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Review

π-ALLYL—METAL COMPOUNDS

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Contents

1. Introduction

Organometallic compounds containing the allyl (C_3H_5) moiety are of three types:

(i) σ-allyl: a terminal carbon atom is σ-bonded to the metal atom with a localised double bond between the two remaining carbon atoms. Examples are $(\sigma\text{-}C_3H_5)_3B$ [1] and $\sigma\text{-}C_3H_5Mn(CO)_5$ [2].

(ii) μ-allyl: the allyl group bridges two metal atoms, being σ-bonded to one metal atom through a terminal carbon atom and to the second metal atom

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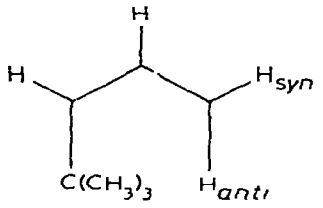
through interaction of the allyl double bond with the metal orbitals. Examples are $[\mu\text{-}C_3H_5Pt(O_2C_5H_7)]_2$ [3], $[\mu\text{-}C_3H_5PtCl]_4$ [3] and $(C_3H_5)_3Cr_2$ [4].

(iii) π-allyl: the bond between the allyl group and the metal atom is delocalised and multicentric.

2. π-Allyl—metal compounds: examples

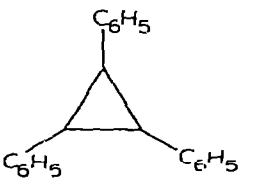
π-Allyl—metal compounds can be of the pure allyl type, such as $(\pi\text{-}C_3H_5)_nM$, n = 2, M = Ni [5, 6], Pd [5, 6], Pt [7]; n = 3, M = Co [8], Rh [9], Ir [10]; n = 4, M = Mo [11], Zr [6], Hf [6]. π-Allyl—metal compounds are also known which have mixed ligands, containing groups such as a halogen [11—15] [e.g. $(\pi\text{-}C_3H_5PdCl)_2$ [13—15]], halogen and carbonyl [16—19][$\pi\text{-}C_3H_5Fe(CO)_3Cl$ [16—18]], halogen and π-cyclopentadienyl [20—22] [$\pi\text{-}C_3H_5Co(\pi\text{-}C_5H_5)I$ [20]], halogen and triphenylphosphine [11, 23—27] [$\pi\text{-}C_3H_5PdClP(C_6H_5)_3$ [25]], carbonyl [28—31] [$\pi\text{-}C_3H_5Co(CO)_3$ [28, 29]], carbonyl and nitrosyl [32—34] [$\pi\text{-}C_3H_5Fe(CO)_2NO$ [32—34]], carbonyl and π-cyclopentadienyl [35—37] [$\pi\text{-}C_3H_5Fe(\pi\text{-}C_5H_5)CO$ [35]], carbonyl and triphenylphosphine [38—40] [$\pi\text{-}C_3H_5Ir(CO)[P(C_6H_5)_3]_2$ [40]], π-cyclopentadienyl [22, 29, 41] [$\pi\text{-}C_3H_5Ni\text{-}(\pi\text{-}C_5H_5)$ [29]], 1,5-cyclooctadiene [42] [$\pi\text{-}C_3H_5Rh(\pi\text{-}1,5\text{-}C_8H_{12})$ [42]], trifluorophosphine [43—45] [$\pi\text{-}C_3H_5Rh(PF_3)_3$ [43]], other tertiary phosphines [46, 47] [$\pi\text{-}C_3H_5Rh[P(C_6H_5)_3]_2$ [46]], and basic groups such as amines [48—51], acetylacetonate ion [15, 52], dimethylsulphoxide [53], pyrazolylborate [54, 55], Schiff bases [56] and thiocyanate ligand [57].

The π-allyl group may be an isolated three-carbon system with substituents at one or more of the terminal and central carbon atoms; it may be cyclic or part of a hydrocarbon ring system. Examples are shown in Ia-Ic.



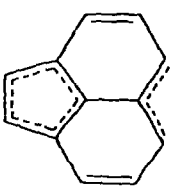
(Ia)

(*anti*-1-$C(CH_3)_3$-π-$C_3H_4PdCl)_2$ (ref 58)



(Ib)

1,2,3-$(C_6H_5)_3$-π-$C_3Ni(\pi\text{-}C_5H_5)$ (ref 59)



(Ic)

π-$C_{12}H_8Fe_2(CO)_5$ (ref 60)

3. Structure: tilting and asymmetric bonding

Many organometallic π-allyl compounds have symmetric π-allyl structures, with the metal—terminal carbon bond lengths nearly identical. For example, the bond lengths in $(2\text{-}CH_3\text{-}\pi\text{-}C_3H_4)_2Ni$ [61] are M—C_1 = M—C_3 = 2.01 Å, M—C_2 = 1.98 Å; $(\pi\text{-}C_3H_5PdCl)_2$ [62, 63]: 2.14, 2.17, 2.02 Å; $(\pi\text{-}C_3H_5)_2Ru[P(C_6H_5)_3]_2$ [64]: 2.25, 2.23, 2.13 Å; $\pi\text{-}C_3H_5Co(CO)_3$ [65]: 2.10, 2.10, 1.98 Å.

The C—C—C angle of the π-allyl group is usually close to 120°, and this is exemplified by the following compounds: $(\pi\text{-}C_3H_5PdCl)_2$ [62, 63] (119.8°);

$(2\text{-}CH_3\text{-}\pi\text{-}C_3H_4PdCl)_2$ [66] (112.4°); $(1,1,3,3\text{-}(CH_3)_4\text{-}\pi\text{-}C_3HPdCl)_2$ [67] (118°); $(\pi\text{-}C_3H_5)_2Ru[P(C_6H_5)_3]_2$ (118° and 120°); $\pi\text{-}C_3H_5Co(CO)_3$ (123°) and $\pi\text{-}C_3H_5Pd(\pi\text{-}C_5H_5)$ [68] (117.5°).

The plane defined by the three-carbon skeleton of the π-allyl group is usually not perpendicular to the plane defined by the metal atom and the terminal carbon atoms of the π-allyl group: examples are $(2\text{-}CH_3\text{-}\pi\text{-}C_3H_4)_2Ni$ (105.5°) and $[(\pi\text{-}C_3H_5)_2RhCl]_2$ [69] (110.3°) but the angle of $(2\text{-}CH_3\text{-}\pi\text{-}C_3H_4)_2Ru[P(OCH_3)_3]_2$ [70] is 88.6°.

The three-carbon π-allyl plane is usually not perpendicular to the coordination plane of the molecule: e.g. in $(\pi\text{-}C_3H_5PdCl)_2$ the dihedral angle between the π-allyl and $PdCl_2Pd$ planes is 108°, with the central carbon atom tipped away from the metal atom. Similarly, the dihedral angle between the metal coordinate plane (that defined by the Pd, Cl and P atoms) and the π-allyl plane in $2\text{-}CH_3\text{-}\pi\text{-}C_3H_4PdClP(C_6H_5)_3$ [71] is 116°. The dihedral angle of $\pi\text{-}C_8H_{11}Pd(CH_3COCHCOCH_3)$ [72] is 121.5°, and of $(2\text{-}C_2H_5CO_2\text{-}\pi\text{-}C_3H_4NiBr)_2$ [73] 106.2°, while the angle between the π-allyl group and the plane defined by the carbonyl carbon atoms of $\pi\text{-}C_3H_5Co(CO)_3$ is 36°. The three-carbon skeleton of the π-allyl group of $(2\text{-}CH_3\text{-}\pi\text{-}C_3H_4PdCl)_2$ makes an angle of 111.6° with the $PdCl_2Pd$ plane and an angle of 108.5° with the plane containing the metal atom and the terminal carbon atoms of the π-allyl group.

When the chemical environment at one terminal carbon atom of the π-allyl ligand is different from that at the other, because of ligands having different *trans*-effects, the bonding of the π-allyl group may deviate from the symmetrical. The shortest Pd—C bond of $2\text{-}CH_3\text{-}\pi\text{-}C_3H_4PdClP(C_6H_5)_3$ [71] is that *trans* to the chlorine atom: Pd—C (*trans* to Cl) = 2.14 Å, Pd—C (*cis* to Cl) = 2.28 Å, and the C—C bond lengths are also unequal: C—C (*trans* to Cl) = 1.47 Å, C—C (*cis* to Cl) = 1.40 Å. The two shortest Rh—C bonds of $[(\pi\text{-}C_3H_5)_2RhCl]_2$ [69] are those *trans* to the two bridging chlorine ligands: Rh—C (*trans* to Cl) = 2.12 Å, Rh—C (*cis* to Cl) = 2.25 Å. Similarly, the compound $(2\text{-}CH_3\text{-}\pi\text{-}C_3H_4)_2Ru[P(OCH_3)_3]_2$ [70], in which the π-allyl ligands are mutually *cis*, has unequal Ru—C bond lengths: Ru—C (*trans* to P) = 2.38 Å, Ru—C (*trans* to C) = 2.18 Å, The Pd—terminal carbon atom bond lengths of $\pi\text{-}C_3H_5PdP(C_6H_5)_3(SnCl_3)$ [74] are equal (2.19 Å) and the *trans*-effect of $SnCl_3$ is therefore comparable to that of $P(C_6H_5)_3$.

The substituted π-allyl ligand is generally non-planar. For example, a methyl substituent in the 2-position of the π-allyl group is bent out of the plane of the π-allyl moiety *towards* the metal atom by 12° in $(2\text{-}CH_3\text{-}\pi\text{-}C_3H_4)_2Ni$, by 11.8° in $(2\text{-}CH_3\text{-}\pi\text{-}C_3H_4PdCl)_2$, by 9.5° in $2\text{-}CH_3\text{-}\pi\text{-}C_3H_4NiBr[P(C_6H_5)_2CH_2]_2$ [75], by 0.5 Å in $2\text{-}CH_3\text{-}\pi\text{-}C_3H_4PdClP(C_6H_5)_3$ and by 0.17 Å in $1,2\text{-}(CH_3)_2\text{-}\pi\text{-}C_3H_3Ti(\pi\text{-}C_5H_5)_2$ [76], whereas the methyl group in $(2\text{-}CH_3\text{-}\pi\text{-}C_3H_3)_2Rh[P(OCH_3)_3]_2$ are bent *away* from the metal atom by 12°. In $[1,1,3,3\text{-}(CH_3)_4\text{-}\pi\text{-}C_3HPdCl]_2$ the methyl groups in the *anti*-positions are bent towards the metal atom by 22.9° and those in the *syn*-positions are bent away from the metal atom by 28.5° [67]. The carboxylate group of $(2\text{-}C_2H_5CO_2\text{-}\pi\text{-}C_3H_4NiBr)_2$, however, is coplanar with the π-allyl plane [73].

The three- and five-membered rings of $1,2,3\text{-}(C_6H_5)_3\text{-}\pi\text{-}C_3Ni(\pi\text{-}C_5H_5)$ [59] are parallel (within 0.8°), but the phenyl substituents are twisted propellor-like out of the cyclic π-allyl plane. Other compounds having strained π-allyl systems

are π-$(CH_3)_4C_4(\sigma$-$C_5H_5)Ni(\pi$-$C_5H_5)$ [77], in which the dihedral angle between the π-allyl and σ-cyclopentadienyl planes is 0.7° and the π-allyl C—C—C angle is 89°, and π-$R_3C_4OCo(CO)_3$ [78] [R = C_6H_5 or CH_3], in which the π-allyl C—C—C angle is also 89°.

The π-allyl group in the hydrocarbon ring system of π-$C_{10}H_8Fe_2(CO)_5$ [79] is not coplanar with the π-cyclopentadienyl group, and the central carbon atom of the π-allyl group is 0.908 Å below the π-cyclopentadienyl plane. The acenaphthylenyl group of π-$C_{12}H_8Fe_2(CO)_5$ [60] and the benzyl group of π-$C_8H_9Mo(CO)_2(\pi$-$C_5H_5)$ [80] are approximately planar. The structure of π-$C_8H_8Fe_2(CO)_5$ [81] is symmetrical about a mirror plane.

The π-cyclopentadienyl group of $[\pi$-$C_3H_4Ni(\pi$-$C_5H_5)]_2$ [82] has a π-allyl-type grouping, while the chlorine bridges of $[1,3$-$(CH_3)_2$-π-$C_3H_3PdCl]_2$ [83] and $[1$-$C(CH_3)_3$-2-CH_3-π-$C_3H_3PdCl]_2$ [84] are bent: the angles between the $Cl—Pd_1—Cl'$ and $Cl—Pd_2—Cl'$ planes are 150° and 148°, respectively.

Substitution of a CO group of π-$C_3H_5Fe(CO)_3I$ [85] by $P(C_6H_5)_3$ [86] changes the M—C(π-allyl) bond lengths from 2.30 Å and 2.09 Å to 2.20 Å and 2.22 Å.

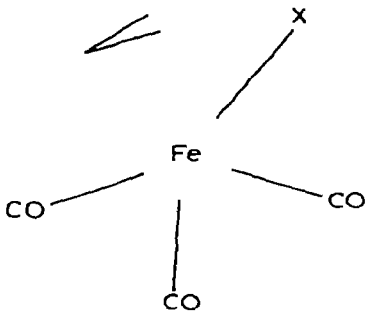
4. Conformational isomerism

π-$C_3H_5Mo(CO)_2(\pi$-$C_5H_5)$ in solution exhibits IR and NMR spectra which indicate the presence of two isomers [87]. The IR spectrum shows doubling of the carbonyl stretching bands, and a temperature-dependence NMR study shows that the isomers interconvert at temperatures above 0°. π-$C_7H_7Mo(CO)_2(\pi$-$C_5H_5)$ also has four carbonyl stretching bands [88, 89] but the low temperature (—100°) NMR spectrum indicates the presence of only one isomer [88]. Two carbonyl bands disappear at —60° and the conformer ratio therefore varies with temperature.

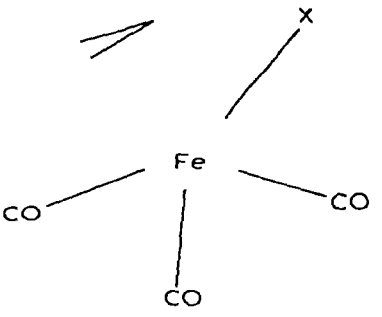
The NMR spectra of π-$C_5H_5W(CO)_3X$ (X = Br, I) both consist of two sets of AM_2X_2 spectra and are interpreted on the basis of the existence in solution of unequal amounts of two isomers [90]. Increasing the temperature to above 80° results in broadening and subsequent collapse of the two spectra into one AM_2X_2 spectrum with a chemical shift intermediate between those of the two isomeric forms. The halogen atom influences the ratio of the isomers. The possibility of a σ-allyl intermediate during the interconversion process is unlikely because averaging of *syn*- and *anti*-protons (which accompanies σ-allyl formation from a π-allyl group) is not observed before decomposition.

The structure of π-$C_3H_5Fe(CO)_3X$ (X = Cl, Br, I, NO_3) and of the $P(C_6H_5)_3$ derivatives is IIa, but in solution structure IIb is also observed, except when X = NO_3 [91]. Only one isomer is observed when the substituent on the central carbon atom of the π-allyl group is CH_3 (X = Cl) or Br (X = Br). The ratio of the two isomers decreases regularly in the series with the halogen, in the order I > Br > Cl. The isomer ratio could be governed by the spatial requirement of X or by the energies of the isomers, the relative energies depending on the relative donor—acceptor interactions of the allyl—metal and metal—halogen bonds.

In the series of compounds π-$C_3H_4RCo(CO)_2X$ [R = H, 1-CH_3, 2-CH_3, 2-Cl, X = $P(C_6H_5)_3$, $P(OC_6H_5)_3$, $P(n$-$C_4H_9)_3$; R = 2-CH_3, X = $P(OCH_2)_3CCH_3$] the multiplicities and intensities of the IR carbonyl stretching bands indicate that isomer-



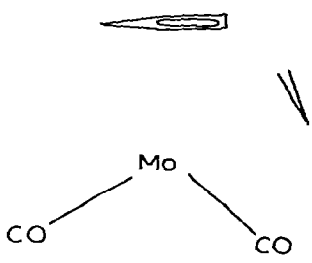
(IIa)



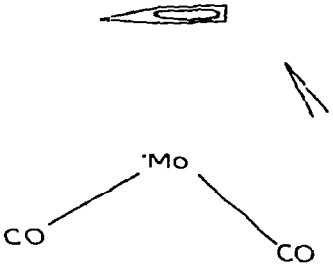
(IIb)

ism exists due to mutual restricted rotation of the substituted π-allyl group and the phosphorus-containing ligand [92]. The major and minor components of the carbonyl bands are separated by 9-16 cm^{-1} and the relative intensities of the components and therefore the proportions of the isomers depend on the substituent and the phosphorus-containing ligand, with the higher proportions of the minor components being produced by the Cl-substituent and the $P(OC_6H_5)_3$ ligand — the set having the greatest steric bulk. The lower frequency band of each pair of bands is always the more intense, indicating that the major component has an identical conformation for each molecule.

The compounds π-$AMo(CO)_2(\pi$-$C_5H_5)$ and π-$AMo(CO)_2(\pi$-$C_9H_7)$ [π-A = π-C_3H_5 or the 2-CH_3, 2-Cl, 2-Br, 1,1-$(CH_3)_2$, 1,1,2-$(CH_3)_3$ derivatives] also consist of isomers [93]. The major isomer configuration of the 2-CH_3, 2-Cl and 2-Br compounds was deduced to be IIIa and the greater intensity of the high



(IIIa)



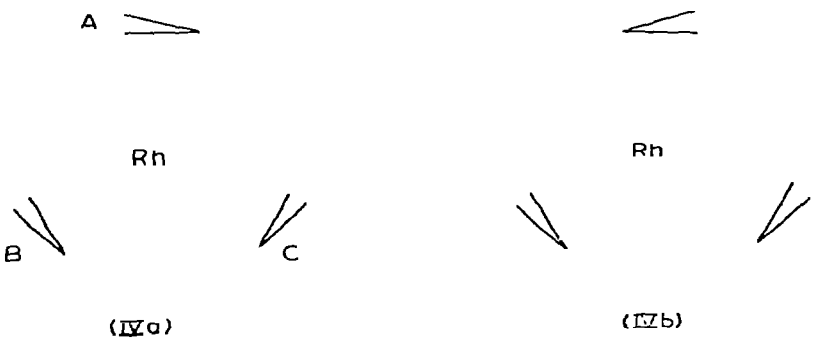
(IIIb)

frequency carbonyl stretching modes led to their assignment to isomer IIIa. In the 1-CH_3, 1,1-$(CH_3)_2$ and 1,1,2-$(CH_3)_3$ compounds the isomer IIIb is predominant. Large changes in the equilibrium constant take place when solvent and temperature are varied, but the principal contribution to the stability is the relative magnitude of steric interactions between allyl substituents and the cyclopentadienyl (or indenyl) ring. *Syn*- and *anti*-protons are not averaged during isomer interconversion and rotation about the metal—π-allyl bond is suggested.

Eclipsed (*cis*) and staggered (*trans*) isomers of $(\pi$-$C_3H_5)_2M$ (M = Ni, Pd) explain the two AM_2X_2 NMR spectra observed [94]. The spectra of $(\pi$-$C_3H_4R)_2Pt$ (R = H, 2-CH_3) are also consistent with the presence of two isomers [7]. The *trans*-isomer of $(\pi$-$C_3H_5)_2Ni$ predominates in the liquid phase, and the proportions are ca. 3/1. The isomer proportions are not influenced by temperature in the

range −70° to 30°, but the relative intensities of the two AM_2X_2 spectra are affected by temperature in the range 10° to 70°. No vibrational evidence has been found for the presence of significant proportions of the *cis*-isomer, and the *trans*-isomer is predominant [95].

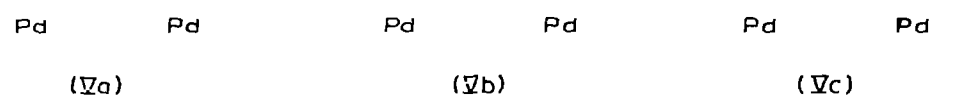
Three sets of AM_2X_2 patterns in the NMR spectrum of $(\pi\text{-}C_3H_5)_3Rh$ [21, 96] at −74° indicate the presence of three distinct types of symmetrically-bonded π-allyl group. Two sets of peaks coalesce on increasing the temperature from −74° to 10°, indicating exchange between two non-equivalent π-allyl groups. The process is explained by an equilibrium between the isomers IVa and IVb



(IVa) (IVb)

caused by a rapid rotation of π-allyl group A at 34°, making the allyl groups B and C magnetically equivalent, while at −70° the more restricted rotation of the allyl group A causes the non-equivalence of allyl groups B and C observed in the NMR spectrum. The NMR spectrum of $(\pi\text{-}C_3H_5)_3Ir$ at room temperature is similar to that of $(\pi\text{-}C_3H_5)_3Rh$, with two sets of π-allyl peaks in the ratio 1/2 [10].

The compound $(\pi\text{-}C_3H_5)_2Pd_2(O_2CCH_3)_2$ has three possible isomeric conformations (Va-c). The structure in the solid state is Va [97], in which the π-allyl



(Va) (Vb) (Vc)

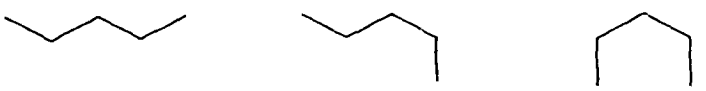
ligands are non-equivalent. At temperatures above 30°, NMR equivalence of the π-allyl ligands is observed [98]. At −20°, in the unsubstituted, 2-CH_3 and 1,1-$(CH_3)_2$ compounds, two overlapping AA'BB'X spectra of relative intensities 1/1, 9/1 and 3.5/1, respectively, are observed. At −60° one of the π-allylic resonances of each compound splits into two further allylic resonances of equal intensity, which are likely to be due to two non-equivalent allyl groups in one isomer (Va). Steric factors suggest that conformation Vb is unfavourable, and the major isomers in solution are therefore likely to be Va and Vc. The Va ⇌ Vc exchange process could involve a bimolecular interaction of $(\pi\text{-}C_3H_5)_2Pd_2(O_2CCH_3)_2$ molecules or a π-allyl rotation. Addition of weak bridge-splitting ligands (e.g. DMSO) results in an increase in the rates of the exchange processes, favouring the former explanation.

The compound $(\pi\text{-}C_3H_5)_2Pd_2[1,3\text{-}(C_6H_5)_2N_3]_2$ has two AM_2X_2 patterns in

the NMR spectrum in the temperature range −60° to +30°, and the spectrum is invariant in this range [99], unlike the analogous acetate complex. There are two non-equivalent π-allyl groups and the predominant isomer is therefore analogous to Va. The 2-CH_3 derivative has only only one M_2X_2 pattern and the structure is therefore analogous to Vc. The temperature invariance of the NMR spectrum is in contrast to that of the acetate compound and precludes the operation of a bridge inversion, a non-dissociative allyl rotation or a bimolecular exchange. A high-energy barrier to inversion due to an electronic effect or to steric repulsions between phenyl substituents during the inversion process is the likely cause of the resistance to bridge-splitting by some reagents.

5. *Syn—anti* isomerism

Isomerism in π-allyl—metal compounds arises from the non-equivalence of the *syn*- and *anti*-proton sites in the π-allyl group. The π-allyl group is usually tilted, with the central carbon atom tipped away from the metal atom (Section 3). In π-allyl—metal compounds substituted at a terminal carbon atom the *syn*-isomer is expected to predominate because of less steric interaction with the metal atom. Accordingly, both *syn*- and *anti*-isomers of 1-CH_3-π-$C_3H_4Co(CO)_3$ exist [29, 100], but the *syn*-isomer predominates, and similarly the *syn*-isomer predominates in 1-CH_3-π-$C_3H_4Co(CO)_2PR_3$ (R = n-C_4H_9, C_6H_5) [101]. The *syn*-isomer of 1-CH_3CH_2-π-$C_3H_4Co(CO)_3$ predominates and thermal isomerisation of the *anti*-isomer is complete at 90° in 1.5 hours [100]. Three isomers are possible in 1,3-$(CH_3)_2$-π-$C_3H_3Co(CO)_3$ (VIa-c), but only VIa and VIb are observed, with VIa predominating [100].



(VIa) (VIb) (VIc)

A structure determination of [1,3-$(CH_3)_2$-π-$C_3H_3PdCl]_2$ shows that the methyl groups each occupy the *syn*-position [83]. However, the tert-butyl group of [1-$C(CH_3)_3$-2-CH_3-π-$C_3H_3PdCl]_2$ occupies the *anti*-position [84] and the percentage of the *anti*-isomer has been shown to increase with the steric bulk of the 1-substituent. The tert-butyl compound has 85% *anti*-isomer, the isopropyl compound 56% and the neopentyl compound 37%. The *syn*-isomer is exclusively formed in the 1-ethyl and 1-methyl compounds. The steric effect of a large substituent of the olefin in a synthetic intermediate is believed to be responsible for the predominance of the *anti*-isomer in the tert-butyl compound [84].

Analysis of the NMR spectrum of (1-CH_3CO-2-CH_3-π-$C_3H_3PdCl)_2$ and the $As(C_6H_5)_3$ derivative suggests that the *anti*-isomer is more favoured in solution, minimising interaction between the acetyl and methyl substituents [102], and the isomer ratio of (1-C_2H_5O-2-CH_3-π-$C_3H_3PdCl)_2$ is *anti*/*syn* = 65/35 [103]. The predominant isomer of 1-CH_3CO-2-CH_3-π-$C_3H_3PdCl(C_5H_5N)$ is also the *anti*-isomer [104], but the only isomer of 1-CH_3CO-π-$C_3H_4PdCl(C_5H_5N)$ is the *syn*-isomer [104]. When the steric bulk of the 1- and 2-substituents is great, as in (1-C_6H_5CO-2-C_6H_5-π-$C_3H_3PdCl)_2$, only the *anti*-isomer is formed, and when the substituents have less steric influence on each other, as in (1-$CH_3CH_2CH_2CO$-

-2-CH_3-π-$C_3H_3PdCl)_2$, 65% of which is the *anti*-isomer, the percentage of *syn*-isomer increases [105].

Addition of a coordinating compound to *anti*-[1-$C(CH_3)_3$-2-CH_3-π-$C_3H_3PdCl]_2$ results in isomerisation to the *syn*-isomer. Prolonged heating of the synthetic reaction mixture also produces the *syn*-isomer [84]. Similarly, 1-CH_3-π-C_3H_4Co-(π-C_4H_6)$P(C_6H_5)_3$, which forms the *anti*-isomer practically free of *syn*-isomer, is rapidly transformed into the *syn*-isomer by the action of $P(C_6H_5)_3$, (C_5H_5N) or $(CH_3)_2SO$, even at room temperature [106]. The fact that isomerisation is caused by coordinating compounds suggests that it occurs through a π—σ—π intermediate, with free-rotation around the metal—carbon bond [106] (Section 6).

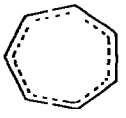
1,1-$(CH_3)_2$-π-$C_3H_3Co(PF_3)_3$ isomerises to *anti*-1-CH_3-2-CH_3-π-$C_3H_3Co(PF_3)_3$ on heating to 60° [44], and 1,1-$(CH_3)_2$-π-$C_3H_3Rh(PF_3)_3$ isomerises to *syn*-1-CH_3-2-CH_3-π-$C_3H_3Rh(PF_3)_3$ at the same temperature but at a faster rate than the cobalt compound. 1,1-$(CH_3)_2$-π-$C_3H_3Co(CO)_3$, however, shows no tendency to isomerise to 1,2-$(CH_3)_2$-π-$C_3H_3Co(CO)_3$ on heating [44]. Addition of $HRh(PF_3)_4$ to isoprene (CH_2=C(CH_3)CH=CH_2) yields initially equal amounts of the *syn*- and *anti*-isomers of 1,2-$(CH_3)_2$-π-$C_3H_3Rh(PF_3)_3$, but the *anti*-isomer isomerises on heating to the *syn*-isomer [44].

6. Fluxional character

A molecule which is fluxional has several configurations which are equivalent in structure and bonding. In many cases, as the molecule passes from one configuration to another, some atoms pass through several different environments within the molecule. An example of a fluxional π-allyl molecule is π-$C_7H_7Co(CO)_3$ (VII), which has only one proton NMR signal at room

$Co(CO)_3$

(VII a)

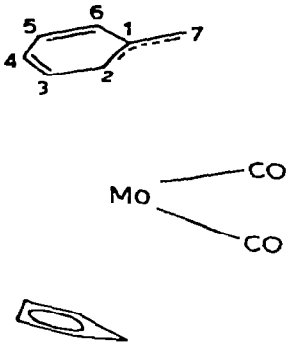


$Co(CO)_3$

(VII b)

temperature due to rapid interconversion (on the NMR time scale) of the instantaneous structures of type VIIa, but at very low temperatures (ca. —140°) a more complex spectrum is obtained [88] due to the existence of only one instantaneous structure. Similarly, π-$C_7H_7Mo(CO)_2$(π-C_5H_5) has only one resonance at room temperature but a more complex spectrum at —100° [88].

The π-allyl compound, π-$C_6H_5CH_2Mo(CO)_2$(π-C_3H_5), which in the solid-state has structure VIII [80], also has a temperature dependent NMR spectrum [107]. At —30° the methylene protons and the protons at carbon atoms 3 and 5 and carbon atoms 2 and 6 are distinct, but become equivalent on increasing the temperature to +64°. Possible mechanisms are (i) rapid rotation of the benzyl group around the C_4—C_1—C_7 axis; (ii) revolution of the $Mo(CO)_2$-(π-C_5H_5) moiety around the ring; (iii) formation of a σ-benzyl intermediate at higher temperatures causing interconversion of the bonding of C_7, C_1 and C_2 of the benzyl group to the $Mo(CO)_2$(π-C_5H_5) moiety to bonding of C_7, C_1 and C_6.

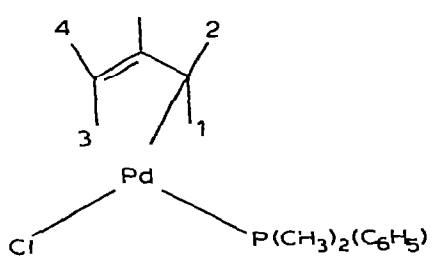


(VIII)

Syn—anti proton-site exchange: π—σ—π-transformations

Exchange of the *syn*- and *anti*-protons on one side of the π-allyl group in some π-allyl—metal compounds takes place under the influence of donor ligands or temperature. The behaviour of the π-allyl group in the compounds π-$C_3H_4RPdClL$ (R = H, 2-CH_3; L = Group V donor ligand) has been studied as a function of the type of ligand L, the ligand-to-metal ratio and the temperature [108]. Interchange of the *syn*- and *anti*-protons of the π-allyl group in π-C_4H_7PdClL via a σ-allyl intermediate is caused by interactions with L [$P(C_6H_5)$ or $As(C_6H_5)_3$] [109—111] or of π-$C_4H_7PdClP(C_6H_5)_3$ with $(\pi$-$C_4H_7PdCl)_2$ at temperatures below 20° [112]. Similarly, addition of pyridine to 2-CH_3-π-$C_3H_4Pd[P(C_6H_5)_2CH_2]_2$ promotes rapid *syn—anti* exchange [113].

Interchange of the *syn*- and *anti*-protons *cis* to the phosphine group in 2-$CH(CH_3)_2$-π-$C_3H_4PdClP(C_6H_5)_3$ is accompanied by exchange of the methyl groups in the 2-isopropyl side-chain, but not of the *syn*- and *anti*-protons *trans* to the phosphine group [114]. Exchange of protons at the carbon atom (C_3) *cis* to the phosphine group in 1-$CH(CH_3)_2$-π-$C_3H_4PdClP(C_6H_5)_3$ occurs at the same rate as that of the methyl groups in the isopropyl side-chain, which, however, remains in the *syn*-position [114, 115]. The interchange of the methyl groups in π-$C_3H_5PdClP(CH_3)_2(C_6H_5)$ is accompanied by interchange of the protons *cis* to the phosphine group. The results therefore indicate a transition state or transient intermediate having a σ-allyl group (IX). In the transition state H_1 and H_2 are equivalent but H_3 and H_4 are distinct.



(IX)

In a compound in which the π-allyl group is *trans* to a sulphur and an oxy-

gen atom, the protons *cis* to the sulphur atom exchange preferentially and this is also interpreted in terms of a short-lived σ-allyl intermediate [116], and so also is the epimerisation of α-phenylethylamine complexes of 1-substituted π-allyl ligands, which is accompanied by proton interchange at the unsubstituted terminal carbon atom [51].

Syn—anti proton-site exchange in the absence of base takes place in $(\pi\text{-}C_3H_5)_4Zr$ [6] at −20°, $(\pi\text{-}C_3H_5)_4Th$ [5] (10°), $(\pi\text{-}C_3H_5)_4Hf$ [6] (−72°) but not in $(\pi\text{-}C_3H_5PdCl)_2$ [117] at 150°, $\pi\text{-}C_3H_5Rh[P(C_6H_5)_3]_2$ [46] (130°), $\pi\text{-}C_3H_5Mn(CO)_4$ [117] (180°) or $(\pi\text{-}C_3H_5)_4Mo$ [11] (170°), and the mechanism of exchange in $(\pi\text{-}C_3H_5)_4Zr$ has been discussed [118].

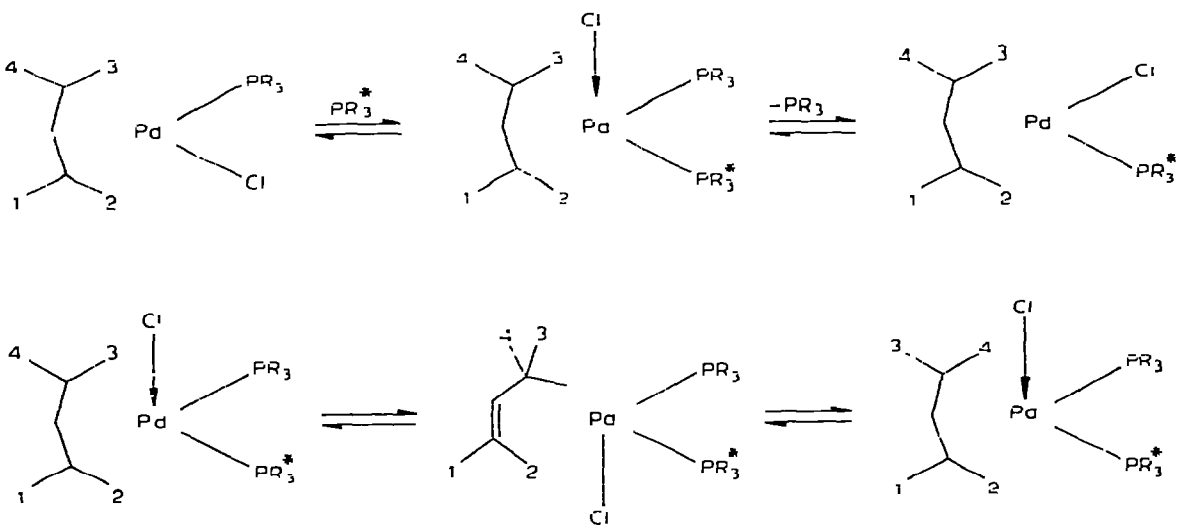
Syn—syn and syn—anti proton-site exchange

Interaction of $\pi\text{-}C_4H_7PdClP(C_6H_5)_3$ with $(\pi\text{-}C_4H_7PdCl)_2$ induces *syn—anti* proton-site exchange *cis* to the phosphine group, at temperatures below 20° [112]. At higher temperatures exchange of *syn*-protons and simultaneous exchange of the *anti*-protons occurs [112]. Similar processes take place in $2\text{-}CH_3\text{-}\pi\text{-}C_3H_4PdClP(C_6H_5)_3$ in the presence of a small excess of $P(C_6H_5)_3$ [119, 120]. *Syn—syn* exchange occurs in $\pi\text{-}C_3H_5Ir(CO)[P(C_6H_5)_3]_2$ and at higher temperatures *syn—anti* exchange is observed [40]. The *syn—syn* exchange process can be explained by a rotation of the π-allyl group about an axis passing through the allyl plane and the metal atom [40].

A mechanism involving a bimolecular S_N2 substitution reaction has been used to interpret the pyridine-promoted *syn—syn* exchange in π-allylpalladium picolinate and oximate complexes [121]. Experimental data on tertiary phosphine-promoted *syn—syn* and *syn—anti* exchange indicate that ligand-promoted proton-site exchange occurs by consecutive S_N2 substitution reactions, and that a low-energy in-plane rotation of the π-allyl ligand is not involved [122]. Mechanisms of PR_3-promoted proton-site exchange in complexes of the type $\pi\text{-}C_3H_5PdClPR_3$ [122] are shown in Scheme 1. The ease of formation of a σ-allyl

SCHEME 1

PR_3-PROMOTED PROTON-SITE EXCHANGE IN $\pi\text{-}C_3H_5PdClPR_3$ COMPLEXES

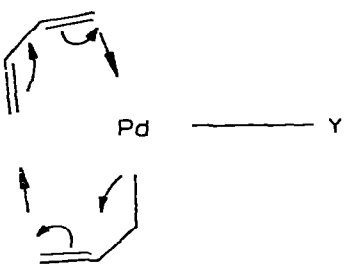


intermediate depends in part on the position and electronic and steric character of the alkyl substituents. Thus *syn—syn* exchange occurs first in the 2-CH_3 compound, for example, but *syn—anti* exchange has priority when the π-allyl group has terminal substituents [122].

7. Insertion reactions

Reactions of π-allyl—metal compounds with 1,3-dienes [123—129], a strained olefin [130], an acetylene [131], fluorocarbons [131—133], isocyanides [134, 135], sulphur dioxide [7] and carbon monoxide [127, 136] result in cleavage of the π-allyl—metal group and formation of products in which the ligand is inserted between the allyl group and the metal atom.

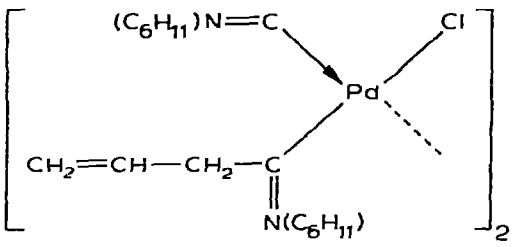
The rate of formation of the insertion products of the reactions of $(\pi\text{-}C_3H_4RPdX)_2$ with substituted 1,3-butadiene compounds increases with increasing electronegativity of the bridging ligand [123, 127], decreases with increasing substitution of the diene [123, 127], and increases with increasing electron withdrawing properties of the substituents of the π-allyl group [123, 126]. The conjugated diene always enters the allyl group at the most substituted carbon atom [127]. The observations of *syn—anti* proton-site exchange during the diene insertion reactions [123], and the stereochemical features [123] indicate that the same kind of σ-allyl intermediate which provides a pathway for base-promoted proton-site exchange also plays a part in an initial stage of the insertion reaction. The factors influencing the reactions suggest that the diene coordinates to the metal atom through the least substituted double-bond to give a σ-allyl intermediate, (σ-allyl)(diene)Pd(Y). The diene adopts a *cis*-configuration within the intermediate and then reacts with the σ-allyl group, with a mechanism of the type shown in X [123]. Support for the mechanism is provided by the



(X)

increase in electric conductivity of $(\pi\text{-}C_3H_5PdCl)_2$ on addition of small quantities of C_4H_6 [129]. The conductivity increases exponentially in the temperature range 0° to 60°, which is the same temperature range in which line broadening and shifting is observed in the NMR spectra, as a result of chemical exchange. Rapid exchange between dimeric and various monomeric forms is the most favoured explanation.

Reaction of the isocyanide $C_6H_{11}NC$ with $(\pi\text{-}C_3H_5PdCl)_2$ gives the product XI [134]. The reaction is favoured by high electron donor ability of the isocyanide group, with the initial stage of the reaction being bridge-cleavage of $(\pi\text{-}C_3H_5PdCl)_2$ [134].



(XI)

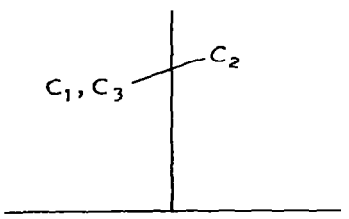
The compounds $(1\text{-}CH_2Cl\text{-}\pi\text{-}C_3H_4PdCl)_2$ and $(1\text{-}C_2H_5OCH_2\text{-}2\text{-}CH_3\text{-}\pi\text{-}C_3H_3\text{-}PdCl)_2$ can be carbonylated at two sites to give different products, depending on reaction conditions [136]. Thus the former compound reacts in a 1/2 ratio in ethanol to give $CH_3CH{=}CHCH_2CO_2C_2H_5$ and in a 3/2 ratio in benzene at room temperature to give $CH_2ClCH{=}CHCH_2COCl$. The latter product can be formed through attack of CO at the carbon atom of the substituent or through a carbonium ion intermediate and Cl attack at the unsubstituted terminal carbon atom of the allyl group. The reaction of CO with $(\pi\text{-}C_3H_5PdCl)_2$ has been studied kinetically. The results are described by a mechanism in which an unstable five-coordinate complex is formed by coordination of CO to Pd and transforms to a four-coordinate species by splitting the bridge [127]. CO always enters at the least substituted carbon atom [127].

Reaction of C_2F_4 with $\pi\text{-}C_3H_4RCo(CO)_3$ (R = H, 2-CH_3) results in coordination of C_2F_4 to the metal atom, with the allyl group σ-bonded [132]. The σ-bonded carbon atom then migrates to C_2F_4, possibly promoted by coordination of the allyl olefinic group. An alternative mechanism involves nucleophilic attack by $\pi\text{-}C_3H_4RCo(CO)_3$ on C_2F_4, forming an ionic intermediate, which collapses by reaction of the carbanion with the cationic π-allyl system [132]. Reaction of $(CF_3)_2CN_2$ with $\pi\text{-}C_3H_4RCo(CO)_3$ (R = H, 1-CH_3, 2-CH_3) gives a similar type of insertion product [137], with evolution of N_2, while reaction of $1\text{-}CH_3\text{-}\pi\text{-}C_3H_4PdClP(CH_3)_2(C_6H_5)$ with $CF_3C{\equiv}CCF_3$ gives insertion of the fluoroacetylene at the unsubstituted terminal carbon atom of the π-allyl group [131].

The reaction of SO_2 with $(\pi\text{-}C_3H_5)_2Pd$ gives $C_3H_5Pd(SO_2C_3H_5)$ [7] but no reaction mechanism has been proposed.

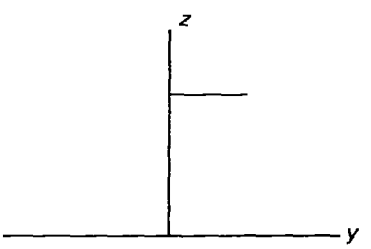
8. Bonding

Overlap integral calculations on the $\pi\text{-}C_3H_5M$ (M = Pd, Pt, Ni) group indicate that the energy of the bonding is optimised when the π-allyl group of $\pi\text{-}C_3H_5Pd$ has an angle of tilt of between 103° and 114° (XII) [138]. However, Slater functions

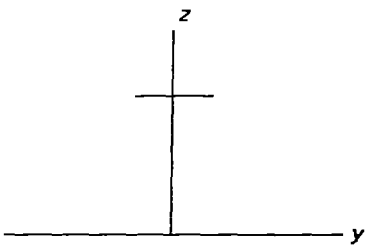


(XII)

have been criticised [139]. A qualitative description of the bonding in $(\pi\text{-}C_3H_5PdCl)_2$ suggests that the principal bonding interaction is between ψ_2* and a metal *d* orbital [108], with the π-allyl group acting as an electron-donor. The bonding between the π-allyl *anion* and a metal atom has been discussed by considering the interactions of ψ_2 and ψ_3 with the metal orbitals [140]. There is no particular steric requirement for maximum ψ_1—M bonding but ψ_2—M bonding is maximised when the structure is XIIIa, with C_1 and C_3 in the *xz*-plane. Maximum ψ_3—M bonding is attained when the ψ_3 node is in the *xz*-plane (XIIIb). The structure is resolved by a tilting of the π-allyl group in structure XIIIb to maximise ψ_2—M bonding.



(XIIIa)



(XIIIb)

Semi-empirical molecular orbital (MO) calculations on $(\pi\text{-}C_3H_5)_2Pd$ [141] show that the ψ_1 orbital interacts mainly with M(*s*, *p*) orbitals, but ψ_2 interacts principally with M(*d*) orbitals, with the π-allyl group acting as an electron-donating ligand. Semi-empirical self-consistent charge and configuration (SCCC) MO calculations on $(\pi\text{-}C_3H_5)_2M$ and $(\pi\text{-}C_3H_5MCl)_2$ (M = Ni, Pd, Pt) show the dual capacity of the π-allyl group to behave as an electron-donor or acceptor, with the ψ_1 orbital acting as an electron-donor in both sets of compounds [142]. The ψ_2 orbital is an electron-donor in the $(\pi\text{-}C_3H_5MCl)_2$ compounds, but an electron-acceptor in the absence of electron-withdrawing ligands in $(\pi\text{-}C_3H_5)_2M$. Self-consistent semi-empirical MO calculations on $(2\text{-}CH_3\text{-}\pi\text{-}C_3H_4)_2M$ (M = Ni, Co, Fe, Cr) show that the relative stability of the Ni compound can be rationalised by two factors: the low energy of the Ni 4*s* orbital, which is the only electro-attractive 4*s* orbital among the four compounds, and the gradual dispersion of the 3*d* orbitals from Ni to Cr [143].

The results of an ab initio MO calculation [145] on $(\pi\text{-}C_3H_5)_2Ni$ have been shown to be consistent with the photoelectron spectrum by taking into account the electronic relaxation upon ionisation [146]. There is no relationship between the sequence of ionisation potentials and the sequence of MO energies, indicating the breakdown of Koopmans' theorem for the molecule [146].

Asymmetric bonding of the π-allyl group of $\pi\text{-}C_3H_5PdClP(C_6H_5)_3$ has been explained by the opposing *trans*-electronic effects of the Cl and $P(C_6H_5)_3$ ligands, with the increased electron density of ψ_2 and ψ_3 on the carbon atom *trans* to the $P(C_6H_5)_3$ ligand weakening the M—C bond [140]. The difference in ligand

---

* Huckel orbitals (depicted in ref. 144) are as follows. $\psi_1 = \frac{1}{2}(\varphi_1 + \sqrt{2}\varphi_2 - \varphi_3)$, $\psi_2 = (1/\sqrt{2})(\varphi_1 - \varphi_3)$, and $\psi_3 = \frac{1}{2}(\varphi_1 - \sqrt{2}\varphi_2 + \varphi_3)$

trans-effects causes a higher degree of σ-bonding in π-$C_3H_5Pd(OCOCH_3)P(C_6H_5)_3$ than in π-$C_3H_5PdClP(C_6H_5)_3$ leading to an intramolecular π—σ—π reaction with *syn*—*anti* proton-site exchange at an attainable temperature in the absence of donor ligands for the former compound but not for the latter [140]. The *trans*-effects of $SnCl_3$ and $P(C_6H_5)_3$ are similar and the NMR spectrum of π-$C_3H_5PdSnCl_3P(C_6H_5)_3$ [147] resembles that of $(\pi$-$C_3H_5PdCl)_2$ rather than that of π-$C_3H_5PdClP(C_6H_5)_3$. The *trans*-effect of the Cl ligand in π-$C_3H_5PdClP(C_6H_5)_3$ increases, and approaches that of the acetate group, in the presence of acceptor molecules, and allows π—σ—π reactions with *syn*—*anti* proton-site exchange to occur at lower temperatures [140].

Conformational isomerism in the compounds π-$C_3H_4RFe(CO)_3X$ (X = Cl, R = H, CH_3; X = Br, R = H, Br; X = I, R = H) has been discussed in terms of ligand—metal interaction [91]. The principal contributions to the π-allyl—metal bonding are regarded as interactions between the π-allyl ψ_1 and ψ_2 orbitals with metal p_z and d_{xz} orbitals, respectively. The central carbon atom contributes to the ψ_1—p_z interaction only, and is ca. 0.2 Å nearer to the metal atom in isomer IIa. With decreasing electron-withdrawing power of the halogen from Cl to I, the ψ_1—p_z contribution to the bonding decreases together with a decrease in the energy difference between the two rotational isomers. At the same temperature there should be a higher proportion of isomer IIb for the iodide than for the bromide or chloride, which has been observed.

9. Substituent effects

The role of substituents in the development of the chemistry of the π-allyl—metal group has been extremely important. Substituents in the π-allyl group may be bent out of the plane of the carbon atoms of the π-allyl group, and can affect the ratio of conformational isomers, originate *syn*—*anti* isomerisation and influence the *syn*—*anti* isomer proportion; they have been useful in understanding *syn*—*anti* proton-site exchange, and influence the rates of insertion reactions.

The carbonyl monosubstitution of π-$C_3H_4RCo(CO)_3$ (R = H, 1-CH_3, 1-Cl, 1-CH_3OCO, 2-CH_3, 2-Cl, 2-Br, 2-C_6H_5) by $P(C_6H_5)_3$ proceeds at a rate which depends on the substituent R and its position in the π-allyl group [38]. The electron-releasing methyl group and the electron-withdrawing chlorine in the 2-position accelerate the reaction, whereas the same substituents in the 1-position decelerate the reaction. The reason for the unusual behaviour cannot be steric because the 2-Br substituent accelerates the reaction less than the 2-Cl substituent, which causes a faster reaction than the 2-CH_3 substituent [38]. The infrared carbonyl stretching frequencies of π-$C_3H_4RCo(CO)_3$ (R = H, 1-CH_3, 1-Cl, 2-CH_3, 2-Cl), however, correlate with the Hammett—Taft σ parameters [148].

The inductive effects of substituents in π-$C_3H_4RFe(CO)_2NO$ (R = H, 1-CH_3, 1-Cl, 2-CH_3, 2-Cl) correlate with the infrared carbonyl stretching frequencies [149] and with the half-wave potentials obtained from polarographic curves [150]. The inductive effects in π-$C_3H_4RFe(CO)_2NO$ (R = H, 2-CH_3, 2-Cl, 2-Br) correlate with the dipole moment values [151], the 2-CH_3 substituent increasing, and the 2-Cl and 2-Br substituents decreasing the dipole moment. The kinetic and polarographic studies show that substituents in the 2-position have a larger influence than substituents in the 1-position.

Substituents (CH_3, C_6H_5) in the 2-position of the π-allyl group lower λ_{max} in the electronic spectra of π-$C_3H_4RTi(\pi\text{-}C_5H_5)_2$, whereas the same substituents in the 1-position raise λ_{max} [41].

The ratio of intensities of peaks characterising ions formed in the mass spectra of π-$C_3H_4RFe(CO)_3X$ (R = H, 1-CH_3, 1-C_6H_5, 2-CH_3, 2-C_6H_5, 2-Br; X = Cl, Br, I, NO_3) depends on R and X [152].

10. Selected physical methods

Kinetics

The rates of monosubstitution of π-$C_3H_4RCo(CO)_3$ (R = H, 1-CH_3, 1-Cl, 1-CH_3OCO, 2-CH_3, 2-Cl, 2-Br, 2-C_6H_5) by $P(C_6H_5)_3$ [38] and of the mono- and di-substitution of π-$C_3H_5Co(CO)_3$ by $P(OCH_2)_3CCH_3$ [153] have been discussed. The rate of reaction of $P(C_6H_5)_3$ with π-$C_3H_5Co(CO)_3$ is independent of phosphine concentration above 0.06*M*, and the data suggest a dissociative-type mechanism.

The compound π-$C_3H_5Fe(CO)_2NO$ reacts relatively slowly with various tertiary phosphine and phosphite compounds, at rates which are unaffected by changes in dielectric constant or coordinating ability of the solvent [154].

The compounds π-$C_3H_5Fe(CO)_3X$ (X = Cl, Br, I) react readily with $P(C_6H_5)_3$ [18]. The bromide and iodide appear to react with second-order kinetics, the rate depending on both the iron complex concentration, and the concentration of phosphine. The chloride is most reactive and the second-order reaction rate constants decrease with time.

Polarography

A general mechanism for the electrochemical reduction of π-$C_3H_4RFe(CO)_2NO$ (R = H, 1-CH_3, 1-Cl, 2-CH_3, 2-Cl) has been proposed [150]. The reaction is a bielectronic process, involving breakage of the π-C_3H_5—Fe bond, whereas reduction of π-$C_3H_5Fe(CO)_3X$ (X = Cl, Br, I) proceeds by addition of one electron to the Fe—X bond [155], leading to Fe—X bond cleavage. The half-wave potentials of $(\pi\text{-}C_3H_5PdX)_2$ (X = Cl, I) and π-$C_3H_5Pd(\pi\text{-}C_5H_5)$ are almost equal, indicating that the electron change is localised on an orbital of the metal atom [156].

Vibrational spectra

The diagnostic peaks of the π-allyl group [ν(C—C—C) 1400 cm^{-1}, δ(C—C—C) 500 cm^{-1}] in the infrared and Raman spectra have been useful for distinguishing between a π-allyl group and a σ-allyl group [ν(C=C) 1550 cm^{-1}].

Partial infrared data are available for many π-allyl—metal compounds [157], but the vibrational spectra, with full assignments of bands, of only $(\pi\text{-}C_3H_4RPdX)_2$ (R = H, CH_3; X = Cl, Br) [158, 159], π-$C_3H_5Mn(CO)_4$ [160], π-$C_3H_5Co(CO)_3$ [161, 162], π-$C_3R_5Fe(CO)_2NO$ (R = H, D) [163], $(\pi\text{-}C_3H_4R)_2M$ (R = H, M = Ni, Pd; R = 2-CH_3, M = Ni) [164] and $(\pi\text{-}C_3H_5)_3M$ (M = Rh, Ir) [164] have been investigated in detail. The detailed vibrational spectra of π-$C_3H_4RCo(CO)_3$ (R = H, 1-CH_3, 1-Cl, 2-CH_3, 2-Cl) have also been investigated [148].

The low-frequency bands of the palladium compounds have been assigned

with the aid of the ^{114}Pd isotopic compounds [159]. The spectrum of π-$C_3H_5Mn(CO)_4$ can be explained on the basis of C_s rather than C_{4v} local symmetry of the $Mn(CO)_4$ group [160], whereas the spectrum of π-$C_3H_5Co(CO)_3$ can be assigned on the basis of a symmetrical $M(CO)_3$ group of C_{3v} local symmetry [148, 161, 162]. Substituents (1-CH_3, 1-Cl, 2-CH_3) on the π-allyl group perturb the C_{3v} symmetry of the $M(CO)_3$ group [148]. The skeletal vibrations of (2-CH_3-π-C_3H_4)$_2$Ni are consistent with C_{2h} symmetry of the molecule and no vibrational evidence has been found for the existence of staggered and eclipsed isomers of (π-C_3H_5)$_2$M [164].

Mass spectra

Fragmentation of π-$C_3H_4RFe(CO)_3X$ (R = H, 1-CH_3, 1-C_6H_5, 2-CH_3, 2-C_6H_5, 2-Br; X = Cl, Br, I, NO_3) proceeds principally through cleavage of Fe—CO and Fe—X bonds. The ratio of peaks characterising the ions formed depends on the nature of R and X [152].

Successive decarbonylation and elimination of the π-allyl group, and of I but not of Br, are observed in the mass spectra of π-$C_3H_5W(CO)_4X$ (X = Br, I) [90]. Successive decarbonylation of π-$C_3H_5Mo(CO)_2(\pi$-$C_5H_5)$ is observed followed by formation of the $[\pi$-$C_3H_5M(\pi$-$C_5H_5)]^+$ and $[M(\pi$-$C_5H_5)]^+$ ions [165]. A similar fragmentation pattern is obtained from π-$C_3H_5Ru(CO)(\pi$-$C_5H_5)$, but π-C_3H_5 $Fe(CO)(\pi$-$C_5H_5)$ gives the mass spectrum of (π-C_5H_5)$_2$Fe [165].

Degradation of the parent ion of 1-CH_3-π-$C_3H_4Ti(\pi$-$C_8H_8)$ occurs via progressive elimination of one- and two-carbon units firstly of the π-allyl group and then of the cyclooctatetraene group [166].

The elimination of chloride and allyl fragments from (π-$C_3H_5PdCl)_2$ occurs with possible formation of a new and stronger Pd—Pd bond [167], and the mass spectra of $[(\pi$-$C_3H_4R)_2RhCl]_2$ (R = H, 2-CH_3) suggest that cyclisation of the metal-bonded allyl moiety occurs to form cyclopropenyl—metal fragment ions [167].

The mass spectra of (π-$C_3H_5)_nM$ (n = 2, M = Ni, Pd, Pt; n = 4, M = Zr, Hf) have also been investigated [6].

Mössbauer spectra

The Mössbauer and infrared spectra of π-$C_3H_4RFe(CO)_2NO$ (R = H, 1-CH_3, 2-CH_3, 1-Cl) indicate that the metal s electron density is relatively unaffected by π-allyl substituents, and that the inductive effects of substituents are conducted via the metal atom to the carbonyl and nitrosyl ligands [149].

The Mössbauer spectra of π-$C_3H_5Fe(CO)_3X$ (X = Cl, Br) and π-$C_3H_5Fe(CO)_2$-$P(C_6H_5)_3X$ (X = Br, I) show that the isomer shift and quadrupole splitting value fall within a narrow velocity range, indicating that the metal electron configuration is not greatly influenced by substitution of a CO group by a $P(C_6H_5)_3$ group [168, 169].

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References

1 B.M. Mikhailov, Organometal. Chem. Revs., 8 (1972) 1.
2 H.L. Clarke and N.J. Fitzpatrick, J. Organometal. Chem., 40 (1972) 379.
3 G. Raper and W.S McDonald, J. Chem. Soc. D., (1972) 265.
4 T Aoki, A. Furusaki, Y. Tomue, K. Ono and K. Tanaka, Bull. Chem. Soc. Japan, 42 (1969) 545.
5 G. Wilke, B. Bogdanović, P. Hardt, P Heimbach, W. Keim, M. Kroner, W. Oberkirsch, K. Tanaka, E. Steinrücke, D. Walter and H. Zimmermann, Angew. Chem. Int. Ed. Engl., 5 (1966) 151.
6 J.E. Becconsall, B.E. Job and S. O'Brien, J. Chem Soc A, (1967) 423.
7 S. O'Brien, J. Chem. Soc. A, (1970) 9.
8 H. Bönnemann, Angew. Chem. Int. Ed Engl., 12 (1973) 964.
9 J Powell and B.L Shaw, Chem. Commun., (1966) 323.
10 P. Chini and S. Martinengo, Inorg Chem., 6 (1967) 837.
11 K.C. Ramey, D C Lini and W.B Wise, J. Amer. Chem. Soc., 90 (1968) 4275
12 J. Powell and B.L Shaw, Chem. Commun , (1966) 236
13 H C. Dehm and J.C.W. Chien, J. Amer. Chem. Soc , 82 (1960) 4429
14 B.L. Shaw and N. Sheppard, Chem. Ind. (London), (1961) 517.
15 S.D. Robinson and B.L. Shaw, J. Chem. Soc , (1963) 4806.
16 F.J Impastato and K.G. Ihrman, J. Amer Chem Soc., 83 (1961) 3726.
17 H D. Murdoch and E Weiss, Helv. Chim Acta, 6 (1962) 1927
18 R.F. Heck and C.R. Boss, J. Amer. Chem. Soc., 86 (1964) 2580.
19 G. Sbrana, G Braca, F. Piacenti and P Pino, J. Organometal Chem , 13 (1968) 240.
20 R.F. Heck, J. Org. Chem., 28 (1963) 604.
21 J. Powell and B.L Shaw, J Chem. Soc. A, (1968) 583
22 H.A. Martin, P J. Lemaire and F. Jellinek, J. Organometal. Chem., 14 (1968) 149.
23 R F. Heck, J.C.W. Chien and D S. Breslow, Chem. Ind. (London), (1961) 386.
24 D.N. Lawson, J A Osborn and G. Wilkinson, J. Chem Soc. A, (1966) 1733.
25 J. Powell and B L Shaw, J. Chem. Soc. A, (1967) 1839.
26 J. Powell and B L Shaw, J Chem Soc. A, (1968) 780.
27 H.C Volger and K. Vrieze, J. Organometal Chem., 9 (1967) 527.
28 R.F. Heck and D.S. Breslow, J. Amer. Chem. Soc., 82 (1960) 750
29 W.R. McClellan, H.H. Hoehn, H.N. Cripps, E.L Muetterties and B W. Howk, J Amer. Chem. Soc., 83 (1961) 1601
30 H.D Murdoch and E A.C. Lucken, Helv. Chim Acta, 47 (1964) 1517.
31 S. O'Brien, Chem Commun., (1968) 757.
32 H.D. Murdoch, Z. Naturforsch. B, 20 (1965) 179.
33 R. Bruce, F M. Chaudhari, G.R. Knox and P.L. Pauson, Z. Naturforsch. B, 20 (1965) 73
34 F.M. Chaudhari, G.R. Knox and P L Pauson, J Chem Soc. C, (1967) 2255
35 M L H Green and P L.I Nagy, J. Chem Soc., (1963) 189
36 M. Cousins and M L.H. Green, J. Chem. Soc , (1963) 889.
37 M L H. Green and A N Stear, J Organometal Chem , 1 (1963) 230
38 R F Heck, J Amer Chem. Soc., 85 (1963) 655.
39 M.I. Bruce, M.Z. Iqbal and F.G.A. Stone, J. Organometal. Chem., 20 (1969) 161.
40 C.K. Brown, W. Mowat, G. Yagupsky and G. Wilkinson, J. Chem. Soc. A, (1971) 850.
41 H A. Martin and F. Jellinek, J. Organometal Chem., 12 (1968) 149.
42 A. Kasahara and K. Tanaka, Bull. Chem. Soc. Japan, 39 (1966) 631.
43 D A. Clement, J F Nixon and B. Wilkins, J. Organometal Chem., 37 (1972) C43.
44 M.A. Cairns, J.F. Nixon and B. Wilkins, Chem. Commun., (1973) 86.
45 M.A. Cairns and J.F. Nixon, J. Organometal Chem , 51 (1973) C27
46 C.A. Reilly and H. Thyret, J. Amer. Chem. Soc , 89 (1967) 5144.
47 M. Cooke, R.J. Goodfellow, M. Green and G. Parker, J. Chem. Soc. A, (1971) 16.
48 H.D. Murdoch and R. Henzi, J. Organometal. Chem , 5 (1966) 552
49 C J. Hull and M.H.B. Stiddard, J. Organometal. Chem., 9 (1967) 519.
50 F. De Candia, G. Maglio, A. Musco and G. Paiaro, Inorg Chim Acta, 2 (1968) 233.
51 J W. Faller and M.E Thomsen, J. Amer. Chem. Soc., 91 (1969) 6871.
52 R.P. Hughes and J. Powell, J. Organometal Chem., 20 (1969) P17.
53 K C. Ramey and G L. Statton, J Amer. Chem. Soc., 88 (1966) 4387.
54 S. Trofimenko, Inorg. Chem., 9 (1970) 2493.
55 S. Trofimenko, J Amer. Chem. Soc., 91 (1969) 3183.
56 B.E. Reichert and B O. West, J Organometal. Chem., 36 (1972) C29.
57 D.L. Tibbetts and T.L.Brown, J. Amer. Chem. Soc., 91 (1969) 1108
58 J. Lukas, S. Coren and J.E. Blom, Chem. Commun., (1969) 1303.
59 R.M. Tuggle and D.L. Weaver, Inorg. Chem., 10 (1971) 1504.

60 M.R. Churchill and J. Wormald, Inorg Chem , 9 (1970) 2239
61 R. Uttech and H Dietrich, Z. Krist , 122 (1965) 60
62 W.E. Oberhansli and L.F. Dahl, J. Organometal. Chem , 3 (1965) 43.
63 A.E. Smith, Acta Crystallogr , 18 (1965) 331.
64 A E Smith, Inorg. Chem , 11 (1972) 2306
65 R Seip, Acta Chem. Scand., 26 (1972) 1966
66 R Mason and A G. Wheeler, J. Chem Soc A, (1968) 2549.
67 R. Mason and A.G. Wheeler, J. Chem. Soc. A, (1968) 2543.
68 M Kh. Minasyants and Yu. T. Struchkov, J. Struct Chem. USSR, 9 (1968) 406.
69 M McPartlin and R. Mason, Chem. Commun , (1967) 16.
70 R. Marsh, J. Howard and P. Woodward, J Chem Soc D, (1973) 778.
71 R Mason and D R. Russell, Chem Commun., (1966) 26.
72 M.R. Churchill, Inorg. Chem , 5 (1966) 1608.
73 M R. Churchill and T A. O'Brien, Inorg. Chem., 6 (1967) 1386
74 R Mason, G.B Robertson and P.O Whimp, Chem Commun , (1968) 1655
75 M.R Churchill and T A O'Brien, Chem. Commun , (1968) 246
76 R.B. Helmholdt, F Jellinek H A Martin and A Vos, Rec. Trav Chim Pays-Bas, 86 (1967) 1263
77 W. Oberhansli and L F. Dahl, Inorg Chem., 4 (1965) 150.
78 J Potenza, R Johnson, D Mastropaolo and A. Efraty, J Organometal Chem., 64 (1974) C13
79 M R. Churchill, Inorg Chem., 6 (1967) 190.
80 F.A. Cotton and M D. LaPrade, J. Amer. Chem. Soc., 90 (1968) 5418.
81 E B Fleischer, A L Stone, R.B K Dewar, J D Wright, C E Keller and R Pettit, J. Amer Chem Soc 88 (1966) 3158.
82 A.E. Smith, Inorg Chem , 11 (1972) 165
83 G.R. Davies, R.H B Mais, S O'Brien and P G Owston, Chem Commun , (1967) 115.
84 J. Lukas, J.E. Ramakers-Blom, T.G Hewitt and J.J de Boer, J. Organometal. Chem , 46 (1972) 167.
85 M Kh. Minasyants and Yu.T. Struchkov, J. Struct. Chem. USSR, 9 (1968) 577.
86 M.Kh Minasyants, V.G. Andrianov and Yu.T. Struchkov, J. Struct. Chem USSR, 9 (1968) 939.
87 A Davison and W C Rode, Inorg. Chem , 6 (1967) 2124.
88 M.A. Bennett, R. Bramley and R. Watt, J. Amer. Chem. Soc., 91 (1969) 3089.
89 R.B. King, Inorg. Chem., 5 (1966) 2242.
90 C.E. Holloway, J.D. Kelly and M.H.B Stiddard, J. Chem. Soc. A, (1969) 931.
91 A N Nesmeyanov, Yu.A Ustynyuk, I I Kritskaya and G.A Shchembelov, J. Organometal Chem , 14 (1968) 395
92 H.L Clarke and N J. Fitzpatrick, Inorg Nucl Chem. Lett., 9 (1973) 75.
93 J.W. Faller, C -C. Chen, M.J. Mattina and A. Jacubowski, J. Organometal. Chem., 52 (1973) 361.
94 H Bönnemann, B Bogdanović and G. Wilke, Angew Chem Int Ed Engl., 6 (1967) 804.
95 D.C. Andrews and G Davidson, J Organometal. Chem , 55 (1973) 383
96 J K. Becconsall and S. O'Brien, Chem. Commun , (1966) 720.
97 M.R. Churchill and R. Mason, Nature (London), 204 (1964) 777
98 J Powell, J. Amer Chem. Soc , 91 (1969) 4311.
99 T. Jack and J. Powell, J Organometal Chem , 27 (1971) 133.
100 J A. Bertrand, H.B. Jonassen and D.W. Moore, Inorg Chem , 2 (1963) 601
101 W W. Spooncer, A C Jones and L H Slaugh, J Organometal Chem., 18 (1969) 327.
102 C W. Fong and W Kitching, Aust J Chem , 22 (1969) 477
103 R. Huttel and H Schmid, Chem. Ber , 101 (1968) 252.
104 J.W. Faller, M E. Thomsen and M.J. Mattina, J. Amer. Chem. Soc., 93 (1971) 2642.
105 J.W. Faller, M.T. Tully and K.J. Lafley, J. Organometal. Chem., 37 (1972) 193.
106 G. Vitulli, L Porri and A.L. Segre, J Chem. Soc. A, (1971) 3246.
107 R.B. King and A Fronzaglia, J Amer Chem Soc , 88 (1966) 709.
108 K. Vrieze, C. MacLean, P. Cossee and C W Hilbers, Rec. Trav. Chim. Pays-Bas, 85 (1966) 1077.
109 K Vrieze, A P Praat and P. Cossee, J Organometal Chem., 12 (1968) 533.
110 K. Vrieze, P. Cossee, C.W. Hilbers and A.P Praat, Rec. Trav. Chim. Pays-Bas, 86 (1967) 769
111 K. Vrieze, P. Cossee, C MacLean and C W. Hilbers, J. Organometal. Chem., 6 (1966) 672.
112 K. Vrieze, P. Cossee, A.P. Praat and C.W. Hilbers, J. Organometal. Chem , 11 (1968) 353.
113 D.L. Tibbetts and T.L Brown, J Amer. Chem. Soc , 92 (1970) 3031.
114 P.W.N.M. van Leeuwen, A.P. Praat and M. van Diepen, J. Organometal. Chem., 24 (1970) C31.
115 C.W. Alexander, W.R. Jackson and R. Spratt, J. Amer. Chem. Soc., 92 (1970) 4990.
116 S.J. Lippard and S.M. Morehouse, J. Amer. Chem. Soc., 94 (1972) 6949.
117 F A. Cotton, J.W Faller and A. Musco, Inorg Chem., 6 (1967) 179.
118 J K Krieger, J.M. Deutch and G.M. Whitesides, Inorg. Chem., 12 (1973) 1535.
119 K. Vrieze, H.C. Volger and P.W.N M van Leeuwen, Inorg. Chim. Acta. Revs., 3 (1969) 109.
120 G. Maglio, A. Musco and R Palumbo, Inorg. Chim. Acta, 4 (1970) 153.

121 E Ban, A. Chan and J. Powell, J. Organometal Chem , 34 (1972) 405
122 M Oslinger and J. Powell, Can. J. Chem., 51 (1973) 274
123 R P Hughes and J Powell, J Amer Chem Soc., 94 (1972) 7723
124 R P. Hughes and J Powell, J Organometal Chem , 30 (1971) C45
125 D. Medema and R. van Helden, Rec. Trav Chim Pays-Bas, 90 (1971) 304.
126 Y Takahashi, S. Sakai and Y Ishii, J Organometal. Chem., 16 (1969) 177
127 D Medema, R. van Helden and C F Kohll, Inorg Chim. Acta, 3 (1969) 255.
128 D.S Guthrie and S M Nelson, Coord. Chem. Revs., 8 (1972) 139.
129 V.N. Sokolov, G.M. Khvostic, I.Ya. Poddubnyi and G.P. Kondratenkov, J Organometal Chem., 29 (1971) 313
130 R P. Hughes and J. Powell, Chem Commun., (1971) 275
131 T.G Appleton, H.C Clark, R.C. Poller and R.J. Puddephatt, J. Organometal. Chem., 39 (1972) C13
132 A Greco, M. Green and F.G A. Stone, J Chem Soc A, (1971) 3476
133 J Browning, M. Green and F.G A Stone, J Chem Soc. A, (1971) 453.
134 T. Boschi and B. Crociani, Inorg. Chim. Acta, 5 (1971) 477
135 T Kanmoto, H Takahashi and J Tsuji, J Organometal. Chem., 23 (1970) 275.
136 J. Tsuji and S. Hosaka, J Amer Chem Soc , 87 (1965) 4075
137 J. Clemens, M. Green and F.G A. Stone, J Chem Soc D, (1974) 93
138 S F.A Kettle and R. Mason, J. Organometal Chem., 5 (1966) 573
139 D A Brown and N.J Fitzpatrick J Chem Soc A, (1967) 316.
140 P.W.N.M van Leeuwen and A P Praat, J. Organometal Chem., 21 (1970) 501
141 I.H Huller and R.M Canadine, Disc. Farad. Soc., 47 (1969) 27.
142 D A. Brown and A Owens, Inorg Chim Acta, 5 (1971) 675
143 G de Brouckère, Theoret. Chim. Acta, 19 (1970) 310
144 M L H Green and P L I Nagy Advan Organometal Chem , 2 (1964) 325.
145 A. Veillard, Chem Commun , (1969) 1022 and 1427
146 M -M. Rohmer and A Veillard, Chem Commun , (1973) 250
147 J.N. Crosby and R.D.W Kemmitt, J. Organometal Chem , 26 (1971) 277
148 H.L Clarke and N J Fitzpatrick, J Organometal Chem , 43 (1972) 405.
149 H.L Clarke and N J. Fitzpatrick, J Organometal. Chem , 66 (1974) 119
150 G. Paiani, S M. Murgia and G Cardaci, J Organometal. Chem., 30 (1971) 221.
151 S. Sorriso, G. Cardaci and S M Murgia, Z Naturforsch. B, 27 (1972) 1316.
152 A N. Nesmeyanov, Yu S. Nekrasov, N.P Avakyan and I.I. Knitskaya, J. Organometal Chem , 33 (1971) 375.
153 R.F. Heck, J. Amer Chem. Soc., 87 (1965) 2572.
154 G. Cardaci and S.M. Murgia, J Organometal. Chem , 25 (1970) 483
155 S P Gubin and L I. Denisovich, J. Organometal. Chem., 15 (1968) 471.
156 S.P. Gubin, A.Z. Rubezhov, B.L. Winch and A.N Nesmeyanov, Tetrahedron Lett (1964) 2881
157 G. Davidson, Organometal Chem. Revs , 8 (1972) 303
158 D.M. Adams and A. Squire, J. Chem. Soc. A, (1970) 1803.
159 K. Shobatake and K. Nakamoto, J Amer. Chem. Soc., 92 (1970) 3339.
160 G. Davidson and D C Andrews, J. Chem. Soc. D, (1972) 126.
161 D.C Andrews and G Davidson, J. Chem. Soc D, (1972) 1381
162 G Paiani, S.M Murgia, G. Cardaci and R Cataliotti, J Organometal Chem , 63 (1973) 407.
163 G. Paiani, A. Poletti, G Cardaci, S.M. Murgia and R. Cataliotti, J Organometal Chem., 60 (1973) 157
164 D.C. Andrews and G. Davidson, J. Organometal. Chem , 55 (1973) 383
165 R.B King and M. Ishaq, Inorg. Chim. Acta, 4 (1970) 258.
166 H F Hofstee, H O. van Oven and H.J de Liefde Meijer, J. Organometal. Chem., 42 (1972) 405.
167 M S. Lupin and M Cais, J Chem. Soc A, (1968) 3095.
168 L. Korecz and K Burger, Acta Chim Acad. Sci. Hung , 58 (1968) 253
169 K. Burger, Inorg. Chim Acta Revs., 6 (1972) 31.