

# Cyclobutadiene–Metal Complexes. IV.<sup>1</sup>

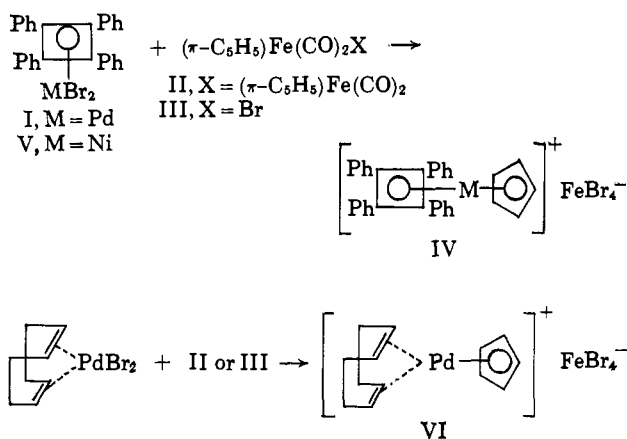
## ( $\pi$ -Cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)palladium Halides and Related Complexes

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Reaction of tetraphenylcyclobutadienepalladium and nickel bromides with  $[(C_5H_5)Fe(CO)_2]_2$  or  $(C_5H_5)Fe(CO)_2Br$  led not to the expected transfer of the tetraphenylcyclobutadiene group onto iron, but to complexes of the type  $[Ph_4C_4]M[C_5H_5]^+FeBr_4^-$  ( $M = Ni$  or  $Pd$ ). These can be converted into the diamagnetic bromides  $[Ph_4C_4]M[C_5H_5]^+Br^-$  which, on treatment with alkoxide, give the ( $\pi$ -cyclopentadienyl)( $\pi$ -alkoxytetraphenylcyclobutenyl) complexes of palladium and nickel. The chemistry of these compounds is discussed and a mechanism for the ligand-transfer reaction proposed.

We recently described a general synthesis of tetraphenylcyclobutadiene–transition metal complexes by transfer of the tetraphenylcyclobutadiene group from the readily accessible tetraphenylcyclobutadienepalladium halides<sup>2,2a</sup> (I) onto other metals by reaction with their carbonyls.<sup>3</sup> An obvious extension of this reaction to the synthesis of other substituted tetraphenylcyclobutadiene–metal complexes is the replacement of carbonyls by substituted carbonyls such as the cyclopentadienylmetal carbonyls. This reaction we anticipated would proceed in the same manner, in that the



tetraphenylcyclobutadiene group would be transferred, for example, from palladium to iron, giving ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)iron bromide,  $(Ph_4C_4)Fe(C_5H_5)Br$ , from the reaction of I with cyclopentadienyliron dicarbonyl dimer II under the usual conditions of these ligand-transfer reactions.

(1) Part III: P. M. Maitlis, A. Efraty, and M. L. Games, *J. Organometal. Chem.*, **2**, 284 (1964).

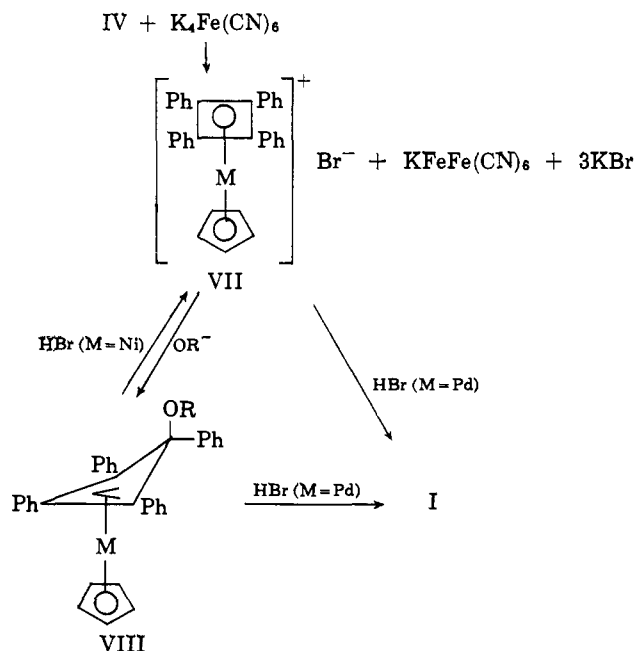
(2) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962); P. M. Maitlis and M. L. Games, *Can. J. Chem.*, **42**, 183 (1964);

(2a) NOTE ADDED IN PROOF. It now appears probable that complexes I and V are halogen-bridged dimers; this does not however materially affect the arguments presented here.

(3) (a) P. M. Maitlis and M. L. Games, *J. Am. Chem. Soc.*, **85**, 1887 (1963); (b) *Chem. Ind.* (London), 1624 (1963).

In fact, as has already been mentioned in a preliminary note,<sup>1</sup> reaction of I with II or preferably cyclopentadienyliron dicarbonyl bromide (III) in refluxing benzene caused transfer of the cyclopentadienyl group onto palladium to give a complex salt of type IV ( $M = Pd$ ). A little ferrocene was the only other product which was isolated from this reaction.

Tetraphenylcyclobutadienenickel bromide (V)<sup>4</sup> underwent an exactly analogous reaction to give ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)nickel tetrabromoferrate (IV,  $M = Ni$ ). 1,5-Cyclooctadienepalladium bromide also reacted with III (and also with II) under the same conditions to give ( $\pi$ -1,5-cyclooctadiene)( $\pi$ -cyclopentadienyl)palladium tetrabromoferrate (VI), again in high yield. The tetrabromoferrates (IV and VI) were all air-stable, dark-colored, highly crystalline, paramagnetic solids. Measurement



of the magnetic susceptibilities gave values of  $\mu_{\text{eff}}$  close to that expected for tetrahedral Fe(III), 5.9 B.M. The cyclooctadiene complex VI was not stable to most reagents, and all attempts to convert it to a diamagnetic salt failed. Both cyclobutadiene complexes (IV,  $M = Pd$  and  $Ni$ ), however, were readily converted into the diamagnetic bromides (VII,  $M = Pd$  and  $Ni$ ) on reaction in dichloromethane with aqueous potassium ferrocyanide. The p.m.r. spectra of VII showed two sharp resonances attributed to phenyl and cyclopentadienyl protons with the expected intensity ratio of

(4) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194 (1961).

**Table I.** N.m.r. Resonances<sup>a</sup> ( $\tau$ )

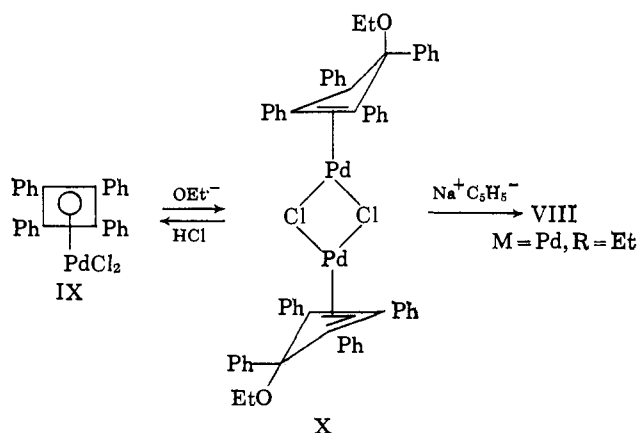
| Compound | M  | R  | C <sub>6</sub> H <sub>5</sub> | C <sub>6</sub> H <sub>5</sub> | OH   | OMe  | OEt        |
|----------|----|----|-------------------------------|-------------------------------|------|------|------------|
| VII      | Pd |    | 2.39                          | 3.66                          |      |      |            |
| VII      | Ni |    | 2.39                          | 4.22                          |      |      |            |
| VIII     | Pd | H  | 2.38; 2.62 <sup>b</sup>       | 4.44                          | 7.23 |      |            |
| VIII     | Pd | Me | 2.26; 2.63 <sup>b</sup>       | 4.55                          |      | 6.58 |            |
| VIII     | Pd | Et | 2.26; 2.85 <sup>b</sup>       | 4.55                          |      |      | 6.36; 8.82 |
| VIII     | Ni | Me | 2.4; 2.8 <sup>b</sup>         | 5.10                          |      | 6.70 |            |

<sup>a</sup> Measured in CDCl<sub>3</sub> with tetramethylsilane as internal reference. <sup>b</sup> The phenyl protons in complexes VIII all show two strong, rather diffuse, resonances, while those in VII show only one very sharp resonance.

20:5. Confirmation of the structures of VII came from analyses and infrared spectra (2–16  $\mu$ ) which were identical with each other, with that of IV, and also with that of the previously prepared ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)cobalt (XIII)<sup>3a,5</sup> showing that the same organic ligands were present in all of them. The presence of the tetraphenylcyclobutadiene group in VII (M = Pd) was also demonstrated by the reconversion of VII (M = Pd) into I in high yield on treatment with hydrogen bromide in dichloromethane.

Both bromides (VII, M = Pd and Ni) reacted with hydroxide or alkoxide to give covalent ( $\pi$ -alkoxytetraphenylcyclobutenyl)( $\pi$ -cyclopentadienyl)metal complexes (VIII). The structures of these complexes were assigned on the basis of analyses and p.m.r. spectra (Table I) which showed the presence of phenyl and alkoxy groups (with the expected intensity ratios) as well as a single unsplit peak due to the cyclopentadienyl protons, showing that addition to the cyclopentadienyl ring had not occurred. In addition, one of the compounds was synthesized by another route (see below) from a compound of known structure.

All the VIII complexes (M = Pd) on treatment with hydrogen bromide gave the cyclobutadiene complex I in high yield, probably *via* VII (M = Pd); however, VIII (M = Ni, R = Me) only gave VII (M = Ni),

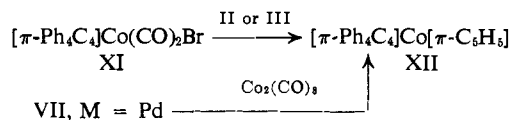


and the reaction did not go through to the cyclobutadiene V. These reactions are very similar to those already described<sup>2</sup> for tetraphenylcyclobutenylpalladium chloride (IX) which on treatment with ethanol gives the  $\pi$ -ethoxytetraphenylcyclobutenylpalladium chloride dimer (X); this reaction is reversible with

(5) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **34**, 452 (1961); J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962).

HCl. X has, moreover, recently been shown to have the ethoxy group *exo* to the metal.<sup>6</sup> Since X could be converted into VIII (M = Pd, R = Et) on treatment with sodium cyclopentadienide, this also fixes the stereochemistry of the VIII complexes.

This novel cyclopentadienylation reaction has also been extended to organocobalt complexes. Thus the recently prepared tetraphenylcyclobutadienecobalt dicarbonyl bromide (XI)<sup>7</sup> reacted with II or III in benzene to give the known<sup>3a,5</sup> ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)cobalt (XII) in high yield. The



cobalt complex XII was also prepared by reaction of ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)-palladium bromide (VII, M = Pd) with dicobalt octacarbonyl in benzene. This is the first reported case of the simultaneous transfer of two organic ligands from one metal onto another and illustrates the utility of the general reaction.

## Discussion

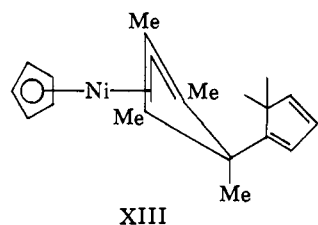
The new cyclopentadienylation reactions which we have described here are of interest from a preparative and mechanistic viewpoint. While they are not likely to supersede the use of the conventional metal cyclopentadienides as cyclopentadienyating agents, II and III do offer some special advantages, since nonpolar and noncomplexing solvents are used and since the reaction appears to be a very mild one. Thus we find no indication that C-cyclopentadienylation occurs. In contrast to Criegee and Ludwig's<sup>8</sup> discovery that tetramethylcyclobutadienenickel chloride reacts with 2 moles of sodium cyclopentadienide to give a complex now shown to have structure XIII,<sup>6,9</sup> our cyclopentadienyating agents do not act as strong nucleophiles toward carbon. On the other hand, as has already been reported,<sup>1</sup> attempts to cyclopentadienylate compounds not already possessing a  $\pi$ -bonded ligand (*e.g.*, TiCl<sub>4</sub> or VOCl<sub>3</sub>) either gave only very low yields of product or none at all.

(6) L. F. Dahl and W. E. Oberhansli, Proceedings of the VIIIth Conference on Coordination Chemistry, Vienna, 1964, p. 242.

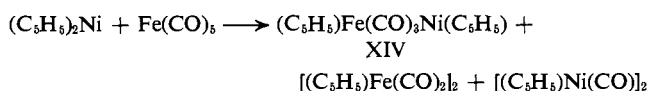
(7) The preparation and properties of this unusual compound will be reported elsewhere shortly.

(8) R. Criegee and P. Ludwig, *Chem. Ber.*, **94**, 2038 (1961).

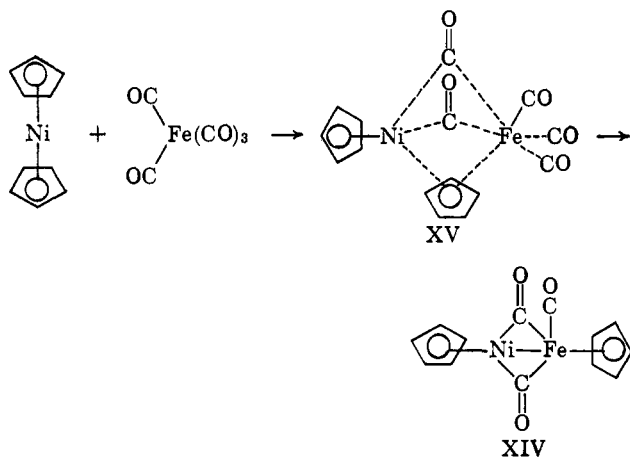
(9) L. F. Dahl, quoted by R. B. King, *Inorg. Chem.*, **2**, 529 (1963), ref. 8a.



One example of the transfer of a cyclopentadienyl group from one transition metal to another under nonpolar conditions has already been described by Tilney-Bassett,<sup>10</sup> who found that reaction of nickelocene with iron pentacarbonyl gave the cyclopentadienyliron dicarbonyl dimer, cyclopentadienylnickel carbonyl dimer, and the mixed complex XIV in unspecified yields. We suggest that this reaction and ours proceed

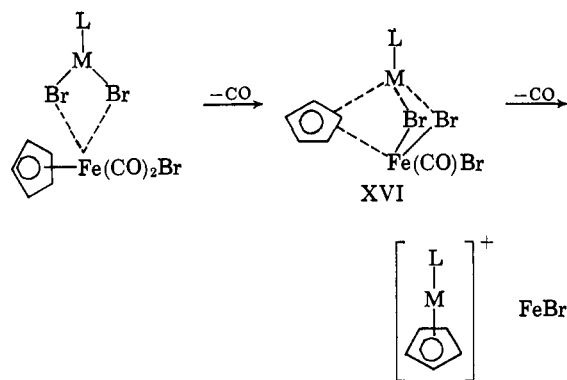


by very similar routes. In the case of Tilney-Bassett's reaction, the first step is probably the formation of a complex such as XV in which one cyclopentadienyl-nickel bond is weakened and where a cyclopentadienyl ring now acts as a bridge between the nickel and the iron. In addition, two of the iron-carbonyl groups now also bridge the two metals. The next stage is accompanied by the expulsion of two carbonyl groups from the iron, the sliding of the cyclopentadienyl group from the nickel wholly onto the iron, as in XIV, and the formation of a nickel-iron bond. XIV can then easily

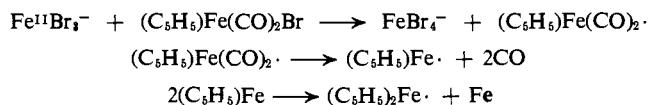


disproportionate to give the cyclopentadienyliron and nickel carbonyl dimers.

In the case of the reactions described here, the intermediate corresponding to XV is now postulated to be a halogen-bridged one (XVI) which then falls apart to give the cation  $[LM(C_5H_5)]^+$  and the  $Fe^{II}Br_3^-$  anion. The latter must then be oxidized to the stable, tetrahedral  $Fe^{III}Br_4^-$  by another molecule of cyclopentadienyliron dicarbonyl bromide *via* the cyclopentadienyliron dicarbonyl radical which decomposes to give ferrocene and iron metal since none of dimer II is formed. When the cyclopentadienyliron dicarbonyl dimer II, rather than the bromide III, is used as the cyclopentadienylating agent, yields of



the tetrabromoferrates IV and VI are much lower since all the bromide in the  $FeBr_4^-$  now must come from the reactant. The synthesis of the cobalt complex XII from tetraphenylcyclobutadienecobalt dicarbonyl bro-



mide probably follows a similar path to the one described; however, as no tetrabromoferrate is formed in this reaction, both II and III give the product XII in similar yields. Since the yields in the double ligand transfer (VII (M = Pd) to XII) are so low, this reaction probably goes in two stages, the first being the formation of cyclopentadienylcobalt dicarbonyl (by transfer of the cyclopentadienyl group) which then reacts with a tetraphenylcyclobutadienepalladium complex to give XII.

It is interesting that at higher temperatures the reaction between I and II produces a small amount of tetraphenylcyclobutadieneiron tricarbonyl. This suggests that the intermediate complex XVI can break down in at least one other way to give transfer of the cyclobutadiene group from palladium to iron as the over-all result.

Unfortunately, most of these reactions are heterogeneous (I, IV, V, and VI all being benzene-insoluble) and thus preclude any meaningful kinetic studies at this moment. However, it is hoped that studies at present being carried out on the ligand transfer of cyclobutadienes and other  $\pi$ -bonded ligands will be able to clarify these reactions further too.

The further reactions of the ( $\pi$ -cyclopentadienyl)-( $\pi$ -tetraphenylcyclobutadiene)metal bromides are also of interest; in particular, the reaction of the palladium bromide salt VII with hydrogen bromide where it is the palladium-cyclopentadiene, and *not* the palladium-cyclobutadiene, ring bond which is broken. This is in agreement with the suggestion of Longuet-Higgins and Orgel<sup>11</sup> that since the cyclobutadiene-metal  $\pi$ -bond involves two electrons, while the cyclopentadiene-metal  $\pi$ -bond involves only one, the former should be stronger. This also provides a dramatic illustration of the stability of some cyclobutadiene-metal complexes.

The addition of alkoxide to the four-membered ring in VII is similar to the reaction already described by Chatt, *et al.*,<sup>12</sup> in which dienepalladium and -platinum-(II) halides undergo nucleophilic attack by alkoxide at

(11) H. C. Longuet-Higgins and L. E. Orgel, *ibid.*, 1969 (1956).

(12) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *ibid.*, 3413 (1957).

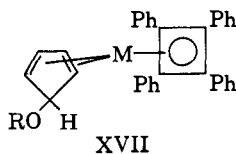
(10) J. F. Tilney-Bassett, *J. Chem. Soc.*, 4784 (1963).

**Table II.** Yields and Analyses of Products from Cyclopentadienylation Reactions

| Compound         | M  | Yield, %                        | Calcd. |      |         |       | Analyses   |          |         |                         |
|------------------|----|---------------------------------|--------|------|---------|-------|------------|----------|---------|-------------------------|
|                  |    |                                 | C      | H    | M       | Br    | C          | H        | M       | Br                      |
| IV               | Pd | 42 <sup>a</sup> 85 <sup>b</sup> | 43.9   | 2.8  | Fe, 6.2 | 35.4  | 44.9, 41.7 | 2.9, 2.9 | Fe, 6.5 | 34.8, 35.0 <sup>c</sup> |
| IV               | Ni | 75 <sup>b</sup>                 | 46.3   | 2.9  | ...     | 37.4  | 48.7, 48.7 | 3.4, 3.4 | ...     | 35.5 <sup>c</sup>       |
| VI               |    | 8 <sup>a</sup> 60 <sup>b</sup>  | 24.05  | 2.64 | ...     | 49.24 | 23.99      | 2.53     | ...     | 48.86                   |
| XII <sup>d</sup> |    | 75 <sup>a</sup> 81 <sup>b</sup> |        |      |         |       |            |          |         |                         |
| VII              | Pd | 83                              | 65.20  | 4.14 | 17.50   | 13.15 | 65.19      | 4.18     | 17.82   | 13.46                   |
| VII              | Ni | 92                              | 70.75  | 4.50 | 10.48   | 14.26 | 70.07      | 4.62     | 10.56   | 14.72                   |

<sup>a</sup> Using II as cyclopentadienylation agent in benzene at 80° for 2 hr. <sup>b</sup> Using III as cyclopentadienylation agent in benzene at 80° for 2 hr. <sup>c</sup> The poor analyses for IV are probably due to the presence of some of the bromide (VII) which cannot be removed. <sup>d</sup> Identified by m.p. (248–252°), m.m.p. with an authentic sample (252–255°), and infrared spectra.

an olefinic carbon. In the case of the complexes VII, the positions of the phenyl and especially of the cyclopentadienyl proton resonances are at somewhat lower field than they are in the uncharged complexes VIII (Table I), suggesting that the positive charge formally on the metal is in fact spread out over the organic ligands. This makes the nucleophilic attack at an unsaturated carbon here very plausible. The formation of a  $\pi$ -cyclobutenyl (*i.e.*,  $\pi$ -allylic) complex VIII rather than a  $(\pi$ -cyclobutadiene)( $\pi$ -cyclopentadiene)-metal complex XVII is also expected, since Fischer and many others<sup>13</sup> have shown that both nickel and palladium prefer to form ( $\pi$ -allyl)( $\pi$ -cyclopentadienyl) rather than ( $\pi$ -diene)( $\pi$ -cyclopentadiene) complexes, *e.g.*



An even closer analogy to the complexes of type VIII is, of course, the Criegee and Ludwig complex XIII. It is also clear that in the formation of complex VIII attack of OR<sup>-</sup> must come from above the cyclobutadiene ring for steric reasons, and therefore must give the product with the alkoxy group *exo* to the metal. This also then fixes the stereochemistry of complex X since VIII can be derived from it, and is thus an interesting confirmation of the X-ray data for X.

### Experimental

The tetraphenylcyclobutadienepalladium halides and related complexes were prepared as already described<sup>2,12</sup>; a sample of tetraphenylcyclobutadiene-nickel bromide was kindly supplied by Dr. H. H. Freedman. Cyclopentadienyliron dicarbonyl dimer (II) was prepared by the method of King and Stone,<sup>14</sup> and the bromide (III) was obtained in 78% yield from the dimer (II) by reaction with bromine in chloroform at 25°. Melting points were determined in evacuated capillaries but are not corrected. The reactions were usually run under a nitrogen atmosphere.

(13) E. O. Fischer and H. Werner, *Chem. Ber.*, **92**, 1423 (1959); **93**, 2075 (1960); **95**, 695, 703 (1962); *Tetrahedron Letters*, No. 1, 17 (1961); B. L. Shaw and N. Sheppard, *Chem. Ind. (London)*, 517 (1961); D. Jones, G. W. Parshall, L. Pratt, and G. Wilkinson, *Tetrahedron Letters*, No. 2, 48 (1961); M. Dubeck and A. H. Filbey, *J. Am. Chem. Soc.*, **83**, 1257 (1961).

(14) R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 110 (1963).

**Cyclopentadienylation Reactions.** The ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)metal tetrabromoferrate (IV, M = Pd, Ni) and the ( $\pi$ -cyclopentadienyl)-( $\pi$ -1,5-cyclooctadiene)palladium tetrabromoferrate (VI) were all prepared in the same way. I and V or 1,5-cyclooctadienepalladium bromide were refluxed in benzene with 2 moles of either II or III for 2 hr.; the suspension was then filtered and the filtrate was usually discarded (except as below) since the product was present in the residue. The residue was washed with a little benzene and then carefully digested with several portions of dichloromethane until the washings were not appreciably colored. The washings were combined, reduced in volume to *ca.* 50 ml. (on a 2-g. scale), and petroleum ether (b.p. 30–60°) was added dropwise with shaking. In this way air-stable crystals of the tetrabromoferrates of IV (M = Pd), VI (red-purple), and IV (M = Ni, brown) were obtained (m.p. above 400°). The yields and analyses are given in Table II. Complexes IV as obtained from either II or III never gave good analyses, owing to the presence of some of the bromides (VII) which could not be removed.

Complexes IV and VI were paramagnetic; the magnetic susceptibilities were measured and these gave the following magnetic moments ( $\mu_{\text{eff}}$ ) after correction for diamagnetism (in B.M.): IV (M = Pd), 6.1; IV (M = Ni), 5.4; VI, 5.8. The dichloromethane-insoluble residues were usually small and contained mainly metallic iron. In one preparation of ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)palladium tetrabromoferrate from I and the bromide III, the benzene-soluble residue was carefully examined. Apart from a small quantity of III which was still present, the only other product which was obtained on chromatography on alumina was a 40% yield of ferrocene.<sup>15</sup> In particular, no trace was found of the dimer II, a material easily recognizable by its characteristic bridging carbonyl band at 5.57  $\mu$ .

The reaction of I and II was repeated in xylene; 1.17 g. (1.88 mmoles) of tetraphenylcyclobutadienepalladium bromide (I) and 2.0 g. (5.65 mmoles) of cyclopentadienyliron dicarbonyl dimer (II) were refluxed in 100 ml. of xylene for 1 hr. and then filtered. The residue gave 0.92 g. of crude ( $\pi$ -cyclopentadienyl)-( $\pi$ -tetraphenylcyclobutadiene)palladium tetrabromoferrate (IV, M = Pd). The filtrate was reduced in

(15) Based on that required for the reaction:  $2(\text{Ph}_4\text{C}_4)\text{PdBr}_2 + 4(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br} \rightarrow 2(\text{Ph}_4\text{C}_4)\text{Pd}(\text{C}_5\text{H}_5)\text{FeBr}_4 + (\text{C}_5\text{H}_5)_2\text{Fe} + \text{Fe} + 8\text{CO}$ .

**Table III.** ( $\pi$ -Cyclopentadienyl)[ $\pi$ -(4-*exo*-alkoxy-1,2,3,4-tetraphenylcyclobutenyl)]-Metal Complexes

| VIII<br>M | R  | Yield,<br>% | M.p., °C.    | Analyses, % |      |       |             |       |      |       |             |
|-----------|----|-------------|--------------|-------------|------|-------|-------------|-------|------|-------|-------------|
|           |    |             |              | Calcd.      |      |       |             | Found |      |       |             |
|           |    |             |              | C           | H    | M     | Mol.<br>wt. | C     | H    | M     | Mol.<br>wt. |
| Pd        | H  | 74          | 158–159 dec. | 72.71       | 4.81 | 19.56 | 545         | 72.58 | 4.99 | 19.48 | 562         |
| Pd        | Me | 61          | 152–154 dec. | 72.40       | 5.15 | 19.45 | 567         | 72.91 | 5.03 | 19.21 | 544         |
| Pd        | Et | 64          | 150–154 dec. | 73.35       | 5.28 | 18.56 | 573         | 73.24 | 5.27 | 18.73 | 595         |
| Ni        | Me | 78          | 139 dec.     | 79.85       | 5.52 | 11.48 | 511         | 79.67 | 5.70 | 11.30 | 520         |

volume and chromatographed on alumina to give 0.2 g. of ferrocene and 0.1 g. (11%) of tetraphenylcyclobutadieneiron tricarbonyl (both identified by melting point and infrared spectra) in addition to *ca.* 0.7 g. of dimer II.

*Conversion of the Tetrabromoferrates (IV) into the Bromides (VII).* A solution of 1.9 g. (2.1 mmoles) of ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)palladium tetrabromoferrate in 200 ml. of dichloromethane was added to a solution of 0.9 g. (2.14 mmoles) of potassium ferrocyanide in 30 ml. of water. The mixture was stirred vigorously (to ensure efficient mixing of the two phases) and, after a few minutes, the aqueous layer became blue owing to the formation of a precipitate of Prussian blue. Stirring continued for 2.5 hr., and the solution was then poured through a large sintered glass funnel (no suction) which retained the aqueous layer and the Prussian blue precipitate and allowed the dichloromethane solution to pass. This was then dried ( $\text{Na}_2\text{SO}_4$ ), filtered, and concentrated to 50 ml. Slow addition of petroleum ether (b.p. 30–60°) caused the formation of 1.06 g. (83%) of orange crystals of ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)palladium bromide, m.p. 193° dec. This compound was diamagnetic and air stable and was recrystallized from dichloromethane-petroleum ether as above.

( $\pi$ -Cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)-nickel tetrabromoferrate (IV, M = Ni) was converted into the diamagnetic bromide VII (M = Ni) in 92% yield by the same method. This was a stable yellow-orange crystalline compound, m.p. 187° dec. The analyses of these compounds are listed in Table II and the proton resonances in Table I.

( $\pi$ -Cyclopentadienyl)[ $\pi$ -(4-*exo*-alkoxy-1,2,3,4-tetraphenylcyclobutenyl)]-Metal Complexes (VIII). A solution (1.3 ml.) of sodium methoxide (from 0.25 g. of sodium) in 13 ml. of methanol (*i.e.*, 1.1 mmoles) was added to a solution of 0.5 g. (0.82 mmole) of ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)palladium bromide (VII, M = Pd) in 30 ml. of methanol. An orange crystalline precipitate (0.4 g.), of the product and sodium bromide, formed immediately and was filtered off. It was recrystallized by dissolving in 15 ml. of benzene, filtering, and adding 60 ml. of methanol. A yield of 0.28 g. (61%) of dark red crystals of ( $\pi$ -cyclopentadienyl)[ $\pi$ -(4-*exo*-methoxy-1,2,3,4-tetraphenylcyclobutenyl)]palladium (VIII, M = Pd, R = Me) was obtained.

The other complexes (VIII) were obtained by similar procedures, except for the ( $\pi$ -cyclopentadienyl)[ $\pi$ -(4-*exo*-hydroxy-1,2,3,4-tetraphenylcyclobutenyl)]palladium (VIII, M = Pd, R = H) where a suspension of VIII (M = Pd) in benzene was shaken with an 0.8%

aqueous solution of sodium hydroxide. The product dissolved in the benzene layer and was obtained by evaporation followed by crystallization. The yields and analyses of these complexes are listed in Table III, the proton resonances in Table I.

( $\pi$ -Cyclopentadienyl)[ $\pi$ -(4-*exo*-ethoxy-1,2,3,4-tetraphenylcyclobutenyl)]palladium was also prepared by another route. A solution of 2.5 mmoles of sodium cyclopentadienide in 1.5 ml. of tetrahydrofuran was added to a suspension of 0.95 g. (1.75 mmoles) of di- $\mu$ -chlorobis[ $\pi$ -(4-*exo*-ethoxy-1,2,3,4-tetraphenylcyclobutenyl)]palladium (X) in 10 ml. of dry tetrahydrofuran under nitrogen at 0°. The solution darkened rapidly, and after 10 min. the solvent was removed on a rotary evaporator at 30°. Extraction of the residual solid with boiling, degassed petroleum ether (b.p. 30–60°) and crystallization from this solvent gave 0.10 g. (10%) of dark red crystals of ( $\pi$ -cyclopentadienyl)[ $\pi$ -(4-*exo*-ethoxy-1,2,3,4-tetraphenylcyclobutenyl)]palladium (VIII, M = Pd, R = Et), m.p. 152° dec., m.m.p., with an authentic sample, 152°. The infrared spectra of the two samples were identical.

*Reconversion of Complexes VII (M = Pd) and VIII (M = Pd) into I.* The ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)palladium bromide (VII, M = Pd) and the ( $\pi$ -cyclopentadienyl)[ $\pi$ -(4-*exo*-alkoxy-1,2,3,4-tetraphenylcyclobutenyl)]palladium complexes (VIII, M = Pd) were all rapidly converted into tetraphenylcyclobutadienepalladium bromide (I) by brief passage of a stream of hydrogen bromide gas through their solutions in dichloromethane. Complex I was obtained in 80% (from IV, M = Pd), 86% (from VIII, M = Pd, R = H), 83% (from VIII, M = Pd, R = Me), and 97% yield (from VIII, M = Pd, R = Et) and identified by melting point and infrared spectra. Since it was probable that the reaction of VIII (M = Pd) with HBr proceeded *via* IV (M = Pd), a reaction was run in benzene with the hope of isolating the intermediate IV. However, although the infrared spectrum showed the presence of some IV (M = Pd) in the product, even in benzene in which IV is insoluble, the major reaction product was again I.

*Reaction of ( $\pi$ -Cyclopentadienyl)[ $\pi$ -(4-*exo*-methoxy-1,2,3,4-tetraphenylcyclobutenyl)]nickel with Hydrogen Bromide.* The methoxynickel complex VIII (M = Ni, R = Me), 50 mg., was treated with dry hydrogen bromide in dichloromethane for 10 min. The solution turned pale orange; the solvent was then removed and the solid residue crystallized from dichloromethane-ligroin (b.p. 80–100°) to give 53 mg. (98%) of ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)nickel bromide, identified by melting point and infrared spectrum. No trace of complex V was found.

( $\pi$ -Cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)cobalt (XII). A. As described above the cobalt complex XII was made from tetraphenylcyclobutadiene-cobalt dicarbonyl bromide (XI)<sup>7</sup> and either cyclopentadienyliron dicarbonyl dimer (II) or the bromide (III). Since XIII is readily soluble in benzene, it was isolated from the reaction mixture by crystallization of the residue, after the solvent had been removed, from benzene–ligroin. The yields are given in Table II.

B. A suspension of 0.20 g. (0.33 mmole) of ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)palladium bromide (VII, M = Pd) in 30 ml. of benzene was refluxed for 5 min. under nitrogen. To this was added 2.0 ml. (0.86 mmole) of a solution of dicobalt octacarbonyl in toluene (Alfa Inorganics) and the refluxing continued for 1 hr. After 15 min. of heating, metal began to be deposited and the solution turned black.

The solution was then filtered and the filtrate evaporated to dryness. The residue was dissolved in 1 ml. of benzene and chromatographed on alumina. A yellow band was eluted with 50% benzene–petroleum ether which gave 15 mg. (10%) of a yellow-brown crystalline solid. This was purified by vacuum sublimation to give pure ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylcyclobutadiene)cobalt, m.p. 250–253°, m.m.p., with an authentic sample, 252–254°. The infrared spectra were identical.

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## Exchange of Parts between Molecules at Equilibrium. VI. Scrambling on Titanium of the Alkoxy, Dimethylamino, and Halogen Substituents

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*Scrambling of substituents on titanium was studied for the systems (1) (RO)<sub>4</sub>Ti vs. [(CH<sub>3</sub>)<sub>2</sub>N]<sub>4</sub>Ti, (2) (RO)<sub>4</sub>Ti vs. (R'O)<sub>4</sub>Ti, (3) (RO)<sub>4</sub>Ti vs. TiX<sub>4</sub> where X stands for bromine or chlorine, and (4) [(CH<sub>3</sub>)<sub>2</sub>N]<sub>4</sub>Ti vs. TiCl<sub>4</sub>. Large enthalpies attributable to association effects were measured for an exchange corresponding to a system 1 above with R = C<sub>2</sub>H<sub>5</sub> and a system 2 exchange with R = C<sub>2</sub>H<sub>5</sub> and R' = (CH<sub>3</sub>)<sub>2</sub>CH. Even larger enthalpies were found for the reactions in systems 3 and 4, as expected for big deviations from random scrambling. An attempt is made to assess the contributions of association and non-association effects to the enthalpy of exchange reactions in system 3. The observed rapid rates of exchange are discussed, as are the structures of the various associated species noted in this study.*

Previous publications from this laboratory dealing with scrambling reactions have primarily been concerned with exchange of substituents on main-group central atoms<sup>1,2</sup> of groups IV, V, and VI in the periodic

(1) E. Schwarzmann and J. R. Van Wazer, *J. Am. Chem. Soc.*, **81**, 6366 (1959); E. Fluck, J. R. Van Wazer, and L. C. D. Groenweghe, *ibid.*, **81**, 6363 (1959); K. Moedritzer, G. M. Burch, J. R. Van Wazer, and H. K. Hofmeister, *Inorg. Chem.*, **2**, 1152 (1963); K. Moedritzer and J. R. Van Wazer, *ibid.*, **3**, 139, 268 (1964); J. R. Van Wazer and L. Maier, *J. Am. Chem. Soc.*, **86**, 811 (1964).

(2) L. C. D. Groenweghe, J. H. Payne, and J. R. Van Wazer, *ibid.*, **82**, 5305 (1960); E. Schwarzmann and J. R. Van Wazer, *ibid.*, **82**, 6009 (1960); L. Maier and J. R. Van Wazer, *ibid.*, **84**, 3054 (1962); K. Moedritzer and J. R. Van Wazer, *ibid.*, **86**, 802 (1964); J. R. Van Wazer, K. Moedritzer, and D. W. Matula, *ibid.*, **86**, 807 (1964); M. D. Rausch, J. R. Van Wazer, and K. Moedritzer, *ibid.*, **86**, 814 (1964); D. Grant and J. R. Van Wazer, *ibid.*, **86**, 3012 (1964).

table. Unlike these central atoms, much of the chemistry of which is characterized by the fact that the low-energy orbitals are filled with spin-paired electrons, many of the transition elements as well as those<sup>3</sup> of groups II and III have readily available orbitals which can accept a pair of electrons from another atom and thereby increase the coordination number of the central atom. This paper is one of several devoted to the study of scrambling reactions which are complicated by intermolecular association due to such increase in coordination number of the central atom.

Recent reviews<sup>4</sup> of the chemistry of titanium show that, although scrambling of substituents on titanium is generally recognized, this phenomenon has received little study, and its significance to titanium chemistry is not well understood. Since the nuclear magnetic resonance (n.m.r.) data obtained in this investigation are pertinent to elucidation of the structure of associated molecules, this popular area for research and speculation in titanium chemistry is also treated herein.

### Experiments and Data

*Reagents and Equilibration.* The ethyl titanate was purchased from Eastman Kodak, the isopropyl titanate from K and K Laboratories (Jamaica 33, N. Y.).

(3) H. K. Hofmeister and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*; in press; M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, **3**, 761 (1964).

(4) J. H. Haslam, *Advances in Chemistry Series*, No. 23, 1959, p. 272; I. Shiihara, W. T. Schwartz, and H. W. Post, *Chem. Rev.*, **61**, 1 (1961).