# ORGANOMETALLIC REACTIONS

Edited by

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VOLUME

4

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## Volume 4

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# Preface

The primary literature on organometallic chemistry has undergone phenomenal growth. The number of papers published from 1955 to 1970 is about equal to all prior literature. Together with this intense activity there has developed a complexity in the literature. Thus specialized texts and teaching texts, a review journal, an advances series, and a research journal have all appeared during this period. The present series also reflects this growth and recognizes that many categories of organometallic compounds now have numerous representatives in the literature.

The purpose of *Organometallic Reactions* is to provide complete chapters on selected categories of organometallic compounds, describing the methods by which they have been synthesized, and the reactions they undergo. The emphasis is on the preparative aspects, although structures of compounds and mechanisms of reactions are briefly discussed and referenced. Tables of all of the compounds prepared in the category under consideration and detailed directions for specific types make these chapters particularly helpful to the preparative chemist. While the specific directions have not been refereed in the same way as are those in *Organic Syntheses* and *Inorganic Syntheses*, the personal experiences of the authors often lend special merit to the procedures and enables the reader to avoid many of the pitfalls frequently encountered in selecting an experimental procedure from the literature.

We acknowledge a debt of gratitude to the contributing authors whose dedication and skill in preparing the manuscripts cannot adequately be rewarded. It has been gratifying to note that virtually all invitations to contribute have been accepted at once. We also owe thanks to the publisher for encouragement and even the "gentle prod" when necessary to see these volumes to their completion.

Ernest I. Becker
Minoru Tsutsui
*September 1970*                                             Editors

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# σ–π Rearrangements of Organotransition Metals

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## I. SCOPE AND LIMITATION

Not until 1957 was it recognized that the polyaromatic chromium complexes isolated by Hein in 1921 were in fact the same π-arene complexes[1] that were obtained from the reaction of phenyl Grignard with chromium(III) chloride via an isolable intermediate, tri-σ-phenylchromium.[2] From this beginning has grown the field known as σ-π rearrangements,[3] in which an organic group σ-bonded to a transition metal rearranges to a π-bonded moiety. The σ-π rearrangements have been observed for almost all of the transition metals with a variety of ligands, including groups bonded through an atom other than carbon. These rearrangements are not only of interest in the field of organometallic chemistry but also involved in such industrially important processes using transition-metal catalysts as the Ziegler–Natta polymerization of olefins, the oxo process (hydroformylation of olefins), and in fact homogeneous catalysis in general. The rearrangement is also proposed in such organic reactions as the Cope reaction, which is induced by stoichiometric or catalytic amounts of metallic compounds, and in the Kharasch coupling reaction, again with the organometallic compound in stoichiometric or catalytic amounts.

This chapter attempts to give a general survey of the field, including both the sparse mechanistic data available and experimental details.

The rearrangements are divided into two broad classifications. (No doubt as the field expands, more distinctly different mechanisms may be elucidated.) The first classification involves addition or abstraction of ligands on the metal atom; the second involves rearrangements induced by reactions on the organic moiety. A special case of the second type, cis-ligand insertion, is considered separately.[4] The few examples that are known to not correspond to such dovetailing are dealt with separately.

## II. REACTIONS ON THE METAL

### A. Arene π-Complexes

The one reaction that has been studied in detail is that which leads to Hein's complexes, i.e., π-arenechromium complexes.[1] The reaction of 3 equivalents of phenylmagnesium bromide with 1 equivalent of chromium(III) chloride tristetrahydrofuranate gives bright-red, crystalline tri-σ-phenyl-chromium tristetrahydrofuranate (1), which either by washing with ether or by heating above the boiling point of tetrahydrofuran, or under reduced pressure loses 3 moles of tetrahydrofuran to give a black, pyrophoric solid. This solid, on treatment with deoxygenated water, gives bis(biphenyl) chromium(0) (2) and benzenebiphenylchromium(0) (3) Hein's complexes.

The black solid is paramagnetic and very sensitive to air and water.[2,5] Solvolysis with deuterium oxide leads to the incorporation of one deuterium
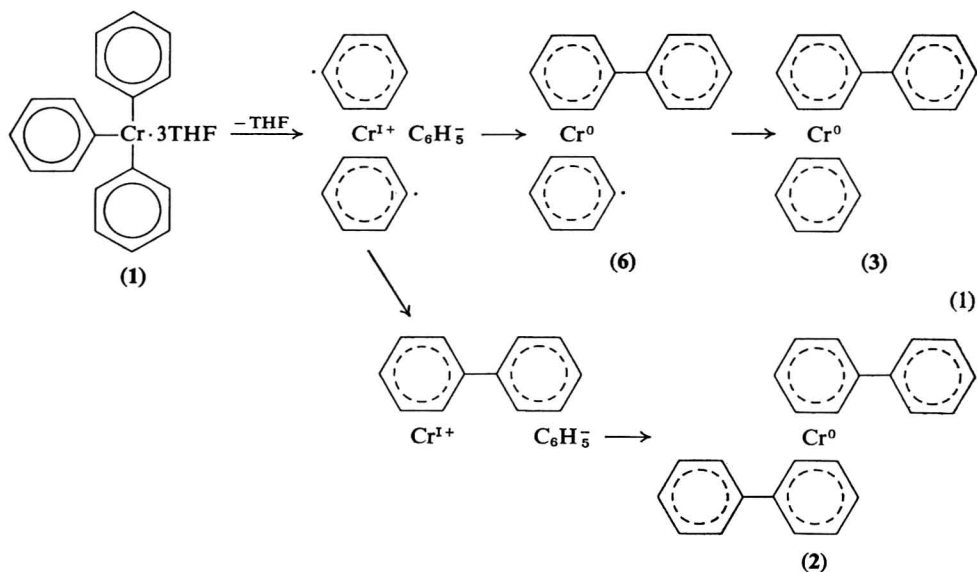
atom into each benzene group but none into the biphenyl moiety.[6] Thermal decomposition gives biphenyl and a complete loss of any $\pi$-character. Zeiss proposed the formation of radical intermediates (the black, pyrophoric solid) to explain these results with reaction scheme (1).[5] The existence of a transition state involving $\pi$-radical hybridization has been postulated, the metal–carbon $\sigma$-bonds cleaving homolytically, with a corresponding three-electron reduction of the chromium to its zero valent state.[7] Investigations with electron-paramagnetic-resonance (EPR) spectroscopy show the homolytic fission of the chromium–carbon bond and the possible formation of radical $\pi$-complexes.[8] A $\pi$-radical hybrid transition state, and proximity of the organic groups to the metal, is supported by the fact that the yield of $\pi$-arenechromium complexes decreases drastically in going from phenyl to benzyl to phenylethyl moieties.[9] From hydrolysis and deuterolysis reactions between phenyl and benzyl Grignards and chromium(III) chloride tristetrahydrofuranate it was concluded that $\pi$-radical formation, hydrogen abstraction, and hydrogen transfer occur within the confines of the intermediate organochromium complexes.[10]

In these examples the $\sigma$-state is stabilized by the fairly good coordinating ability of the tetrahydrofuran ligand and the synergic stabilizing effect of the $\pi$-orbitals on the phenyl group. With cyclopentadienyl groups little stabilization is obtained in the $\sigma$-form: di-$\sigma$-cyclopentadienyliron(III) chloride tetrahydrofuranate rearranges to the $\pi$-ferricinium complex on losing the tetrahydrofuran above $-50°$, on treatment with an organic solvent at $-60°$, or under vacuum at $-60°$.[11]

## B. Addition and Elimination of Carbon Monoxide

Many rearrangements involve the addition or elimination of carbon monoxide from the organometallic compound. The elimination, being accompanied by a σ–π rearrangement, is achieved by irradiation with ultraviolet light or by heating, whereas the reverse reaction is achieved under pressure of carbon monoxide. The question of timing in this reaction—i.e., whether elimination or rearrangement occurs first or whether they occur concurrently—has not been reported.

Thus on irradiation with ultraviolet light σ-alkyl π-cyclopentadienyl-molybdenum tricarbonyl (4)[12] and σ-alkyl π-cyclopentadienyltungsten tricarbonyl (5)[13] compounds give the corresponding π-allene complexes (6) and (7) with the loss of one molecule of carbon monoxide. Irradiation of σ-benzyl π-cyclopentadienylmolybdenum tricarbonyl in hexane gives, with
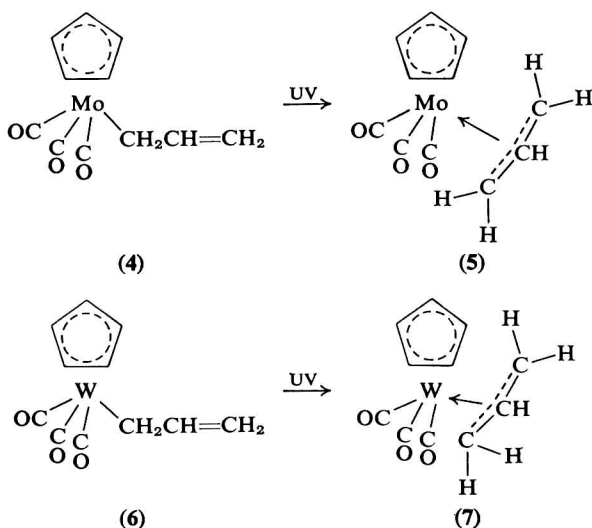


loss of carbon monoxide, a low yield of π-benzyl π-cyclopentadienyl-molybdenum dicarbonyl. The benzyl group is bonded through an allylic system involving three of the carbon atoms. From variable-temperature nuclear-magnetic-resonance (NMR) measurements it is found that the π-benzyl group is sterochemically dynamic.[14] Heating or irradiating with ultraviolet light causes rearrangement of σ-bonded methylthiomethyl π-cyclopentadienylmolybdenum tricarbonyl with loss of carbon monoxide. The structure of the π-complex obtained in this reaction could not be determined unambiguously.[15] Heating σ-allylmanganese pentacarbonyl to 100° causes evolution of one molecule of carbon monoxide, leaving π-allyl-manganese tetracarbonyl.[16,17]

The reaction of carbon monoxide on $\pi$-allylic rhodium complexes of the type $L_2Rh(\pi\text{-}C_3H_4R)Cl_2$ (where $L = Ph_3P$, $Ph_3As$, or $Ph_3Sb$; $R = H$ or $CH_3$) gives $L_2Rh(CO)Cl$, with a methallyl chloride being eliminated. The reaction proceeds via a number of intermediates ($\pi$- and $\sigma$-bonded allylic trivalent rhodium complexes and insertion products). With sulfur dioxide the $\pi$-allylic rhodium complexes give rise to $\sigma$-allylrhodium sulfur dioxide compounds. Ethylene also causes the $\pi$-methallyl group to rearrange to a $\sigma$-bonded moiety.[18]

## C. Addition and Elimination of the Cyanide Ion

Because of the formal similarity of RNC, $CN^-$, and $NO^+$ to CO, similar rearrangements might be expected, but only rearrangements involving addition and abstraction of $CN^-$ are reported. Isomerization is found between $\sigma$- and $\pi$-allylcobalt cyanides: $\sigma$-bonded compounds (8) lose a cyanide ion to give the $\pi$-bonded complexes (9), the rearrangement being reversed on addition of the cyanide ion. Rearrangement of the phenacyl



(8)                    (9)



(10)                    (11)
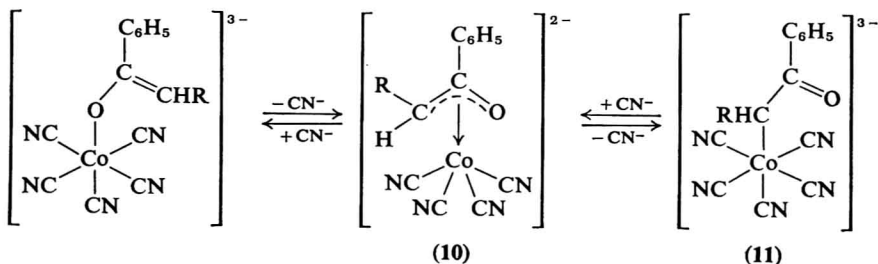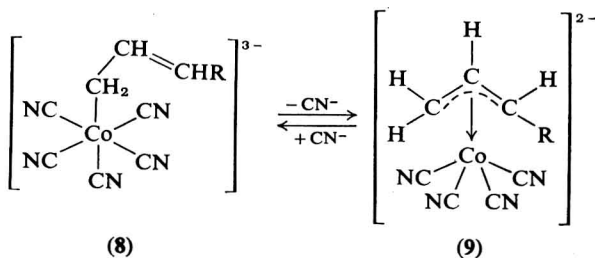
group is also noted, although complexes (10) and (11) were not obtained in a pure state.[19]

Analogous $\sigma$–$\pi$ structures have been proposed as determining the stereoselectivity of the butene products obtained by the hydrogenation of butadiene, catalyzed by the pentacyanocobaltate(II) ion. With excess ion, 1-butene is the major product formed exclusively from a $\sigma$-butenyl intermediate. In the absence of excess cyanide ion trans-2-butene is the major product and

may derive from either a π-butenyl complex or an isomeric σ-butenyl compound in equilibrium with the π-structures.[20]

## D. Temperature- and Solvent-Dependent Equilibrium and Nonrigidity

Recently considerable discussion has arisen on the nature of the stereochemically nonrigid metal allyl compounds. Variable-temperature NMR measurements have been used extensively in attempts to understand their nature. On sufficient cooling a spectrum of a static, rigidly bound π-allyl is often observed. On warming, however, the static π-allyl resonances coalesce to the more simple spectrum of a dynamic allylic group. Internal rotation[21,22] and σ-π rearrangements have been proposed as explanations of the phenomenon.

Allylpalladium chloride (12) is dimeric in the solid state,[23] but in benzene and dioxane solutions a dimer–monomer (75:25%) equilibrium has been suggested from cryoscopic and dipole-moment measurements.[24] The NMR spectrum of compound (12) in dimethyl sulfoxide (DMSO) shows only one proton-resonance peak, explained by the following rapid equilibrium (coordinated DMSO not being shown):[25]

$$CH_2{=}CX{-}\overset{*}{C}H_2{-}Pd{-}Cl \rightleftarrows \overset{*}{C}H_2{=}CX{-}CH_2{-}Pd{-}Cl \qquad (2)$$
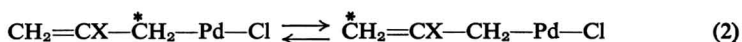
It has been suggested, however, that the variable-temperature (from 25 to 65°) NMR spectrum can be explained by a π-bonded structure for the allylpalladium chloride with hindered rotation of the $CH_2$-group about the C—C bonds.[21] The temperature dependence of the NMR spectra of a number of allylic palladium complexes with various strongly bonding ligands has been studied, and the results have been explained by ligand exchange, followed by a head-over-tail equilibration.[26]

Ligand exchange:

$$\qquad (3)$$

(12)

π–σ Equilibration:

$$\qquad (4)$$

Head-over-tail equilibration:

$$\qquad (5)$$
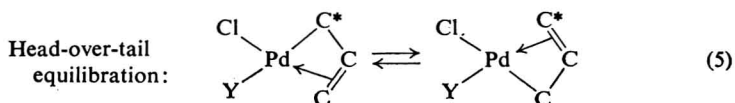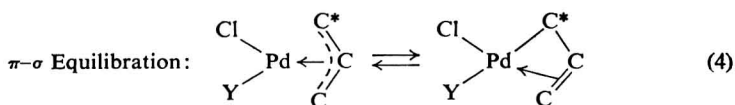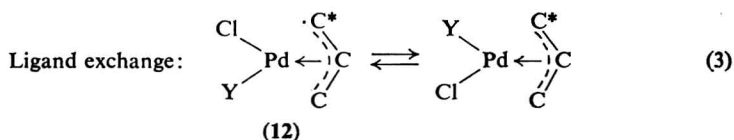
Addition of triphenylphosphine to $\pi$-methallylpalladium chloride (up to 2 moles of phosphine being added) has been observed by study of the NMR spectra and their changes, which indicate that a $\sigma$-compound is formed and then undergoes a rapid head-to-tail exchange of the allylic group. Methallyl-palladium chloride triphenylphosphine is isolated from the reaction mixture, and its NMR spectrum indicates that its structure might be (13), with two carbon atoms weakly bonded to the palladium.[27] X-Ray analysis of (13)



(13)
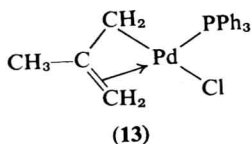
supports this structure.[28] Further work casts doubt on the structure of the intermediate proposed by Shaw et al.[27]

The reactions of $\pi$-allylpalladium chloride with the ligands $PPh_3$, $P(n-C_4H_9)_3$, $P(OCH_2)_3CCH_3$, $AsPh_3$, and $SbPh_3$ have been studied by variable-temperature NMR measurements. It appears that at least three different conformational rearrangements may occur. In the phosphine systems a change occurs, giving rise at a low temperature to an interchange of protons (3) and 4) in compound (14). The fact that protons (1) and (2) maintain their positions is explainable by an intermediate with structure



(14)



(15)
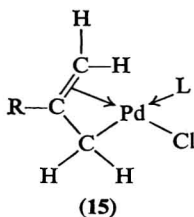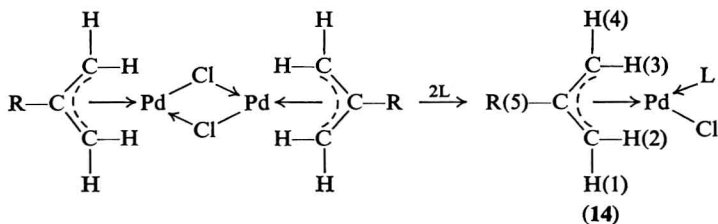
(15). However, study with a high-resolution spectrometer and very low temperatures has demonstrated nonequivalence for all protons. This is explained by an equilibrium between $\pi$- and $\sigma$-moieties, with the equilibrium lying almost completely on the $\pi$-bonded side. The second observable process