Ring-Slippage Chemistry of Transition-Metal Cyclopentadienyl and Indenyl Complexes

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Contents

I. Introduction

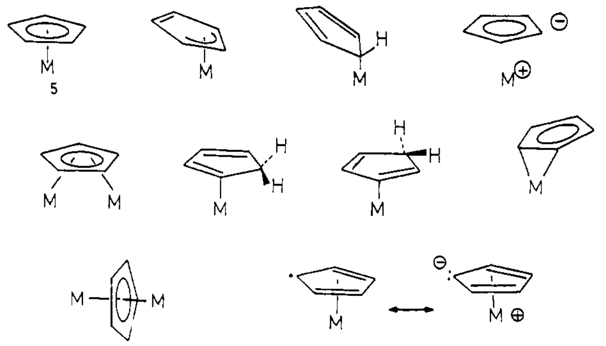
Cyclopentadienyl transition-metal chemistry dates back to the synthesis and characterization of ferrocene over 30 years ago.[1-3] The cyclopentadienyl ligand has since become one of the most extensively utilized ligands in organotransition metal research. At least 10 distinct bonding modes for the C_5H_5 ligand have been structurally characterized to date (Chart I). Of these, the η^5-C_5H_5, η^3-C_5H_5, and η^1-C_5H_5 ligands are of particular interest due to their interconversion chemistry ("ring slippage") and the consequent implications for the design of catalytic systems.

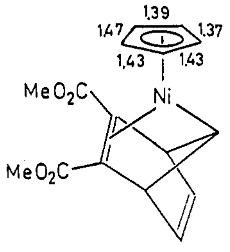
This review concentrates on η^5-, η^3-, and η^1-C_5H_5 ring isomerizations in transition-metal complexes.[4] Coverage includes the historical development, structural and spectroscopic properties of the ligand types, and illustrative examples of the role that C_5H_5 isomerizations have in a number of fundamental organometallic reactions. Related chemistry of the η^5-indenyl ligand is also presented.

II. η^5-Cyclopentadienyl Ligands

For a number of years it was believed that the bonding in all η^5-cyclopentadienyl transition-metal complexes involved a uniform interaction between the five carbon atoms of the C_5H_5 ring and the metal atom. However, in 1963 Dahl and Wei reported structural evidence for localized metal–C_5H_5 bonding in (η^5-C_5H_5)Ni[$C_7H_5(CO_2CH_3)_2$] (1).[5]

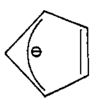
CHART I





1

The following year Bennett made similar bonding observations for a number of π-cyclopentadienyl transition-metal complexes.[6] A localized π-allyl-ene formulism, 2, was suggested in which the allyl portion is always trans to the relatively strong field ligand on the opposite side of the metal.



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In 1967 Wheatley pointed out difficulties in determining the significance of crystallographically observed η^5-C_5H_5 distortions and brought into question whether or not distortions were actually detected.[7] The concept of localized η^5-C_5H_5 bonding in some "noncylindrical" complexes has only recently been verified by Smith for [(η^5-C_5H_5)Ni(η^3-C_3H_4)]$_2$ (3)[8] and by Dahl for (η^5-C_5Me_5)Co(CO)$_2$ (4).[9,10]

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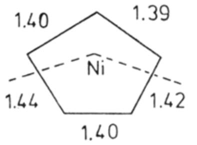

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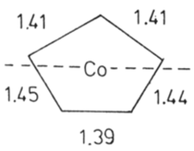

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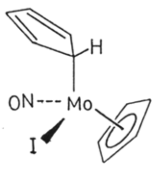
III. η^3-Cyclopentadienyl Ligands

The η^3-cyclopentadienyl ligand proved to be a controversial species for a number of years. In 1968 King reported the synthesis of the neutral, diamagnetic complex $(C_5H_5)_2Mo(NO)(I)$ (**5**), for which a linear nitrosyl stretch was observed at 1648 cm^{-1} in the IR spectrum.[11] King suggested that **5** avoided a 20-electron valence shell configuration by donating only three electrons from one of the C_5H_5 ligands. Although Basolo earlier recognized cyclopentadienyl ring slippage[12] (section VE), this report by King was the first in which a cyclopentadienyl ligand was formulated with η^3 bonding. A crystal structure determination on **5** later disproved the presence of an η^3-C_5H_5 ligand.[13]



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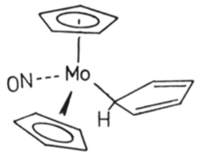
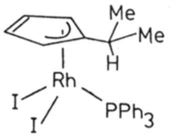
In 1969 Cotton reported the X-ray crystal structure of $(C_5H_5)_3Mo(NO)$ (**6**), for which an $(\eta^1$-$C_5H_5)(\eta^3$-$C_5H_5)(\eta^5$-$C_5H_5)Mo(NO)$ formulation seemed plausible on the basis of the 18-electron rule.[14] However, the structure was shown to consist of an $(\eta^1$-$C_5H_5)(NO)Mo$ unit and two additional cyclopentadienyl ligands in which all 10 carbons had significant bonding interactions with molydenum. Cotton noted that simple geometry requires that a metal atom equidistant from three carbons of a regular planar pentagonal cyclopentadienyl ligand is necessarily equidistant from all five ring carbons. This makes η^3-C_5H_5 and η^5-C_5H_5 geometries indistinguishable, and Cotton stated that "the *concept* of a (trihaptocyclopentadienyl)metal bond... is mythical."[15] However, this rationale leaves open the possibility of a nonplanar η^3-C_5H_5 ligand or a planar η^3-C_5H_5 ligand with unequal carbon–metal distances.



6

Later the same year, King proposed the concept of "interligand resonance" to explain why the X-ray structure of **6** failed to show a distinct η^3 ligand.[16] It was suggested that the skewed C_5H_5 ligand in **6** be considered a resonance hybrid of the η^3 and η^5 ring forms. The structure of **6** was addressed again in 1975 when Cotton referred to the skew C_5H_5 ligands as formally 4-electron donors and designated them as η^4-C_5H_5 ligands.[17]

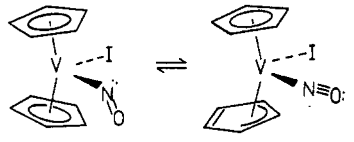
In 1974 Wakatsuki and Yamazaki reported that $(\eta^5$-$C_5H_5)Rh(PPh_3)_2$ reacts with isopropyl iodide to give the (isopropylcyclopentadienyl)(triphenylphosphine)-rhodium diiodide complex **7**.[18] In the ^1H NMR of **7** only two of the four C_5H_4R ring protons were coupled



7

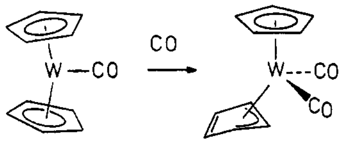
to phosphorus. On the basis of the phosphorus–hydrogen couplings, it was suggested that 7 might be an η^3-C_5H_4R complex. It is not clear why the 5-coordinate, 16-electron, η^3-C_5H_4R formulation of 7 might be preferred over an alternative 6-coordinate, 18-electron η^5-C_5H_4R species, and the authors did not rule out the latter possibility.

Bottomley, Darkwa, and White reported the synthesis of the fluxional, paramagnetic molecule, $(\eta^5$-$C_5H_5)_2V$-(I)(NO) (**8A** and **8B**) in which linear and bent nitrosyl groups interconvert (IR: 1690, 1590 cm^{-1}).[19] For **8B** to adhere to the 18- (17-) electron rule, one C_5H_5 ring may have nonplanar η^3-C_5H_5 bonding or both rings may be bonded in a planar η^4-C_5H_5 fashion.



8A 8B

The proposal of an η^3-cyclopentadienyl ligand was unambiguously substantiated in 1978 when Huttner, Brintzinger, and Bell reported the crystal structure of $(\eta^5$-$C_5H_5)(\eta^3$-$C_5H_5)W(CO)_2$ (**9**).[20,21] The η^3-C_5H_5 ligand in **9** has a 20° angle between the planes of the allyl (C_1, C_2, C_3) and alkene (C_1, C_3, C_4, C_5) portions of the η^3-C_5H_5 ligand. The carbon atoms of the alkene group are 2.98 Å from the metal atom—clearly a nonbonding distance. The η^5-C_5H_5 and η^3-C_5H_5 ligands of **9** interconvert on the NMR time scale as indicated by a singlet in the ^1H NMR spectrum at δ 5.17. The reaction of $(\eta^5$-$C_5H_5)_2W(CO)$ with CO to give **9** represents the first report in which an η^5-C_5H_5 complex was converted into an isolable η^3-C_5H_5 complex.



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IV. η^1-Cyclopentadienyl Ligands

Within 3 years of the determination of the structure of ferrocene, the first η^1-C_5H_5 transition-metal complexes were reported in the literature.[22,23] X-ray studies indicate that the five-carbon ring is nearly planar and that the angle between the metal, the sp^3 ring carbon, and the ring center of gravity is ~120°.[24]

The η^1-C_5H_5 ligand in **6** has a Mo–C distance of 2.29 Å and C–C distances of 1.47 (C_1–C_2), 1.35 (C_2–C_3), 1.44 (C_3–C_4), 1.34 (C_4–C_5), and 1.47 (C_5–C_1). The largest deviation of a carbon from the mean plane of the ring is 0.013 Å.[14]

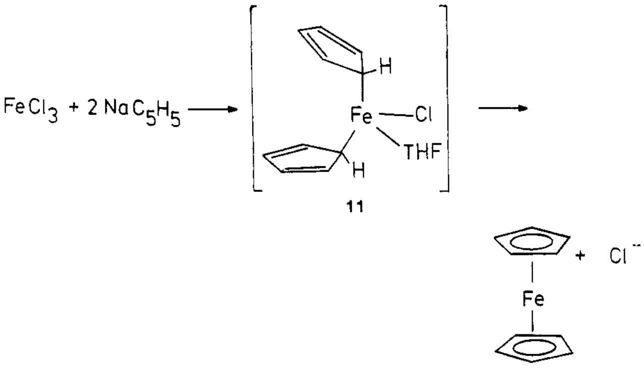
The room-temperature NMR spectra of η^1-C_5H_5 ligands typically exhibit one resonance for the protons due to rapid migration of the metal around the ring via a series of sequential 1,2-shifts. Although is some cases such as $(\eta^5$-$C_5H_5)(\eta^1$-$C_5H_5)Fe(CO)_2$ this fluxional process may be frozen out on the NMR time scale, more often this is not possible.[25] Faller, Murray, and Saunders utilized isotopic perturbation of degeneracy to distinguish fluxional η^1- and η^5-C_5H_5 rings by NMR spectroscopy.[26]

V. Interconversions of Cyclopentadienyl Ligands

By 1968 it was clear from various physical studies (vide infra) that the C_5H_5 ligand was capable of η^5, skew η^5, and η^1 forms, yet there were no reports of η^5 to η^1 interconversions.

In 1968 Ustynyuk reported that $(\eta^5$-$C_5H_5)_2$ Ni reacts with PPh_3 at 50 °C to give a green unstable solid formulated as $(\eta^1$-$C_5H_5)(\eta^5$-$C_5H_5)Ni(PPh_3)$ (**10**).[27] Compound **10** was not isolated, and characterization consisted of reaction with CCl_4/HCl to give $(\eta^5$-$C_5H_5)Ni$-$(PPh_3)Cl$ and with I_2 to give $(\eta^5$-$C_5H_5)Ni(PPh_3)I$.

In 1969 Tsutsui and co-workers reported evidence for an η^1-C_5H_5 intermediate, **11**, in the reaction of $FeCl_3$ and NaC_5H_5 to give ferrocenium chloride.[28,29] The spectroscopic evidence for **11** was an IR stretch at 1620 cm^{-1} attributed to the conjugated double bonds in the η^1-C_5H_5 ring. Other evidence for **11** was reaction with CH_3OH/HCl to give $FeCl_3$ and polymeric cyclopentadiene and reaction with maleic anhydride to give an uncharacterized compound that could be hydrolyzed to *endo*- and *exo*-bicyclo[2.2.1]hept-5-ene 2,3-anhydrides.



Cross and Wardle reported that a low yield of $(\eta^1$-$C_5H_5)Pd(PEt_3)_2Br$ was formed from the reaction of $(\eta^5$-$C_5H_5)Pd(PEt_3)Br$ and PEt_3.[30] The evidence was a ^1H NMR resonance at δ 6.37 attributed to the η^1-C_5H_5 ligand.

In 1971 Cotton reported the variable-temperature ^1H NMR of $(\eta^5$-$C_5H_5)_2Ti(\eta^1$-$C_5H_5)_2$ (**12**), for which he was able to observe η^1 to η^5 cyclopentadienyl interconversions.[31,32] Although no intermediates were observed, Cotton later proposed an $(\eta^1$-$C_5H_5)(\eta^4$-$C_5H_5)_2(\eta^5$-$C_5H_5)Ti$ intermediate, **13**, for these η^1 to η^5 interconversions.[17] Atwood and co-workers have structurally characterized the related complex $(C_5H_5)_4Zr$ and found one η^1-C_5H_5 ligand and three η^5-C_5H_5 ligands in which the Zr–C distances are longer than expected.[33]

$$(\eta^1\text{-}C_5H_5^*)_2(\eta^5\text{-}C_5H_5)_2Ti$$

12

$$\rightleftharpoons$$

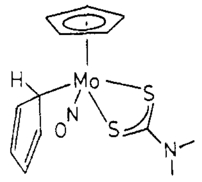
$$(\eta^1\text{-}C_5H_5^*)(\eta^4\text{-}C_5H_5^*)(\eta^4\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Ti$$

13

$$\rightleftharpoons$$

$$(\eta^1\text{-}C_5H_5^*)(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5^*)(\eta^5\text{-}C_5H_5)Ti$$

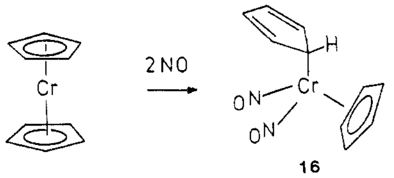
Cotton also proposed $(\eta^4$-$C_5H_5)_2$ intermediates for the η^5- to η^1-C_5H_5 interconversions observed by McCleverty[34] in the variable-temperature ^{1}H NMR of $(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Mo(NO)(S_2CNMe_2)$ (**14**).[17] Cotton suggested that the ring exchange in **14** was facilitated by the conversion of a 3-electron NO or S_2CNR_2 ligand to a 1-electron-donor ligand. McCleverty later expressed reservations concerning Cotton's proposed η^4-cyclopentadienyl intermediate and suggested an $\eta^3\text{-}C_5H_5$ intermediate as an alternative.[35]



14

Werner and Kraus also observed η^5- to $\eta^1\text{-}C_5H_5$ ligand exchange in $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Pd(P(i\text{-}Pr)_3)$ (**15**) and proposed a $(\eta^3\text{-}C_5H_5)_2$ intermediate.[36]

In 1978 Hames, Legzdins, and Martin reported the first case in which an $\eta^5\text{-}C_5H_5$ complex, $(\eta^5\text{-}C_5H_5)_2Cr$, was converted to an isolable, well-characterized $\eta^1\text{-}C_5H_5$ complex, $(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Cr(NO)_2$ (**16**).[37]



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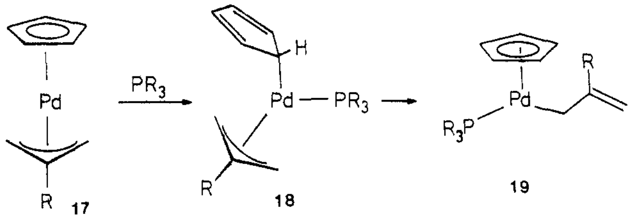
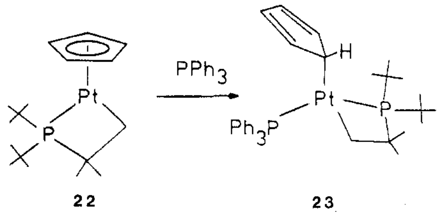
The following year, Werner and Kühn reported the conversion of an $\eta^5\text{-}C_5H_5$ complex, **17**, to an isolable $\eta^1\text{-}C_5H_5$ complex, **18**, induced by addition of a neutral 2-electron-donor ligand.[38] In solution, **18** was shown to be in equilibrium with an $(\eta^5\text{-}C_5H_5)(\eta^1\text{-allyl})$ complex, **19**.



17 **18** **19**

In 1980 Casey and Jones reported that $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_3)$ (**20**) reacts reversibly with 2 equiv of PMe_3 to produce $(\eta^1\text{-}C_5H_5)Re(CO)(NO)(CH_3)(PMe_3)_2$ (**21**) (vide infra).[39]

Goel and co-workers reported the related reaction of $(\eta^5\text{-}C_5H_5)Pt(CH_2CMe_2P(t\text{-}Bu)_2)$ (**22**) and PPh_3 to give $(\eta^1\text{-}C_5H_5)Pt(CH_2CMe_2P(t\text{-}Bu)_2)(PPh_3)$ (**23**).[40] The ^{1}H NMR resonance for the $\eta^1\text{-}C_5H_5$ ligand in **23** is a triplet at δ 6.24 (J_{PH} = 3.4 Hz).

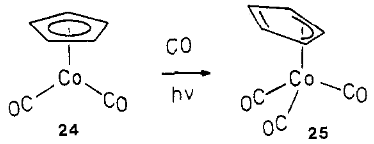


22 **23**

The structures of **18**, **21**, and **23** were confirmed by X-ray crystallography.

A. Photoinduced $\eta^5\text{-}C_5H_5$ to $\eta^3\text{-}C_5H_5$ Ring Slippage

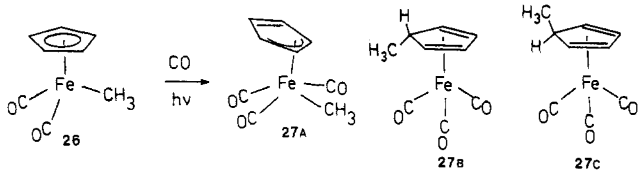
In some cases it is possible to photochemically generate $\eta^3\text{-}C_5H_5$ metal complexes from $\eta^5\text{-}C_5H_5$ precursors. Crichton, Rest, and Taylor have reported that photolysis of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (**24**) in a pure CO matrix (12 K) led to a decrease in the IR bands for **24** (2032, 1972, 817 cm^{-1}) and the appearance of a new bands at 2075, 2018, and 781 cm^{-1}, attributed to **25**.[41] A comparison



24 **25**

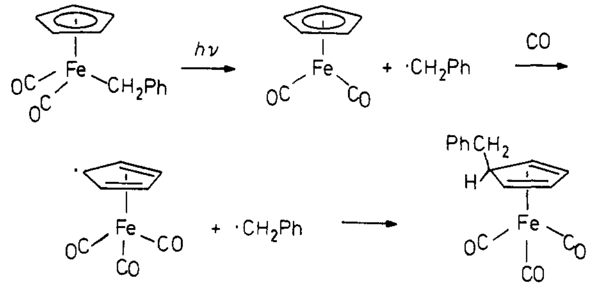
of the observed and calculated spectra for ^{13}CO-substituted **24** and **25** indicated that **25** contained an $M(CO)_3$ fragment with C_{3v} symmetry. Additional support for an $\eta^3\text{-}C_5H_5$ ligand in **25** came from the similarity of its IR spectrum to that of $(\eta^3\text{-}C_3H_5)Co(CO)_3$, which has IR bands at 2076 and 2025 cm^{-1} in the gas phase.

Rest and co-workers carried out a related study on $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ (**26**) and again observed a shift of the ν(CO) IR bands to higher wave number (2050, 1982, 1975 cm^{-1}), as expected for an increase in the number of CO ligands.[42,43] A low conversion to the presumed $\eta^3\text{-}C_5H_5$ tricarbonyl product, **27A**, precluded ^{13}CO labeling studies. An additional complication in this case arises from the potential for metal to ring methyl migration upon addition of CO to give **27B**.



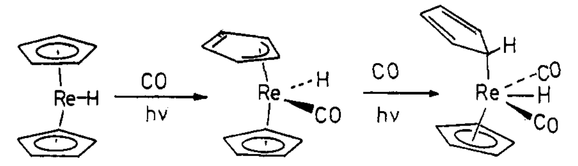
26 **27A** **27B** **27C**

Blaha and Wrighton studied the related photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Ph$ in the presence of added ligand (CO, PPh_3) and observed the formation of $(\eta^4\text{-}C_5H_5CH_2Ph)Fe(CO)_2L$.[44] Their mechanism involved



generation of $(\eta^4\text{-}C_5H_5)Fe(CO)_2L$ and $CH_2C_6H_5$ radicals that couple to give $(\eta^4\text{-}C_5H_5CH_2Ph)Fe(CO)_2L$. It was also noted that $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ exhibits IR bands at 2050, 1982, and 1975 cm^{-1} of relative intensities nearly identical with those attributed to **27A** by Rest.[42,43] It thus appears that $(\eta^4\text{-}C_5H_5CH_3)Fe(CO)_3$ (**27B** or **27C**) must be considered as an alternative to **27A**.

More recently, Perutz and co-workers obtained evidence for the formation of $(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Re(CO)H$ (**28**) upon photolysis of $(\eta^5\text{-}C_5H_5)_2ReH$ (**29**) in a CO matrix.[45] Compound **28** is formulated as an $\eta^3\text{-}C_5H_5$ monocarbonyl species on the basis of a CO stretch at 1918 cm^{-1}, which is shifted to 1921 cm^{-1} in the deuteride **28**-d_1. In a ^{12}CO/^{13}CO (1/1) matrix, bands are observed



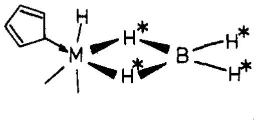
29 28 30

at 1918 and 1872 cm^{-1}. The absence of bands between 1918 and 1872 cm^{-1} supports the monocarbonyl formulation. Continued irradiation leads to the formation of the (η^1-C_5H_5) dicarbonyl complex **30**.

The validity of the conclusions arrived at in these matrix studies requires adherence of the compounds to the 18-electron formalism. Characteristic infrared data for the η^3-C_5H_5 ligand are not firmly enough established to permit direct observation of an η^3-C_5H_5 ligand by IR spectroscopy.

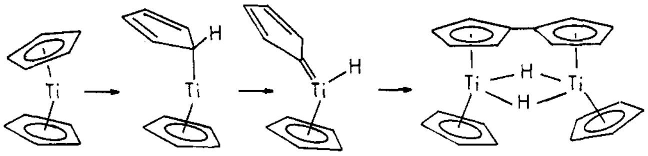
B. α-Hydrogen Abstraction

Marks and Kolb observed the exchange of η^5-C_5H_5 hydrogens with BH_4 hydrogens in the complex (η^5-C_5H_5)$_2$Zr(H)(BH_4) and suggested the possibility of η^1-C_5H_5, η^3-C_5H_5, and cyclopentadienylidene (**A**) zirconium intermediates.[46] Direct evidence for a cyclopentadienylidene transition-metal complex has not yet been reported in the literature.



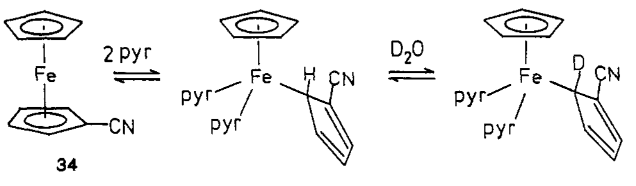
A

For the rearrangement of (η^5-C_5H_5)$_2$Ti to dimer **31**, Brintzinger and Bercaw suggested formation of an η^1-C_5H_5 titanium complex, **32**, followed by α-H abstraction to give titanafulvene intermediate **33**.[47] Neither **32** nor **33** was observed, although there is ample precedent for η^5-C_5H_5 to η^1-C_5H_5 ring slippage in other titanium complexes (vide infra).[31,32] There is no clear precedent for α-H abstraction from η^1-C_5H_5 ligands.



32 33 31

Slocum and co-workers observed isotopic exchange of deuterium for hydrogen in ferrocenes containing electron-withdrawing substituents on the cyclopentadienyl ligand.[48,49] When 9% D_2O–pyridine solutions of cyanoferrocene were refluxed for 6 h, (η^5-C_5H_5)Fe(η^5-C_5D_4CN) (**34**) was formed in low yield.



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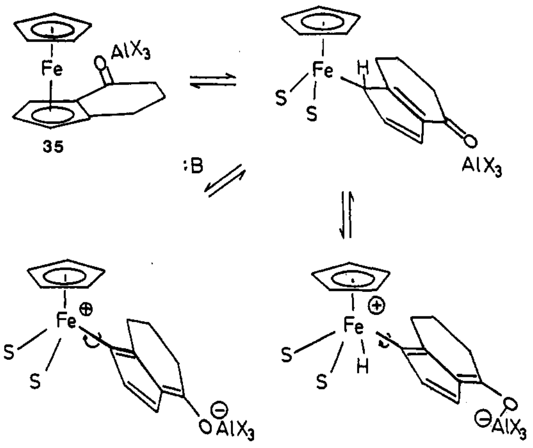
Deuterium exchange occurred only in the substituted cyclopentadienyl ring. Examination of a variety of substituents indicated that the exchange did not correlate with π-cyclopentadienyl ring proton acidity. Added NaOD increased the reaction rate by about 2 and led Slocum to suggest a mechanism involving a rate-determining η^5 to η^1 rearrangement followed by deuterium exchange with the proton on the sp^3 carbon.

Chiral ferrocenylcyclohexenone–aluminum trichloride complex **35** has been proposed by Astruc[50] and Slocum[51,52] to undergo η^5 to η^1 interconversions, followed by either base abstraction of an α-hydrogen or insertion of Fe into a C–H bond, to explain an intramolecular racemization reaction. The proposed intermediates were not observed.



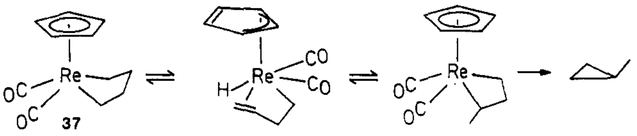
C. β-Hydrogen Elimination

Marks reported that (η^5-C_5H_5)$_3$Th(i-C_3H_7) (**36**), which is thermally inert toward β-hydride elimination, gives (C_5H_5)$_3$Th (92%), propane (53%), and propene (47%), upon photolysis.[53] Marks interpreted this reaction as the result of a β-hydride elimination sequence in which a photoinduced C_5H_5 ring slip opens up the necessary coordination site on thorium.

$$\underset{\mathbf{36}}{(C_5H_5)_3ThCH(CH_3)_2} \xrightarrow{h\nu} (C_5H_5)_3ThH + CH_2{=}CHCH_3$$

$$(C_5H_5)_3ThH + (C_5H_5)_3ThCH(CH_3)_2 \longrightarrow 2(C_5H_5)_3Th + CH_3CH_2CH_3$$

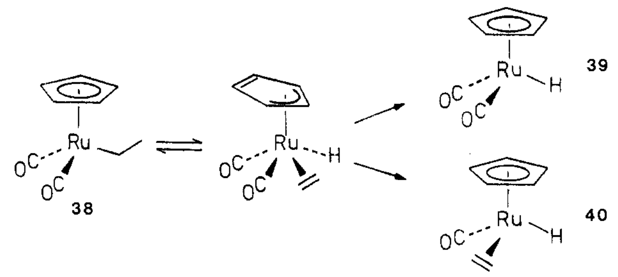
Bergman and Yang observed the conversion of a metallacyclopentane complex, (η^5-C_5H_5)Re(CO)$_2$(CH_2)$_4$ (**37**), to methylcyclopropane.[54] Labeling studies provided evidence in support of a β-hydride elimination/readdition mechanism in which an η^5 to η^3 ring slip was proposed as an intermediate step.



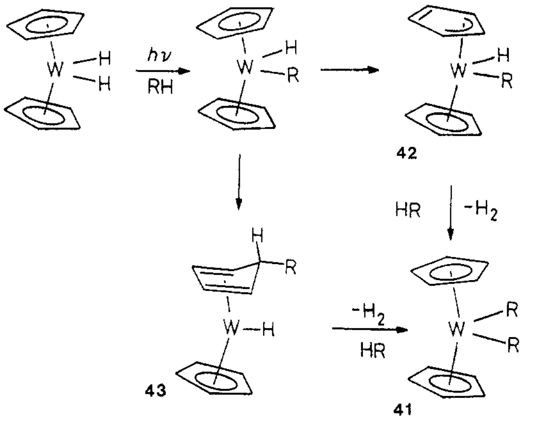
More recently, Rest, Alt, and Mahmoud found that photolysis of (η^5-C_5H_5)Ru(^{12}CO)$_2$(CH_2CH_3)* (**38**) in ^{13}CO-doped CH_4 matrices gave (η^5-C_5H_5)Ru(^{12}CO)$_2$H (**39**) and (η^5-C_5H_5)Ru(^{12}CO)(C_2H_4)H (**40**).[43] Photolysis of **38** at high dilution in a pure CO matrix led to the observation of new IR bands tentatively assigned to (η^3-C_5H_5)Ru(CO)$_3$(CH_2CH_3).

D. C–H and C–C Bond Cleavage

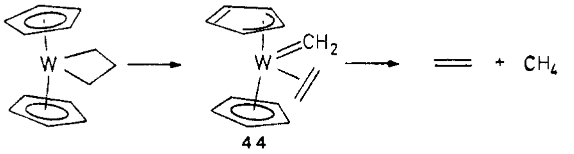
M. L. H. Green has suggested photochemically induced η^5- to η^3-C_5H_5 rings shifts to explain both the insertion of tungsten into carbon–hydrogen bonds[55] and the decomposition of tungsten metallacyclobutanes.[55,57]



When $(\eta^5\text{-}C_5H_5)_2WH_2$ was irradiated in *p*-xylene, a dialkyl product **41** was isolated. Green proposed an $\eta^3\text{-}C_5H_5$ intermediate, **42**, as a possibility in this and related C–H insertion reactions. Reversible metal to ring alkyl migration to give intermediate **43** could not be ruled out.



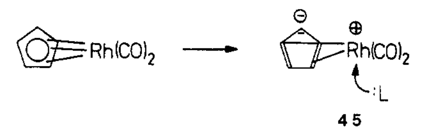
Irradiation of $(\eta^5\text{-}C_5H_5)_2W(CH_2CH_2CH_2)$ in hexane is reported to give ethylene in low yield.[56] Green used circumstantial evidence such as the reaction of $\eta^3\text{-}C_5H_5$ complex **9** to give $(\eta^5\text{-}C_5H_5)_2W(CO)$[20] as support for $\eta^3\text{-}C_5H_5$ intermediate **44** in the formation of ethylene.



Rest, Graham, and co-workers observed the formation of $(\eta^5\text{-}C_5R_5)Ir(CO)(CH_3)H$ upon photolysis of $(\eta^5\text{-}C_5R_5)Ir(CO)_2$ in CH_4 matrices at 12 K.[58] In Ar or N_2 matrices only a trace amount of $(\eta^5\text{-}C_5R_5)Ir(CO)$ was formed. In ^{13}CO-doped matrices exchange with ^{12}CO was very slow. On the basis of these observations, the authors suggested an $\eta^5\text{-}C_5R_5$ to $\eta^3\text{-}C_5R_5$ ring slip may open up the coordination site necessary for interaction with CH_4.

E. Ligand Substitution

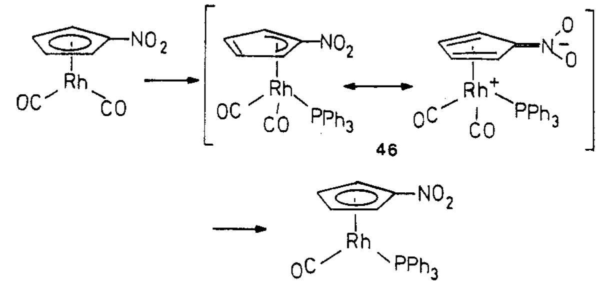
In 1966 Basolo noted that the rate of reaction between PPh_3 and the coordinatively saturated complexes $(\eta^5\text{-}C_5H_5)M(CO)_2$ (M = Rh, Co) to give $(\eta^5\text{-}C_5H_5)M(CO)PPh_3$ was unusually fast and depended on the concentration of both metal complex and phosphine.[12] To explain these associative substitution reactions, it was proposed that slippage of the cyclopentadienyl ring occurs as phosphine attacks to produce the $\eta^4\text{-}C_5H_5^-$ intermediate **45**. This proposal was the first recognition that reversible $\eta^5\text{-}C_5H_5$ ring slippage reactions have a role in the ligand substitution chemistry of cyclopentadienyl metal complexes.



In 1983 Basolo reformulated this $\eta^4\text{-}C_5H_5^-$ intermediate as an $\eta^3\text{-}C_5H_5$ complex and proposed a similar intermediate for the related associative substitution reactions of $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$.[59]

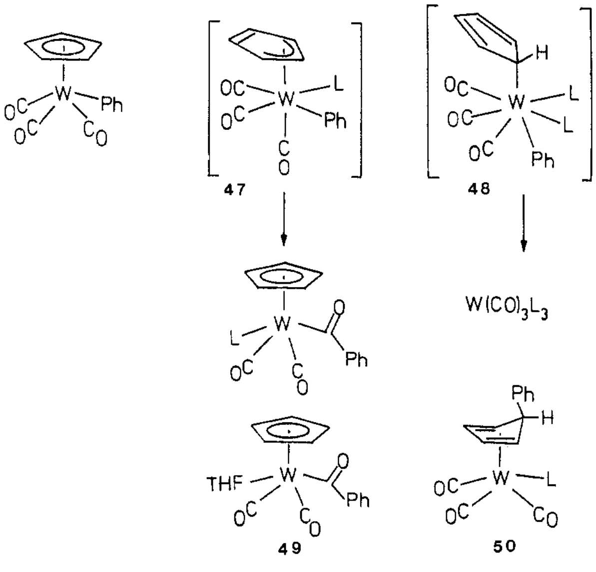
More recently, Basolo and Rerek studied the kinetics and mechanism of PPh_3 substitution reactions for other $(\eta^5\text{-cyclopentadienyl})(\text{dicarbonyl})$rhodium derivatives.[60] Again the reactions are first order in both metal complex and PPh_3. The rates of reaction follow the order $(\eta^5\text{-}C_9H_7)Rh(CO)_2 > [\eta^5\text{-}C_9(CH_3)_7]Rh(CO)_2 > (\eta^5\text{-}C_5H_4NO_2)Rh(CO)_2 > (\eta^5\text{-}C_5H_4PPh_3)Rh(CO)_2^+ \gg (\eta^5\text{-}C_5H_5)Rh(CO)_2$.

For nitro derivative $(\eta^5\text{-}C_5H_4NO_2)RhCO)_2$, a fulvenic resonance structure, **46**, at the transition state, apparently accelerates the reaction rate relative to that for $(\eta^5\text{-}C_5H_5)Rh(CO)_2$.

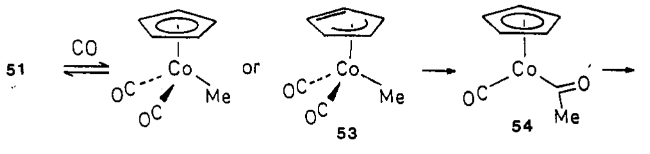


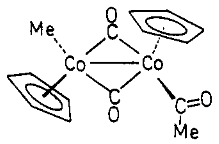
Cramer previously used a kinetic argument to support a proposed $(\eta^3\text{-}C_5H_5)Rh(C_2H_4)_2(PPh_3)$ intermediate in the associative C_2H_4 substitution reactions of $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2$.[61]

Nesmeyanov suggested both $\eta^3\text{-}C_5H_5$ and $\eta^1\text{-}C_5H_5$ intermediates, **47** and **48**, in the reaction of $(\eta^5\text{-}C_5H_5)W(CO)_3(C_6H_5)$ with PPh_3 to give $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(COC_6H_5)$ and $W(CO)_3(PPh_3)_3$.[62] Intermediates **47** and **48** were not supported by spectroscopy or kinetic evidence, and Nesmeyanov suggested compounds **49** and **50** could also be feasible intermediates.



Bergman and co-workers carried out kinetic studies on the reaction of $[(\eta^5\text{-}C_5H_5)Co(CO)CH_3]_2$ (**51**) with CO to give $[(\eta^5\text{-}C_5H_5)Co(CO)]_2(CH_3)(COCH_3)$ (**52**) and suggested the involvement of mononuclear η^5-C_5H_5 or η^3-C_5H_5 odd-electron intermediates, **53** and **54**.[63]

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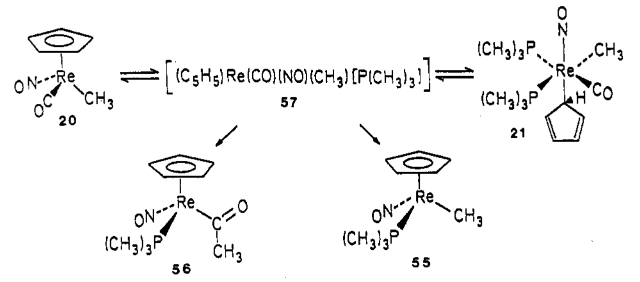
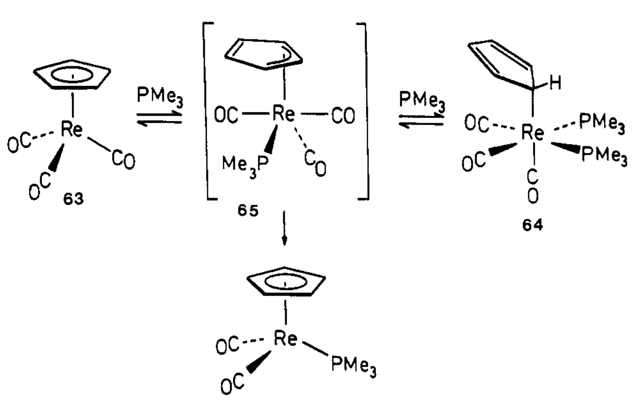
Casey and co-workers reported structural evidence for the formation of η^1-C_5H_5 intermediates in the phosphine substitution reactions at coordinatively saturated η^5-C_5H_5 metal centers. The reaction of (η^5-C_5H_5)Re(NO)(CO)(CH_3) (**20**) with 2 equiv of PMe_3 at 25 °C yields the bis(phosphine) adduct (η^1-C_5H_5)Re(NO)(CO)(CH_3)(PMe_3)$_2$ (**21**) in which the η^5-C_5H_5 ring has slipped all the way to an η^1-C_5H_5 configuration.[39,64,65] Upon being heated to 90 °C, **20** and **21** equilibrate and are converted to a mixture of phosphine-substituted methyl compound **55** and the phosphine-substituted acetyl compound **56**. The rate of formation of **21** depends on the concentration of both **20** and PMe_3 and thus requires a mono(phosphine) adduct **57** as an intermediate. Three possible 18-electron structures for such an intermediate are an η^3-C_5H_5 linear nitrosyl, an η^4-$C_5H_5CH_3$ linear nitrosyl, or an η^5-C_5H_5 bent nitrosyl compound.



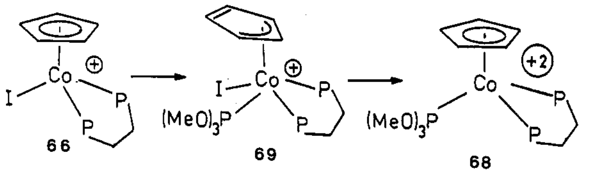
The reactions of (η^5-C_5H_5)Mo(CO)$_2$(NO) (**58**) and (η^5-C_5H_5)W(CO)$_2$(NO) (**59**) with PMe_3 at -60 °C also give observable bis(phosphine) η^1-cyclopentadienyl compounds (η^1-C_5H_5)Mo(CO)$_2$(NO)(PMe_3)$_2$ (**60**) and (η^1-C_5H_5)W(CO)$_2$(NO)(PMe_3)$_2$ (**61**).[64,65] Compounds **60** and **61** are unstable at room temperature and decompose to starting material and η^5-C_5H_5 mono(phosphine) adducts. The reactions of **58** and **59** with PMe_3 also show second-order kinetics and require a mono(phosphine) intermediate, **62**. Since both **58** and **59** contain a nitrosyl ligand, there are two possible 18-electron formulations for **62**: an η^3-C_5H_5 linear nitrosyl compound and an η^5-C_5H_5 bent nitrosyl compound.

The non-nitrosyl-containing compound (η^5-C_5H_5)Re(CO)$_3$ (**63**) reacts reversibly with PMe_3 at +64 °C to give a stable η^1-C_5H_5 bis(phosphine) adduct, (η^1-C_5H_5)Re(CO)$_3$(PMe_3)$_2$ (**64**), which was characterized by X-ray crystallography.[66] The rate of reaction of **63** depended on the concentration of both Re and PMe_3, and a mono(phosphine) intermediate is again required. The only reasonable 18-electron structure for this intermediate is the η^3-C_5H_5 complex **65**. When the equilibrium mixture of **63** and **64** is heated at 100 °C for long periods, the phosphine substitution product is formed.

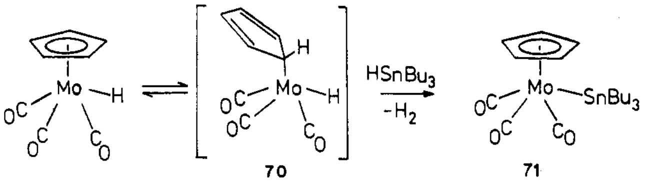


To date, these associative PMe_3 substitution reactions are the only reports of the direct observation and isolation of "ring-slipped" intermediates in ligand substitution and CO-insertion reactions.

Brill studied the kinetics of an Arbusov Rearrangement involving (η^5-C_5H_5)Co(dppe)(I)$^+$ (**66**) and P(OCH_3)$_3$ to give (η^5-C_5H_5)Co(dppe)[P(O)(OCH_3)$_2$]$^+$ (**67**) and CH_3I.[67] The formation of an intermediate species, (η^5-C_5H_5)Co(dppe)[P(OCH_3)$_3$]$^{2+}$ (**68**), was observed to follow second-order kinetics and led Brill to propose (η^3-C_5H_5)Co(dppe)(I)(P(OCH_3)$_3$)$^+$ (**69**) as an intermediate in the conversion of **66** to **67**.



Brown also relied on kinetic evidence to support a proposed, but unobserved, (η^1-C_5H_5) intermediate, **70**, in the reaction of (η^5-C_5H_5)Mo(CO)$_3$H and HSn(n-Bu)$_3$ to give (η^5-C_5H_5)Mo(CO)$_3$Sn(n-Bu)$_3$.[68]

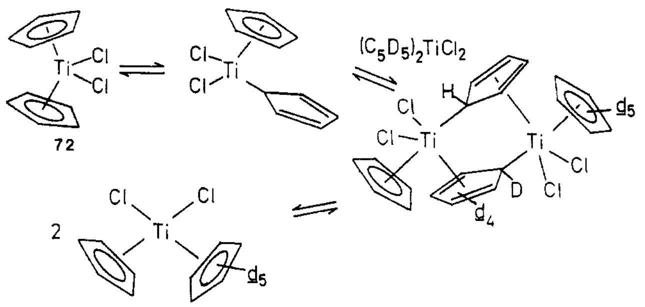


An η^5-C_5H_5 formyl intermediate is also possible for **70**. Brown observed a slower reaction for the tungsten analogue and pointed out that the W–H bond strength is greater than the Mo–H bond strength, an observation consistent with a formyl intermediate. However, CO insertion into metal–hydride bonds is rare and Casey has previously observed faster PMe_3-induced η^5- to η^1-C_5H_5 ring slippage for (η^5-C_5H_5)Mo(CO)$_2$(NO) (**58**) than for (η^5-C_5H_5)W(CO)$_2$(NO) (**59**).[64,65]

F. Cyclopentadienyl Ligand Transfer

Cyclopentadienyl ligand-transfer reactions have been known since 1956 when Wilkinson, Cotton, and Birmingham reported that the reaction of chromocene and ferrous chloride gave ferrocene.[69] However, mechanistic details have not been well established in most cases.

The most detailed work with early metal complexes is that of Brubaker and co-workers.[70-72] Photolysis of (η^5-C_5H_5)$_2$MCl_2 and (η^5-C_5D_5)$_2$MCl_2 (**72**) mixtures (M = Ti, V, Hf) results in intermolecular exchange of the



cyclopentadienyl ligands. The irradiation of 1/1 titanocene dichloride/carbon tetrabromide gives $(\eta^5\text{-}C_5H_5)TiCl_3$ and $(\eta^5\text{-}C_5H_5)TiCl_2Br$, an indication of a photoinitiated free-radical mechanism. However, the fact that $(\eta^5\text{-}C_5H_5)TiCl_3$ is not found in the absence of a sensitizer led Brubaker to suggest that in some cases a photochemically induced ring slippage may open up the coordination sites necessary for a bimolecular C_5H_5-bridged mechanism.

Brubaker found that in thermal C_5H_5 exchange reactions the rate of exchange depends directly on the conductivity of a given complex: $(\eta^5\text{-}C_5H_5)_2Cr > (\eta^5\text{-}C_5H_5)_2U \gg (\eta^5\text{-}C_5H_5)_2UCl$. To explain these observations a mechanism involving free C_5H_5 anions was proposed:

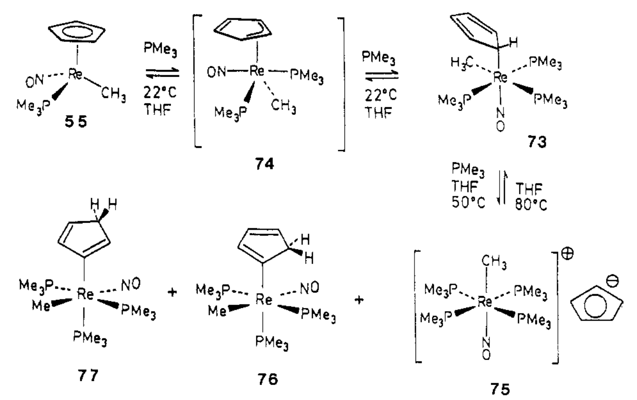
$$(C_5H_5)_2M \rightleftarrows C_5H_5^- + C_5H_5M^+$$

$$(C_5D_5)_2M \rightleftarrows C_5D_5^- + C_5D_5M^+$$

$$C_5D_5^- + C_5H_5M^+ \rightarrow (C_5H_5)(C_5D_5)M$$

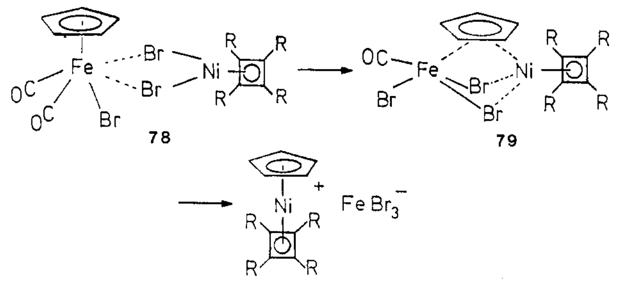
$$C_5H_5^- + (C_5D_5)_2M \rightarrow (C_5H_5)(C_5D_5)M + C_5D_5^-$$

Loss of a coordinated η^5-C_5H_5 ligand to give a $C_5H_5^-$ anion is well established. In 1966, Behrens and Meyer speculated that $(C_5H_5)_2Ni$ might reversibly dissociate to $[Ni(NH_3)_6]^{2+}[C_5H_5]_2^-$ in liquid ammonia.[73] In 1979 Booth and Smith reported that reaction of $(C_5H_5)_2Ni$ and 2 equiv of $CH_2{=}PPh_3$ gave an air-sensitive brown precipitate that, although itself uncharacterized, gave $[(\eta^5\text{-}C_5H_5)Ni(CH_2PPh_3)_2]^+[BPh_4]^-$ upon treatment with $NaBPh_4$.[74] Fabian and Labinger reported that $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Fe(CO)_2$ reacts rapidly with PMe_3 to give a yellow precipitate, which they formulated as $[(\eta^5\text{-}C_5H_5)Fe(CO)(PMe_3)_2]^+[C_5H_5]^-$ on the basis of its reactions with water and $CHCl_3$.[75] Due to poor solubility of the compound in polar solvents, the only spectroscopic characterization was an IR band at 1940 cm^{-1}.



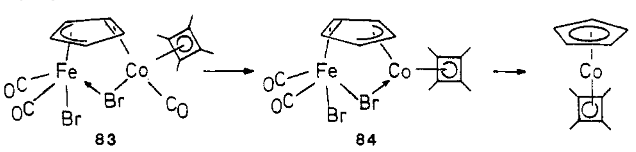
Casey, O'Connor, and Haller reported spectroscopic and structural evidence for the interconversion of η^5-C_5H_5, η^1-C_5H_5, and ionic "η^0"-$C_5H_5^-$ compounds in the reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(CH_3)(PMe_3)$ (**55**) with PMe_3.[76] When a THF solution of **55** and 4 M PMe_3 was monitored by ^1H NMR, the clean conversion to η^1-C_5H_5 tris(phosphine) complex **73** was observed. The authors proposed that the conversion of **55** to **73** involves an η^3-C_5H_5 intermediate, **74**. When THF solutions of **55** and PMe_3 were heated at 50 °C, the cyclopentadienyl ligand was cleaved from rhenium and the ionic "η^0"-$C_5H_5^-$ compound **75** crystallized from hot THF. Compound **75** was characterized by X-ray crystallography; the closest distance between anion and cation is 3.65 Å between a carbon of the C_5H_5 anion and a carbon of a PMe_3 ligand. When solid **75** was heated in THF, it slowly dissolved to re-form the η^5-C_5H_5 complex **55**. In addition to **75**, the reaction of **55** and PMe_3 gave a 1/1 mixture of 1-η^1-(1,3-cyclopentadiene) compound **76** and 2-η^1-(1,3-cyclopentadiene) compounds **77**. These products are formally the result of hydrogen 1,5-shifts around the rhenium-substituted ring.

A number of groups have suggested the formation of cyclopentadienyl-bridged intermediates to explain C_5H_5 transfer between metal centers. Maitlis, Efraty, and Games suggested cyclopentadienyl-bridged binuclear intermediates **78** and **79** to explain C_5H_5 transfer from $(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$ (**80**) to $(\eta^4\text{-}C_4Ph_4)Ni(Br)_2$ (**81**).[77]

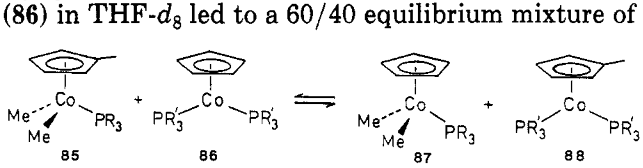


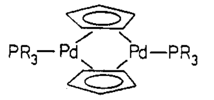
Rubezhov and Gubin noted that coordinatively saturated **80** was unlikely to associate with **81** via halide bridges. They suggested initial dissociation of CO or Br from **80** followed by reaction with **81**.[78]

Efraty has proposed that **80** transfers a C_5H_5 ligand to $(\eta^4\text{-}C_4R_4)Co(CO)_2Br$ (**82**) by initial loss of CO from **82** and η^5-C_5H_5 to η^3-C_5H_5 ring slippage to generate the C_5H_5-bridged intermediates **83** and **84**.[79]



Bryndza and Bergman found that heating $(\eta^5\text{-}C_5H_4Me)Co(Me)_2(PMe_3)$ (**85**) and $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ (**86**) in THF-d_8 led to a 60/40 equilibrium mixture of





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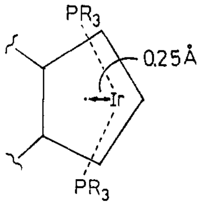
$(\eta^5\text{-}C_5H_5)Co(Me)_2(PMe_3)$ (**87**) and $(\eta^5\text{-}C_5H_4Me)Co(PPh_3)_2$ (**88**).[80] Through a series of reactivity studies, evidence was obtained for cyclopentadienyl ligand exchange rather than exchange of the methyl and phosphine ligands. Excess PPh_3 failed to inhibit the exchange process. The authors suggested that exchange occurs by interaction of two coordinatively saturated complexes or that its rate is controlled by some other process such as an η^5 to η^3 rearrangement. It was pointed out that Werner's unusual C_5H_5-bridged complex, **89**, could be an interesting model for the transition state.[38]

VI. η^5-Indenyl Ligands

η^5-Indenyl complexes exhibit a localized allyl-ene structure similar to that observed in some "noncylindrical" η^5-C_5H_5 complexes.[81] The distortion is more pronounced than in the η^5-cyclopentadienyl ligand due to incorporation of the ene unit into the aromatic six-membered ring. An illustrative example is the crystal structure of $[(\eta^5\text{-}C_9H_7)Ir(PPh_3)_2H]^+BF_4^-$ (**90**).[81] The projection of the iridium atom on the plane of the five-carbon ring is 0.24 Å from the ring centroid.



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As was observed for localized η^5-C_5H_5 systems, the ligand with the greatest trans influence is trans to the ene portion of the five-membered ring.

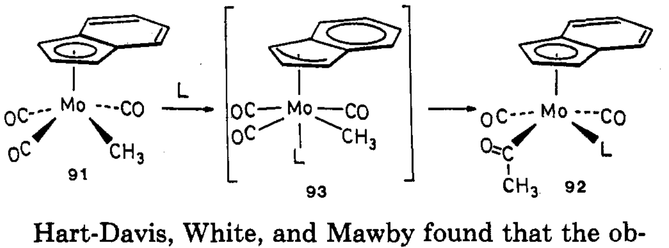
A number of methods for the quantitative description of η^5-allyl-ene distortions have been proposed.[81-83] The degree of allyl-ene distortion in η^5-C_9H_7 complexes is reflected in the ^{13}C NMR signals of the ring junctions carbons: the greater the distortion, the more downfield the chemical shift.[84,85]

A number of groups have correlated the barrier to η^5-indenyl rotation about the metal–ring axis with the degree of allyl-ene distortion: the greater the distortion, the lower the barrier to rotation.[85,86]

A. η^5-C_9H_7 to η^3-C_9H_7 Rearrangements

The presence of the fused benzene ring in η^5-C_9H_7 complexes results in more facile η^5 to η^3 ring isomerizations for indenyl ligands than for cyclopentadienyl ligands. This effect has been aptly termed the "indenyl ligand effect" by Basolo.[87]

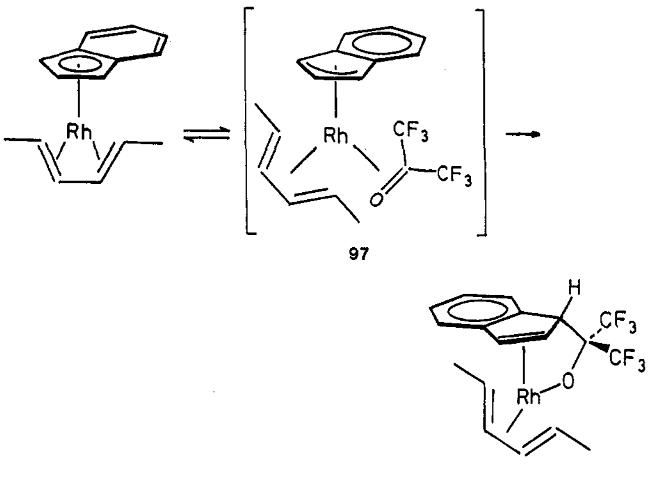
More rapid substitution reactions of η^5-indenyl complexes compared to η^5-cyclopentadienyl complexes were first observed by Hart-Davis and Mawby for the reaction of $(\eta^5\text{-}C_9H_7)Mo(CO)_3CH_3$ (**91**) and PPh_3 to give $(\eta^5\text{-}C_9H_7)Mo(CO)_2(PPh_3)(COCH_3)$ (**92**).[88] To explain the rate acceleration and the observed second-order kinetics, η^3-indenyl intermediate **93** was proposed.



91 93 92

Hart-Davis, White, and Mawby found that the observed rate constants for reaction of $(\eta^5\text{-}C_9H_7)Mo(CO)_3X$ (X = Cl, Br, I) (**94**) with phosphine and phosphite ligands fit the expression $K_{obsd} = K_A + K_B[L]$, where K_A is a dissociative rate constant and K_B an associative rate constant.[89-91] For both the associative and dissociative reactions, the rates were faster than for the corresponding η^5-C_5H_5 complexes. This acceleration is explained by an η^5 to η^3 ring slippage in the associative reactions. For the dissociative component, it was suggested that the rate acceleration could be due to a loss of planarity of the indenyl ligand, with the six-membered ring bending toward the metal. Alternatively, it was suggested that the intermediate may involve movement of the metal toward a more central position above the planar indenyl ligand.

Green and co-workers proposed η^5- to η^3-C_9H_7 ring slippage to account for the higher reactivity of $(\eta^5\text{-}C_9H_7)Rh(CH_2CH_2)_2$ (**95**) than $(\eta^5\text{-}C_5H_5)Rh(CH_2CH_2)_2$ (**96**) toward ligand substitution.[92,93] Green proposed a similar η^3-intermediate, **97**, to account for the reaction of η^5-indenyl complex **98** with CF_3COCF_3 to give indenyl alcoholates **99**.[94]



97

99

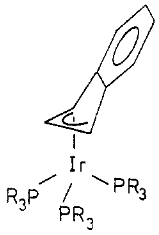
The barrier to alkene rotation in $(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2$ (**95**) is 10.3 kcal mol^{-1},[95] while the barrier in $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2$ (**96**) is 15 kcal mol^{-1}.[96,97] The lower barrier in **95** has been attributed to an indenyl ligand electronic effect.[86] Back-bonding to the ethylene π^* orbital reduces the repulsion between a filled polyene level and a filled metal d orbital. In a 90° ethylene rotation, the back-bonding is lost and an η^5 to η^3 ring slip reduces the increase in repulsion at the transition state.[86]

B. Structural Characterization of the η^3-C_9H_7 Ligand

Struchkov and co-workers were the first to structurally characterize an η^3-C_9H_7 metal complex, $(\eta^5\text{-}C_9H_7)(\eta^3\text{-}C_9H_7)W(CO)_2$ (**100**).[98] As was observed for the analogous η^3-C_5H_5 complex, **9**, the η^3 ligand is bent 26° with 3.2-Å carbon–metal distances for the ene unit. In the ^1H NMR spectrum of **100** resonances are observed at δ 6.6 (8 H), 4.8 (4 H), and 3.4 (2 H), indicative of rapid η^5 to η^3 interconversions on the NMR time scale. For comparison, the ^1H NMR of $[(\eta^3\text{-}C_9H_7)PdCl]_2$ (**101**) in acetone-d_6 consists of resonances at δ 7.08 (8 H), 6.99 (t, 2 H, J = 3 Hz, H-2), and 6.30 (d, 4 H, J = 3 Hz, H-1,3). The ^{13}C NMR of **101** has resonances at δ 85.4

(C-1,3), 114.0 (C-2), 127.4 (C-4,7), 118.8 (C-5,6), and 136.9.[99,100]

Recently Merola isolated and structurally characterized an η^3-C_9H_7 complex, **102**, formed by the reaction of (η^5-C_9H_7)Ir(C_2H_4)$_2$ (**103**) and PMe_2Ph.[101] Again the η^3-C_9H_7 ligand is bent (28.5°). When **102** is treated with a large excess of PMe_3, the indenyl ligand is completely displaced from the metal to give $[Ir(PMe_3)_4]^+[C_9H_7]^-$ (**104**). Marder and Williams also observed displacement of the η^5-indenyl ligand from (η^5-C_9H_7)Rh(C_2H_4)$_2$ (**90**) to give $[Rh(dmpe)_2]^+[C_9H_7]^-$,[102] which was structurally characterized. Unlike the formation of $[Re(PMe_3)_4(NO)(CH_3)]^+[C_5H_5]^-$ (**75**), no η^1 intermediate was observed and the reaction does not appear to be reversible.



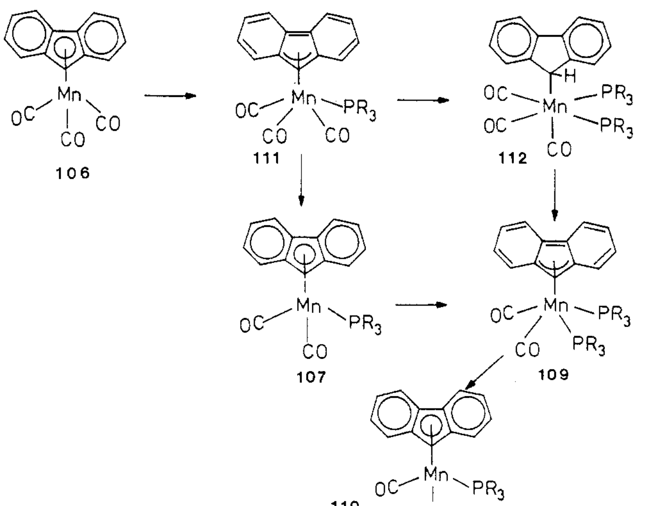
102

$[Ir(PR_3)_4]^+ [C_9H_7]^-$

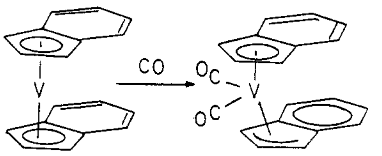
104

Ji, Rerek, and Basolo compared the kinetics of the phosphine substitution reactions of the indenyl complex (η^5-C_9H_7)Mn(CO)$_3$ (**105**) and the fluorenyl complex (η^5-$C_{13}H_9$)Mn(CO)$_3$ (**106**), both of which are first order in metal complex and in phosphine.[103] Phosphine substitution with P(n-Bu)$_3$ at 140 °C occurs 250 times faster with fluorenyl complex **106** than with indenyl complex **105** to produce the monophosphine products (η^5-$C_{13}H_9$)Mn(CO)$_2$(P(n-Bu)$_3$) (**107**) and (η^5-C_9H_7)Mn(CO)$_2$(P(n-Bu)$_3$) (**108**). The related cyclopentadienyl complex (η^5-C_5H_5)Mn(CO)$_3$ is inert to thermal CO substitution. The rates of reaction of **105** and **106** with phosphines depend on both the size and basicity of the incoming ligand. These results support an associative mechanism in which ring slippage to form an (η^3-C_9H_7) mono(phosphine) intermediate occurs in the rate-determining step.

With high concentrations of P(n-Bu)$_3$, the fluorenyl complex **106** is converted to the bis(phosphine) substitution product **110**. The mono(phosphine) substitution product **107**, however, is not an intermediate in the formation of **110** from **106** under these conditions, since the conversion of mono(phosphine) complex **107** to bis(phosphine) complex **110** is 70 times slower than the direct formation of **110** from **106**. To explain the rapid bis substitution of **106**, the sequential formation of η^3-$C_{13}H_9$ mono(phosphine), **111**, η^1-$C_{13}H_9$ bis(phosphine), **112**, and η^3-$C_{13}H_9$ bis(phosphine), **109**, intermediates was proposed. At low phosphine concentration, η^3-$C_{13}H_9$ mono(phosphine) intermediate **111** loses CO to form the relatively inert mono(phosphine) product **107**; at high phosphine concentration, this intermediate adds a second phosphine to form the key intermediate η^1-$C_{13}H_9$ bis(phosphine) complex, **112**. A $^{13}C\{^1H\}$ NMR of the reaction mixture at an intermediate time revealed **112** was the major component in solution as indicated by a resonance at δ 51.9 (C-9). There are to date no additional examples of η^5- to η^1-$C_{13}H_9$ isomerizations. The conversion of mono(phosphine) complex **107** to bis(phosphine) complex **110** was suggested to occur via slow addition of phosphine to form (η^3-$C_{13}H_9$) bis(phosphine) intermediate **111**.



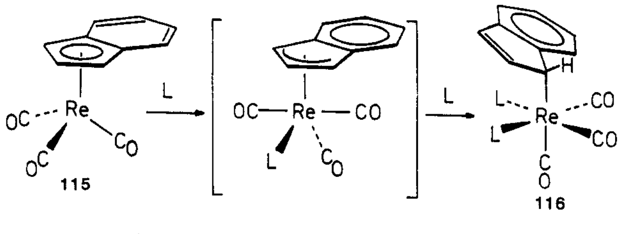
Trogler, Basolo, Rheingold, and Kowaleski demonstrated that the odd-electron species (η^5-C_9H_7)$_2$V reacts with CO to form (η^5-C_9H_7)(η^3-C_9H_7)V(CO)$_2$ (**113**).[104] Although the complex should be more crowded than the isostructural tungsten complex **100**, the dihedral angle between the η^3-carbons and the remaining carbon atoms of the η^3-indenyl ligand is only 12.0°.



113

Unlike the η^3 complexes **9** and **100**, the η^3-fluorenyl ligand in (η^3-$C_{13}H_9$)(η^5-$C_{13}H_9$)CrCl$_2$ (**114**) is planar.[105]

Casey and O'Connor reported much faster rates of bis(phosphine) η^1 complex formation for the reaction of PMe_3 with (η^5-C_9H_7)Re(CO)$_3$ (**115**) than with η^5-C_5H_5)Re(CO)$_3$ (**63**).[106] The difference in $\Delta G^‡$ of about 14 kcal mol^{-1} between these two reactions is comparable to the $>10^8$ rate enhancement ($\Delta\Delta G^‡ > 10.7$ kcal mol^{-1}) reported by Basolo and Rerek for the phosphine substitution reactions of (η^5-C_5H_5)Rh(CO)$_2$ and (η^5-C_9H_7)Rh(CO)$_2$.[87] Once again, the large rate differences are probably related to the generation of a fully aromatic benzene ring in the proposed η^3-indenyl intermediates. Unlike η^5-C_5H_5 complex **63**, the η^5-C_9H_7 complex **115** gives isolable η^1-C_9H_7 complexes, **116**, with both the bulky P(n-Bu)$_3$ ligand and the less nucleophilic 2,2′-bipyridyl ligand. These η^5- to η^1-C_9H_7 conversions represent the only examples of η^5-C_9H_7 isomerizations to isolable η^1-C_9H_7 complexes. In 1977 Green reported that (η^5-C_9H_7)Rh(C_2H_4)$_2$ reacts with excess t-BuNC to form (σ-C_9H_7)Rh(t-BuNC)$_4$, which was characterized by its infrared spectrum.[92]



Cyclopentadienyl and indenyl ligand isomerizations often play a significant role in the chemistry of their transition-metal complexes. Although the factors that control these processes are not yet fully understood, it is clear that these ligands offer promise in the design of new stoichiometric and catalytic reactions for which accessible open coordination sites are of crucial importance.

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