution of 100 ml. of diethyl ether containing 0.090 mole of *n*-butyllithium was added rapidly under nitrogen to a suspension of 3.48 g. (0.015 mole) of ruthenocene in 100 ml. of tetrahydrofuran maintained at −50°. After the addition was complete, the reaction mixture was allowed to warm slowly to room temperature over about a 1 hr. period, during which time all the ruthenocene dissolved. The reaction mixture was stirred for an additional 17 hr. at room temperature, then cooled, carbonated and hydrolyzed. After Soxhlet extraction of the crude acid (4.175 g.), evaporation of the ether extracts and recrystallization of the residue gave 0.035 g. (1% yield) of ruthenocenemonocarboxylic acid, m.p. 235–238° dec. The insoluble residue was recrystallized from glacial acetic acid, yielding 4.102 g. (86% yield) of yellow crystals of ruthenocenedicarboxylic acid, which melted with much decomp. at approximately 325°, with slight charring from 300°; neut. equiv. calcd., 159.9; neut. equiv. found, 161.3.

Anal. Calcd. for $C_{12}H_{10}O_4Ru$: C, 45.05; H, 3.15; O, 20.01; Ru, 31.79. Found: C, 44.97; H, 3.38; O, 20.50; Ru, 31.70.

In a similar experiment in which ruthenocene was replaced with an equimolar quantity of ferrocene, the yields of ferrocenemonocarboxylic acid and ferrocene-1,1′-dicarboxylic acid were 35 and 39%, respectively.

The preparation of osmocene acids was made in an analogous manner from 0.700 g. (0.00218 mole) of osmocene and 0.0131 mole of *n*-butyllithium in diethyl ether–tetrahydrofuran 1:1. The crude osmocene acids were vacuum sublimed at 220°, producing a white crystalline sublimate (0.600 g.) and leaving an appreciable dark residue. The sublimate began to decompose slowly at 245° and decomp. was complete at 333°.

Anal. Calcd. for $C_{11}H_{10}OsO_2$: C, 36.25; H, 2.77; Os, 52.20; O, 8.78. Calcd. for $C_{12}H_{10}OsO_4$: C, 35.28; H, 2.47; Os, 46.57; O, 15.67. Found: C, 35.32; H, 2.94; Os, 48.75; O, 12.90.

On this basis, the sublimate consisted of approximately 42 mole % osmocenemonocarboxylic acid and 58 mole % osmocenedicarboxylic acid. It is quite possible that partial decarboxylation occurred during the sublimation at 220°, since later tests with the sublimate indicated that some decomposition began to occur at this temperature.

Phenylation of ruthenocene was made according to procedures reported for the facile arylation of ferrocene.[11,14] In general, experiments involving the use of acetone or glacial acetic acid as the solvent were less successful, due to the marked decrease in solubility of ruthenocene in these solvents compared to ferrocene.

In an experiment in which 0.0034 mole of ruthenocene in diethyl ether solution was treated for 17 hr. with a 12 molar excess of benzenediazonium chloride, chromatography of the reaction product on an alumina column (eluting with benzene–ether mixtures) produced considerable unreacted ruthenocene and developed several orange-yellow bands. Selective elution of these bands resulted in only traces of products, although one band gave 0.067 g. of an orange solid, m.p. 203–205°. An infrared spectrum of this material exhibited 3 bands in the carbon–hydrogen stretching region (3012, 2899 and 2841 cm.$^{-1}$), bands at 1733, 1595 and 687 cm.$^{-1}$ attributable to a phenyl group, a very strong band at 827 cm.$^{-1}$ attributable to ruthenocene (carbon–hydrogen bending vibration), as well as ruthenocene bands at 1002 and near 1100 cm.$^{-1}$, which would indicate the presence of an unsubstituted cyclopentadienyl ring.

Acknowledgments.—The authors wish to thank Dr. H. P. Fritz for aid in interpretation of the infrared spectra and Mr. W. Semmlinger for determination of the dissociation constants of the carboxylic acids. We also wish to express our appreciation to Baker and Co., Inc., Newark, N. J., for a gift of ruthenium chloride which made possible a portion of this investigation. M. D. R. is indebted to the National Science Foundation for a post-doctoral fellowship for the year 1957–1958.

MUNICH, WEST GERMANY

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY AND LABORATORIO DE FÍSICA NUCLEAR UNIVERSIDAD DE CHILE]

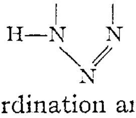
Metal Tetrazole Complexes: Bis-(5-aminotetrazolato)-copper(II)

BY CARL H. BRUBAKER, JR.[1]

RECEIVED JUNE 5, 1959

Two crystalline forms of bis-(5-aminotetrazolato)-copper(II) have been prepared and characterized. Visible and ultraviolet spectra of aqueous copper(II)–5-aminotetrazole solution have been examined. Continuous variation experiments reveal 1:2 interactions and a formation constant for the complex in solution has been determined and is about 10^{12}. Infrared studies suggest coördination involves the ring and not the 5-amino group. Acids decompose the complexes and bring about rupture of the tetrazole ring, while decomposition by ammonia does not affect the ring.

Since tetrazole and a variety of substituted tetrazoles are available at Michigan State University,[2] it appeared to be worthwhile to examine the possible coördination of several, especially tetrazole and some 5-substituted tetrazoles, with metallic ions. One can envision a number of possible ways in which the class of compounds



might engage in coördination and in inner complex formation, if the acidic 1-H were replaced by a metal–nitrogen bond.

Preliminary experiments revealed interactions between copper(II), nickel(II) and platinum(II) and tetrazole. 5-Aminotetrazole was more plenti-

---

[1] 1958 Fulbright Lecturer in Radiochemistry, Universidad de Chile. Correspondence should be sent to Michigan State University.

[2] R. M. Herbst, Department of Chemistry.