Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

π-ALLYLIC COMPLEXES OF RHODIUM(III) AND PLATINUM(II)
III. CHEMICAL REACTIVITY OF π-ALLYLIC RHODIUM(III) COMPLEXES

H. C. VOLGER AND K. VRIEZE
Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.) (The Netherlands)

(Received March 7th, 1968)

SUMMARY

The reactions of $L_2Rh(\pi\text{-}C_3H_4R)Cl_2$ [$L = (C_6H_5)_3P, (C_6H_5)_3As$ or $(C_6H_5)_3Sb$ and $R = H$ or CH_3] with sulfur dioxide, ethene and carbon monoxide were studied.

Sulfur dioxide gives rise to the formation of a σ-allylic rhodium–sulfur dioxide complex. With carbon monoxide $L_2Rh(\pi\text{-}C_3H_4R)Cl_2$ (L = triphenylphosphine or arsine) produces $L_2(CO)RhCl$ and (meth)allyl chloride in quantitative yields. The reaction proceeds via a number of intermediates (trivalent rhodium π- and σ-allyl and insertion products). Ethylene dimerizes into a mixture of butenes; the catalytic activity of the complex is rather poor.

The ease of displacement of the ligand by either ethylene or carbon monoxide decreases in the order $(C_6H_5)_3As > Cl > (C_6H_5)_3P$.

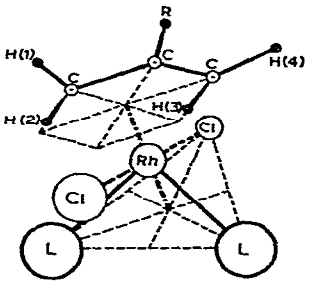
No specific correlation has been found between the destabilizing influence of the ligand L on the metal–π-methallyl bond and the rate of the reaction with carbon monoxide.

INTRODUCTION

Previously we reported on the synthesis of π-allylic rhodium(III) complexes $L_2Rh(\pi\text{-}C_3H_4\text{-}R)X_2$ with L a group V donor ligand, X halogen and R either hydrogen or an alkyl group by reaction of the appropriate allylhalide with L_3RhX at room temperature[1]:

$$L_3RhX + CH_2{=}CH{-}CH_2X \rightleftarrows L_2Rh(\pi\text{-}C_3H_5)X_2 + L$$

On the basis of the molecular weight determined, the NMR and IR spectra and the dipole moments, the following configuration was assigned to these isostructural complexes[1]*:



---

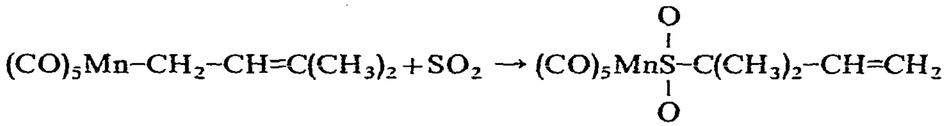
* The configuration was confirmed for $L{=}AsPh_3$ by a structural determination (T. G. Hewitt and K. Anzenhofer, private communication).

Furthermore we reported on the temperature dependence of the NMR spectra[2,3]. Two borderline types of the π-allyl spectrum were observed, *viz.* the stable π-allyl and the dynamic π-allyl types. The latter type of spectrum was ascribed to the occurrence of an intramolecular interconversion process proceeding via a σ-allyl form (either transition state or intermediate).

The tendency for a dynamic π-allyl type to occur decreases in the series $L = R_3P > R_3As > R_3Sb$ and was discussed in terms of the donating properties of the ligand and the destabilization of the π-allyl form[2].

The present report deals with the chemical reactivity of the π-methallylrhodium(III) complexes towards compounds such as sulfur dioxide, carbon monoxide and ethylene, which are known to be capable of inserting in metal–carbon bonds.

Insertion of sulfur dioxide, reported for the Fe[4], Mo[5], Hg[4], Mn[6] alkyl compounds, yields compounds with metal–sulfur–carbon bonds. Klein[7] reported the formation of $CH_3{-}CH_2{-}SO_2{-}CH_2{-}CH{=}CH{-}CH_3$ in the palladium chloride-catalysed reaction of ethylene and sulfur dioxide. It is interesting that for a manganese σ-allyl carbonyl complex the insertion yields a product having SO_2 between the metal and the γ carbon atom:



$$(CO)_5Mn{-}CH_2{-}CH{=}C(CH_3)_2+SO_2 \rightarrow (CO)_5Mn\underset{\underset{\displaystyle O}{|}}{\overset{\overset{\displaystyle O}{|}}{S}}{-}C(CH_3)_2{-}CH{=}CH_2$$

whereas $(CO)_4Mn(\pi\text{-}C_3H_5)$ does not react at all under identical conditions[6]. Insertion in π-allyl complexes has only been observed for $[(C_6H_5)_3P]_2Pt(\pi\text{-allyl})Cl$ (Part IV).

Insertion of carbon monoxide in metal–alkyl bonds and metal–π-allyl bonds has been studied extensively and has found wide-spread application in organic synthesis[8-12]. One of the most promising results seems to be the di-π-allylpalladium chloride catalysed insertion in $CH_2{=}CH{-}CH_2X$ with $X = Cl$, OR, OCOR, yielding $CH_2{=}CH{-}CH_2{-}C(O)X$.

Rhodium complexes are known to exhibit a strong affinity towards carbon monoxide. Striking examples are the decarbonylations of aldehydes[13], acid chlorides[13,14] and alcohols[15,16] under fairly mild conditions. Lawson, Osborn and Wilkinson recently reported the reaction of $[(C_6H_5)_3P]_2Rh(\pi\text{-}C_3H_5)Cl_2$ with CO, which yields $[(C_6H_5)_3P]_2Rh(CO)(\sigma\text{-}C_3H_5)Cl_2$[17].

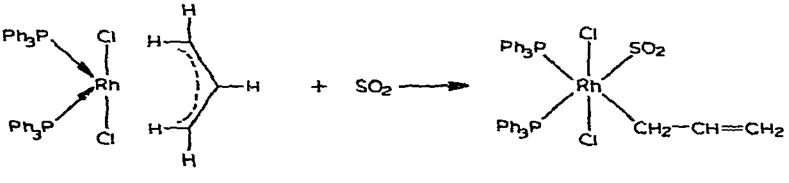
Two important mechanistic studies have been presented on the interaction of olefins with rhodium complexes, *viz.* the rhodium chloride-catalysed dimerization of ethylene to butene by Cramer[18] and the catalysed hydrogenation of olefins by $[(C_6H_5)_3P]_3RhCl$ by Wilkinson and coworkers[19].

In the present work we have studied the reactivity of $L_2Rh(\pi\text{-}C_4H_7)Cl_2$ towards CO, ethylene and sulfur dioxide.

RESULTS

Sulfur dioxide

Bis(triphenylphosphine)-π-allylrhodium dichloride (I) reacts with sulfur dioxide to yield a SO_2-containing rhodium complex, under a variety of reaction conditions. The complex is often contaminated with impurities. The best results were obtained by dissolving the rhodium complex (I) in liquid sulfur dioxide at room temperature. According to the elemental analysis the product formed is a fairly pure 1 : 1 adduct (II). A similar adduct was obtained from the π-methallyl complex. The reaction can be depicted as follows:



(I) (II)

The structure of the complex is based on the IR spectrum, which shows the presence of a terminal double bond (1640 cm^{-1} and 915 cm^{-1}, CH_2 out of plane deformation) and of the SO_2 group (1095 cm^{-1} sym. str. freq.; 1120 and 1164 assym. str. freq.). The formation of an insertion product seems unlikely, since only free SO_2, rather than organic sulfur dioxide-containing fragments, could be detected by mass-spectrometric analysis*. NMR measurements in $CDCl_3$ and in liquid SO_2 did not provide additional evidence; owing to the poor solubility of the product the spectrum had a low intensity. It showed very broad signals; presumably an exchange process of SO_2 occurs.

A number of complexes containing SO_2 as a ligand are already known[20]. In the case of rhodium the only example is $(SO_2)(CO)[(C_6H_5)_3P]_2RhCl$.

Ethylene

a. $[(C_6H_5)_3As]_2Rh(\pi\text{-}C_4H_7)Cl_2$. Preliminary qualitative experiments showed that initially ethylene (1 atm) is consumed by a solution of bis(triphenylarsine)-π-methallylrhodium dichloride in chloroform, while in a later stage of the reaction gas evolution was observed, so that the overall gas consumption was only small. Analysis of the gas revealed the presence of 1-butene, *cis*- and *trans*-2-butene, isobutene and ethylene; isobutene, derived from the methallyl group may in part explain the small overall gas consumption. The amount of unbranched butenes was no more than twice the amount of the catalyst. The poor catalytic activity of the arsine complex for dimerization is due to decomposition of the catalyst. A somewhat larger activity towards hydrogenation of olefins was observed; *e.g.* twenty moles of ethane was produced per mole of catalyst from a mixture of ethylene and hydrogen. It should be recalled that $RhCl_3$ (in ethanol)[18] and $[(C_6H_5)_3P]_3RhCl$[19] are known to be very active homogeneous catalysts for dimerization and hydrogenation of olefins, respectively.

More information with respect to the interaction of ethylene and the π-methallylrhodium complex was obtained from the NMR spectra of the reaction mixture and the electrical conductivity measurements as a function of the reaction time.

---

* Fragmentation into SO_2-containing fragments was observed for the reaction product of SO_2 and $[(C_6H_5)_3P]_2Pt(\pi\text{-}C_3H_5)^+Cl^-$ (Part IV).

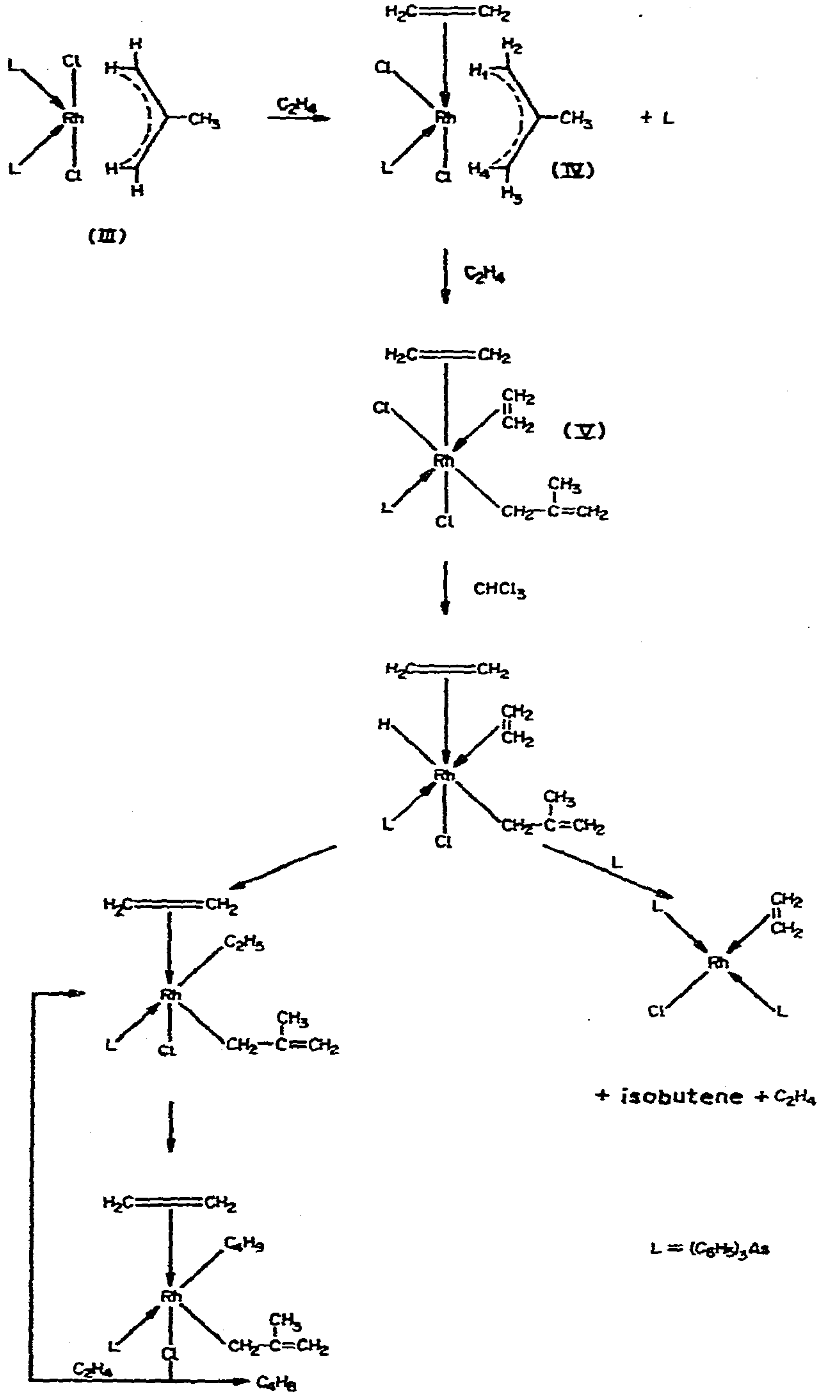


Fig. 1. Suggested path of the reaction of ethylene with bis(triphenylarsine)-π-methallylrhodium dichloride.

A brief description will be given, followed by a detailed discussion of the individual steps (Fig. 1).

The starting complex, (III), is rapidly converted by ethylene into the asymmetric π-methallyl ethylene complex, (IV). The latter complex subsequently reacts with another mole of ethylene to give the σ-methallyl bis(ethylene) complex, (V). The suggestion that both (IV) and (V) are present is experimentally supported. The final steps are not very clear. They are proposed in accord with the reported mechanism for the dimerization of ethene with $RhCl_3$ as catalyst. Substitution of a chloride for a hydride by the reaction of (V) with chloroform may yield a hydride complex, which is either converted into a σ-ethyl(ethylene)Rh^{III} complex or into isobutene and rhodium bis(ethylene) complex. The latter complex is apparently not converted into a hydride bis(ethylene) complex, so that the cycle ends at this stage. The cycle via the σ-ethyl(ethylene)Rh^{III} complex, insertion and hydride shift, presumably ends by hydride shift from the σ-butyl group to the σ-isobutenyl group, giving also a bis(triphenylarsine)bis(ethylene)rhodium chloride species and isobutene (Fig. 1).

Our supposition as regards the intermediate formation of complexes (IV) and (V) is based on the following evidence. Complex (IV) is formed within ten minutes of ethylene being passed through a chloroform solution of (III). The electrical conductivity in that time does not show any change, indicating the substitution of an arsine ligand by ethylene. The NMR spectrum of (IV) showed four signals for the methylene protons at 3.97 ppm (H_1), 3.54 ppm (H_2), 4.70 and 4.78 ppm ($H_{3,4}$); the assignment is analogous to the one given to the asymmetric triphenylphosphine-π-methallylpalladium chloride[21,32]. The CH_3 signal (1.95 ppm) was present as a doublet (J 1.4 cps) owing to coupling with the rhodium nucleus, which seems characteristic of all π-methallylrhodium complexes[1,22]. Signals due to the coordinated ethylene molecule were not visible probably owing to the occurrence of a rapid process of exchange with the ethylene molecules in solution. The coordination site of the ethylene molecule in (IV) at one of the apices of the pseudo octahedron is proposed, since it appears that the changes in the NMR spectrum of complex (III) due to either ethylene or carbon monoxide are exactly the same (Fig. 6). Coordination of ethylene or CO *trans* to the methallyl group would not influence the chemical shifts of the methylene protons in a similar way.

Prolonged reaction with ethylene causes a decrease in the concentration of both (III) and (IV); a third species, the σ-methallyl complex (V), appears. The CH_3 signal is now present at 1.45 ppm (singulet), the vinylic protons at 4.30 and 4.62 ppm and the CH_2 group bonded to the rhodium at 3.83 ppm (singulet); this value lies well in the range observed for ethylrhodium complexes*,**.

The proposed *trans* position of the σ-methallyl group relative to chlorine is based on the fact that in $[(C_6H_5)_3P]Pd(\pi\text{-}C_4H_7)Cl$ the distance between palladium and the terminal carbon (of the methallyl group) *trans* to chlorine is smaller than that between palladium and the carbon *trans* to phosphine. As in complex (IV), no proton signals are observed for the coordinated ethylene molecules.

---

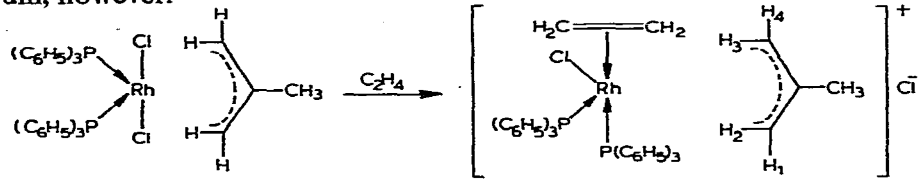
* It should be noted that the deshielding effect of a double bond as compared with CH_3 is about 0.8 ppm.

** Cramer[18] reported for δ(ethyl-CH_2) in (solvent)$(C_2H_4)Rh(CH_2CH_3)Cl_3$ and $(C_2H_4)Rh(CH_2CH_3)(\pi\text{-}C_5H_5)Cl$ 4.47 and 3.00 ppm, respectively.

In the final stage of the reaction, the NMR spectrum of the reaction mixture became very complicated. At any rate, signals characteristic of an ethyl group and of isobutene [$\delta(CH_3)$ 1.70 ppm and $\delta(CH_2)$ 4.68 ppm] appeared. The presence of isobutene, 1-butene and 2-butene (*cis* and *trans*) in the liquid and gas phases was confirmed by GLC.

b. $[(C_6H_5)_3P]_2Rh(\pi\text{-}C_4H_7)Cl_2$. A chloride ion rather than triphenylphosphine is displaced in the reaction of ethylene with bis(triphenylphosphine)-π-methallylrhodium dichloride, as was evidenced by the considerable increase in electrical conductivity of the reaction mixture.

The asymmetric π-methallyl complex (VII) and finally isobutene could be detected by NMR in the reaction mixture. The NMR signal of (VII) [CH_3 1.70 ppm, $J(CH_3\text{–}Rh)$ 1.4 cps; $H_{2,3}$ 2.66 and 2.74 ppm and $H_{1,4}$ 4.90 and 5.02 ppm] were assigned in a similar way as was given for complex (IV). The rather broad signals at 0.7, 4.1 and 5.2 ppm presumably result from olefin exchange reactions. During the replacement of Cl by ethylene the chloride and triphenylphosphine ligands have apparently changed their coordination sites in order to achieve an asymmetric π-methallyl complex. In analogy with the arsine case the complex is assumed to be converted into the σ-methallyl complex, which could not be detected in the NMR spectrum, however.



(VI) (VII)

The results described above for the interaction of ethylene with phosphine and arsine π-methallylrhodium dichloride complexes indicate that the ease of replacement of a ligand by ethene decreases in the order $(C_6H_5)_3As > Cl > (C_6H_5)_3P$.

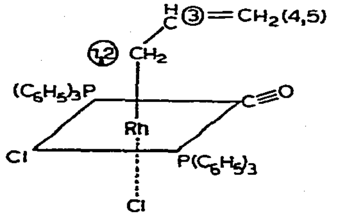
With the triphenylstibine complex, no experiments with ethylene were performed.

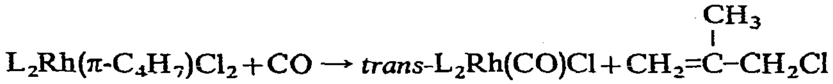
Carbon monoxide

Both the triphenylphosphine- and triphenylarsine-π-methallylrhodium dichloride complexes react in chloroform or benzene solutions at room temperature with one equivalent of carbon monoxide (1 atm) to yield the thermodynamically very stable *trans*-bis(triphenylphosphine)- or *trans*-bis(triphenylarsine)carbonylrhodium chloride and methallyl chloride quantitatively*:

---

* The same reaction was very recently described by Wilkinson and coworkers[17]. They reported the isolation of a σ-allylcarbonylRh^{III} complex as an intermediate, the structure of which was established by IR data [$\nu(C{=}O)$ 2035 cm^{-1}, $\nu(C{=}C)$ 1611 cm^{-1}] and by NMR data [$H_{1,2}$ 2.8 ppm (doublet $J = 8$ cps), H_3 6.58 ppm and $H_{4,5}$ 4.82 ppm (complex peak)].





$$L_2Rh(\pi\text{-}C_4H_7)Cl_2 + CO \rightarrow trans\text{-}L_2Rh(CO)Cl + CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_2Cl$$

Preliminary examination by infrared spectroscopy of the reaction of CO with the phosphine and arsine complexes revealed that the reaction is much more complicated than one would expect on the basis of the stoichiometry. Therefore, the reaction was also followed by measuring simultaneously the electrical conductivity, the gas uptake and the NMR spectra.

Particularly important information was obtained from the carbonyl stretching frequency, which is known to be very sensitive to the nature and the state of oxidation of the metal and to the nature of the ligand at the trans position with respect to the

TABLE 1

CARBONYL STRETCHING FREQUENCIES FOR SOME TRANSITION METAL CARBONYL COMPLEXES AS INFLUENCED BY THE *trans*-LIGAND AND THE OXIDATION STATE OF THE METAL

Complex	Metal	Oxid. state	*trans*-ligand of CO	ν(C=O)(cm^{-1})	Ref.
$[(C_6H_5)_3P]_2(CO)RhCl$	Rh	I	Cl	1960	26
$[(CO)_2RhCl_2]_2$	Rh	I	μ-Cl	2015, 2076	26
$[(C_6H_5)_3P]_2(CO)Rh(CH_2{-}CH{=}CH_2)Cl_2$	Rh	III	Cl	2035	17
$[(C_6H_5)_3P]_2(CO)IrCl$	Ir	I	Cl	1972	24
$[(C_6H_5)_3P]_2(CO)IrCl_3$	Ir	III	Cl	2079	24
$[(C_6H_5)_3P]_2(CO)IrH_2Cl$	Ir	III	H	2010	25
$[(C_6H_5)(C_2H_5)_2P]_2(CO)IrBr_3$	Ir	III	Br	2056	27
$[(C_2H_5)_3P]_2(CO)IrCl_3$	Ir	III	$(C_2H_5)_3P$	2073	27
$[(C_6H_5)_3P](CO)_4Mn[C(O)CH_3]$	Mn	I	CO	1631	23

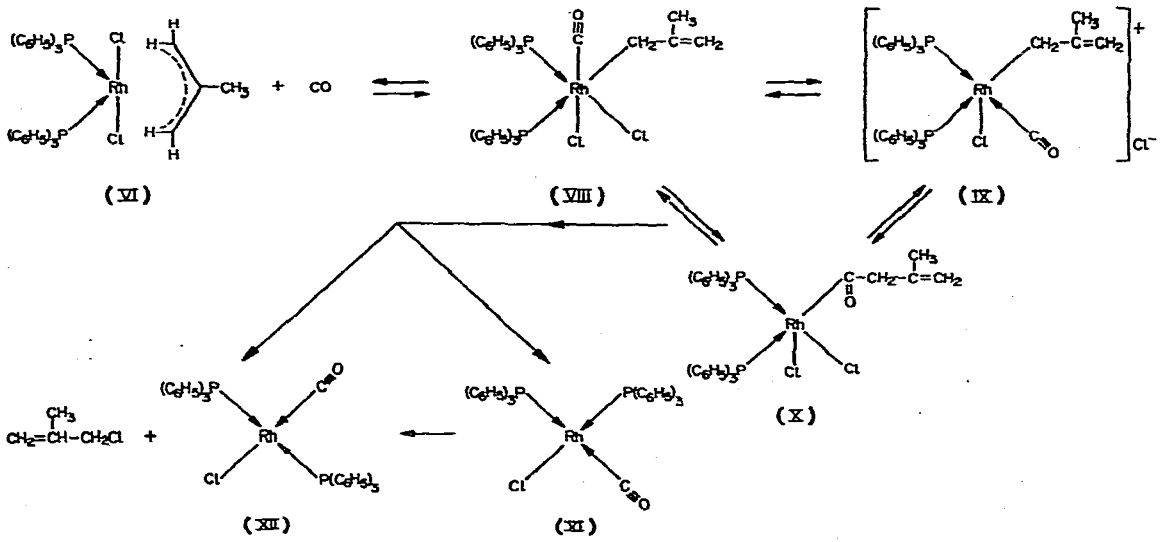


Fig. 2. Suggested path of the reaction of carbon monoxide with bis(triphenylphosphine)-π-methallylrhodium dichloride.

carbonyl group. In addition, a carbonyl group inserted in a metal–carbon bond also shows a characteristic stretching frequency. Some literature data of the carbonyl stretching frequencies are summarized in Table 1.

a. $[(C_6H_5)_3P]_2Rh(\pi\text{-}C_4H_7)Cl_2$. The reaction of CO (1 atm) with bis(triphenylphosphine)-π-methallylrhodium dichloride dissolved in chloroform at 0° can be described by the scheme shown in Fig. 2.

From the beginning of the carbon monoxide consumption onwards a number of carbonyl-containing species were formed, *viz.* a π-methallylcarbonylrhodium(III) complex, (VIII), which was about 20% dissociated into (IX), an insertion product, (X), and two carbonyl rhodium(I) complexes, (XI) and (XII). The infrared spectra (Fig. 3) show carbonyl stretching frequencies at 2080 (VIII), 2015 (IX), 1710 (X) and a broad signal at 1985–1970 [(XI)+(XII)]. The NMR spectra (Fig. 4) show a pattern characteristic of the σ-methallyl group (VIII), *viz.* (CH_3 1.44 ppm, $H_{3,4}$ 3.48 ppm, H_1 4.60 ppm and H_2 4.20 ppm); the signals due to (IX) and (X) were of too low intensity to be resolved. Complex (VIII) is about 20% dissociated, as was inferred from the increase in electrical conductivity of the reaction mixture during CO consumption. The conductivity cannot be explained by dissociation of X, since experiments at 20° show that the insertion product is hardly formed at this temperature while the electrical conductivity remains constant. We assume an equilibrium between the species (VIII), (IX) and (X)*, and formation of the final product (XII) from one of these species. The appearance of two carbonyl stretching frequencies at 1985 cm^{-1} and 1970 cm^{-1} initially and only one at 1970 cm^{-1} finally may be due to the initial formation of *cis*-$[(C_6H_5)_3P]_2Rh(CO)Cl$ (XI) which isomerizes to the *trans* product on being left standing. Replacing π-methallyl by π-allyl leads to a complex similar to (VIII). The NMR spectrum shows signals at 5.90 ppm (H_5), at 5.13, 5.21 and 5.37 ppm (ratio 1 : 2 : 1, $H_{3,4}$) and 4.00 ppm (doublet $J = 7$ cps, $H_{1,2}$).

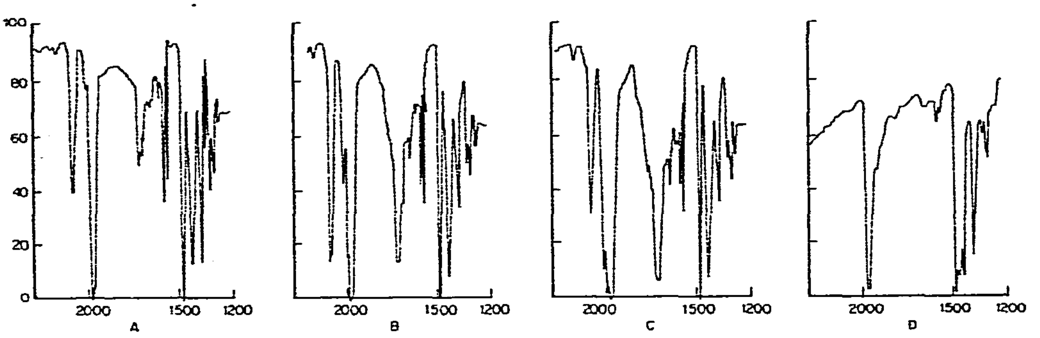


Fig. 3. Infrared spectra of a solution of $[(C_6H_5)_3P]_2Rh(\pi\text{-}C_4H_7)Cl_2$ in $CHCl_3$ at 0° when CO is passed through. A, reaction time 18 min^{-1}; B, reaction time 27 min^{-1}; C, reaction time 60 min^{-1}; D, reaction time infinity.

b. $[(C_6H_5)_3As]_2Rh(\pi\text{-}C_4H_7)Cl_2$. The reaction of carbon monoxide (1 atm)

---

* Similar equilibria have recently been noted for $RhCl_2(COCH_3)(PPh_3)_2$[31].

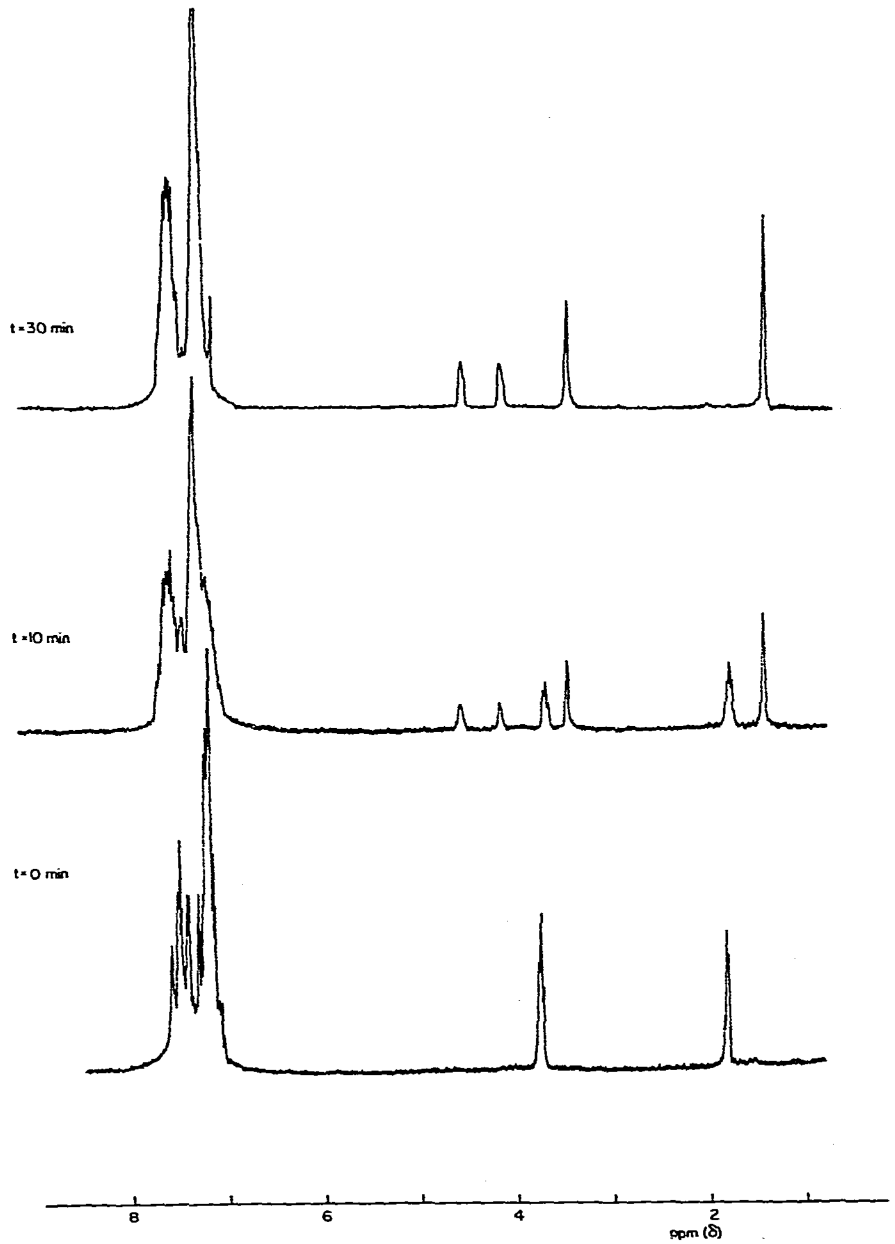


Fig. 4. Time dependence of the NMR spectrum of a reaction mixture of $[(C_6H_5)_3P]_2Cl_2Rh(\pi\text{-}C_4H_7)$ and carbon monoxide in $CDCl_3$ at 0°.

with bis(triphenylarsine)-π-methallylrhodium dichloride dissolved in chloroform can be pictured as follows:

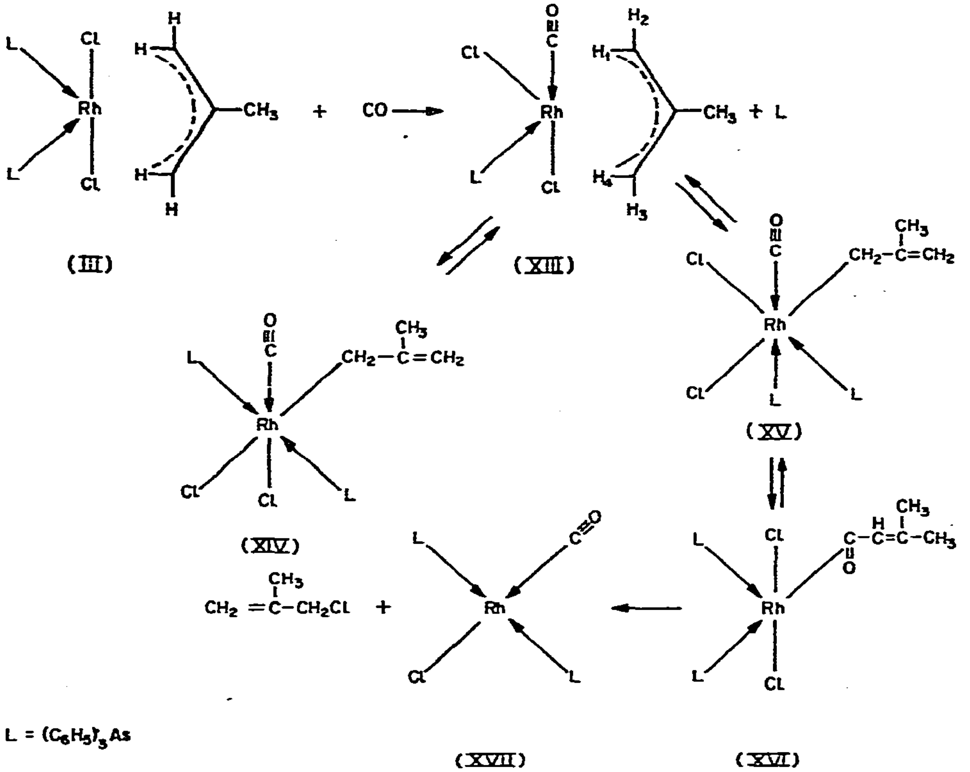


Fig. 5. Suggested path of the reaction of carbon monoxide with bis(triphenylarsine)-π-methallylrhodium dichloride.

In contrast to the triphenylphosphine case, an asymmetric π-methallyl complex (XIII) is initially formed by displacement of a triphenylarsine ligand. On further progress of the reaction σ-methallyl-containing species (XIV) and (XV) and subsequently the insertion product (XVI) are formed. Finally *trans*-bis(triphenylarsine)carbonylrhodium chloride and methallyl chloride are quantitatively obtained.

The reaction course is evidenced by the following observations. During the CO consumption the electrical conductivity increased only to a very small extent, in contrast to the triphenylphosphine case. It is an interesting fact that in the reaction with ethene an analogous first reaction step was observed. This is in particular deduced from the NMR spectra (Fig. 6) of complexes (XIII) and (XIV) or (XV), which were completely identical with the ones observed for the intermediates in the ethylene reaction [as (IV) and (V), respectively]. This similarity of the reaction patterns excluded the possibility of assigning the NMR signals to a Rh–C(O)–CH_2–C(CH_3)=CH_2 entity. It indicates, however, that the ethylene and the carbonyl ligands are not located *trans* with respect to the σ-methallyl group, since in that position a strong *trans* effect would influence the NMR pattern of the σ-methallyl group in a different way. The infrared spectra show first the appearance of two C=O bands at 2060 cm^{-1} and 2015 cm^{-1}; in the later stage of the reaction these bands disappear in part at the

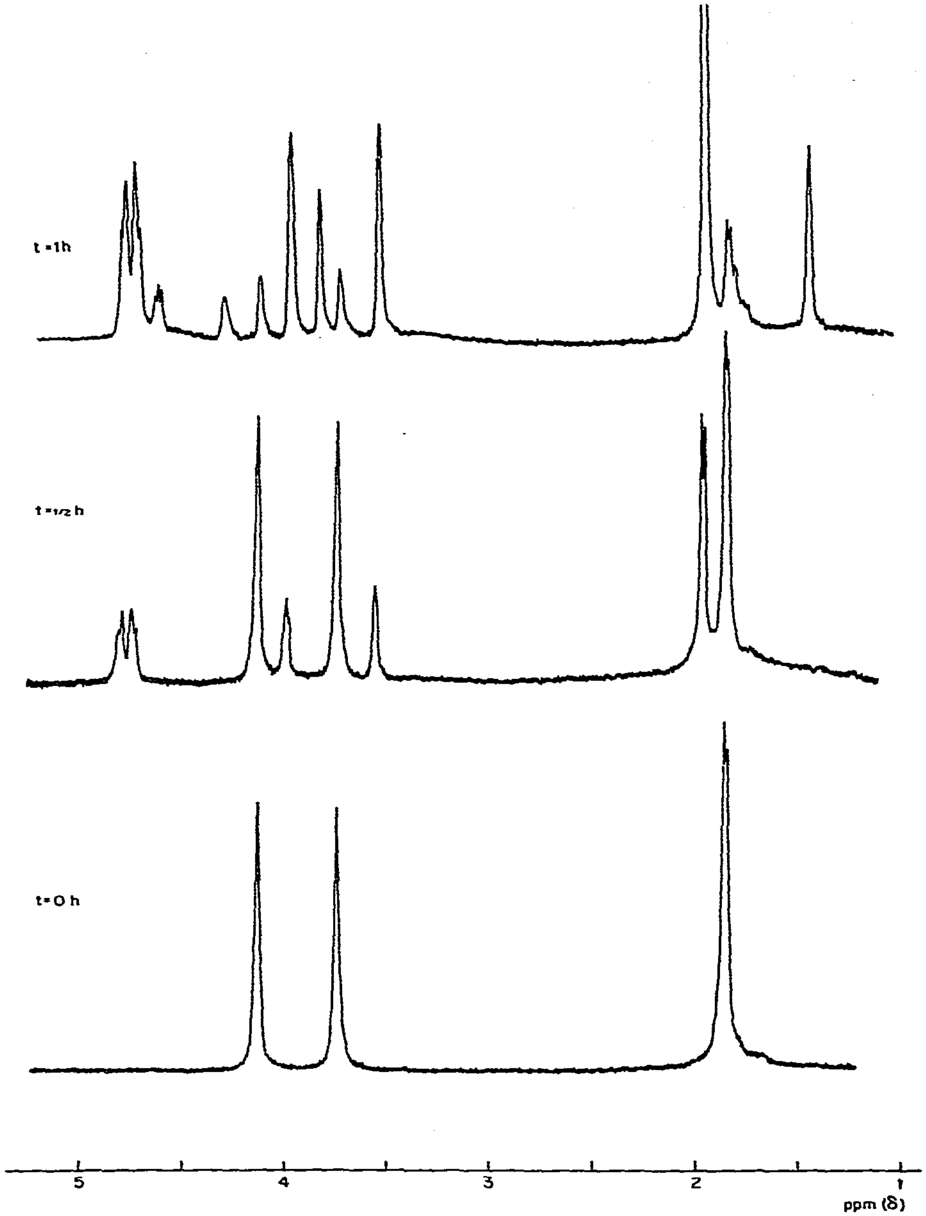


Fig. 6. Time dependence of the NMR spectrum of a reaction mixture of $[(C_6H_5)_3As]_2Rh(\pi\text{-}C_4H_7)Cl_2$ and carbon monoxide in $CDCl_3$ at 0°.

cost of two new bands at 2090 cm^{-1} and 1710 cm^{-1}. Finally, at 1970 cm^{-1} an absorption band was observed for the end product, (XVII).

The bands at 2060 cm^{-1}, 2015 cm^{-1} and 2090 cm^{-1}—indicative of trivalent rhodium carbonyl complexes—are tentatively assigned to (XIII), (XIV) and (XV), while the band at 1710 cm^{-1} is ascribed to the insertion product, (XVI).

c. $[(C_6H_5)_3Sb]_2Rh(\pi\text{-}C_4H_7)Cl_2$. In contrast with the phosphine and arsine cases, about three moles of carbon monoxide were consumed by a solution of bis(triphenylstibine)-π-methallylrhodium dichloride in chloroform. Another difference is the fact that methallyl chloride is not produced. A black reaction product is formed, to which a definite structure could not be assigned.

A similar result was obtained from the reaction of tris(triphenylstibine)rhodium chloride and carbon monoxide. The reaction does not proceed via the intermediate formation of $[(C_6H_5)_3Sb]_3(CO)RhCl$, as was demonstrated in a separate experiment.

The extension of the coordination of square planar rhodium(I) complexes to five coordination is known to be strongly favoured by ligands like triphenylstibine with a strong π-acceptor character, thus reducing the electron density at the metal atom.

Examples are the reaction of amines with (1,5-cyclooctadiene)(triphenylstibine)rhodium chloride[28] yielding (amine)(1,5-cyclooctadiene)(triphenylstibine)rhodium chloride and the formation of tris(triphenylstibine)carbonylrhodium chloride[26,29].

KINETICS

The reaction of carbon monoxide with $L_2Rh(\pi\text{-}C_4H_7)Cl_2$ dissolved in chloroform was found to be first-order in the concentration of the complex and, at least for the triphenylphosphine and arsine ligands first-order in the carbon monoxide pressure. By measuring the solubility of carbon monoxide in chloroform values for the experimental second-order rate constants k_2 were obtained.

TABLE 2

SECOND-ORDER RATE CONSTANTS OF THE REACTION OF CO WITH $L_2Rh(\pi\text{-}C_4H_7)X_2$ IN CHLOROFORM AT 0°

L	X	k_2(l·mole^{-1}·sec^{-1})
$(C_6H_5)_3Sb$	Cl	0.07
$(C_6H_5)_3As$	Cl	1.7
$(C_6H_5)_3P$	Cl	1.3
$(C_6H_5)_3P$	Br	0.9
$(C_6H_5)_3P$[a]	Cl	0.7

[a] $\pi\text{-}C_3H_5$ instead of $\pi\text{-}C_4H_7$.

Replacement of the halide, the ligand L or the methallyl group for allyl does not affect the rate of carbon monoxide consumption to an appreciable extent. The low value found for the stibine case must be due to the reaction course being different.

Addition of the ligand L to a solution of $L_2Rh(\pi\text{-}C_4H_7)Cl_2$ in chloroform results in an increase in the rate of carbon monoxide uptake. For arsine one would expect a decrease on the basis of the mechanism pictured in Fig. 5. However, the increase observed can be rationalized by the fact that in the presence of excess L the complex is in equilibrium with methallyl chloride and L_3RhCl; the latter is known to be more reactive towards carbon monoxide than $L_2Rh(\pi\text{-}C_4H_7)Cl_2$.

CONCLUSION

The main results can be summarized as follows.

Sulfur dioxide coordinates in the reaction with $[(C_6H_5)_3P]_2Rh(\pi\text{-}C_4H_7)Cl_2$ to the rhodium atom, but does not insert perceptibly.

Ethylene dimerizes to butenes to a small extent.

The best-studied reaction is that between carbon monoxide and $L_2Rh(\pi\text{-}C_3H_4R)Cl_2$, which was found to proceed by a complicated mechanism even if the final products are simple ones: *trans*-$L_2(CO)RhCl$ and $CH_2{=}C(R){-}CH_2Cl$ (for $L =$ phosphine or arsine).

Intermediate complexes of rhodium(III) with π- and σ-methallyl groups and an insertion product were identified.

The ease of displacement of a ligand L by either CO or ethylene decreases in the order $(C_6H_5)_3As > Cl > (C_6H_5)_3P$.

The π-allyl complexes show a tendency to give σ-allyl carbonyl complexes rather than π-allyl carbonyl compounds. Furthermore, the CO insertion product seems less labile than the analogous σ-methallyl carbonyl complex; these results fit in with the greater lability of the π-allyl–metal bonding relative to the π-methallyl–metal bonding.

No specific correlation has been found between the nature of the ligand L and the rate of the reaction of the complexes $L_2Rh(\pi\text{-}C_4H_7)Cl_2$ with carbon monoxide. The difference in the primary reaction products in this reaction, *viz.* a σ-methallyl carbonyl complex (VIII) for $L=(C_6H_5)_3P$ and a π-methallyl carbonyl complex (XIII) for $L=(C_6H_5)_3As$ may be reflected by the destabilizing influence of the ligand L.

EXPERIMENTAL*

Apparatus for gas consumption

The apparatus consisted of a flask of 50–100 ml provided with a side tube carrying a small teflon beaker containing the complex. The top of the flask was connected to a gas burette and to vacuum and gas supply lines. The apparatus was immersed in a thermostat bath. The air in the apparatus was replaced by either ethylene or carbon monoxide.

After temperature equilibrium had been reached the reaction was started by adding the complex to the solvent, which was stirred magnetically.

NMR measurements

The NMR spectra were determined with a Varian HA 100 spectrometer. Tetramethylsilane was used as an internal reference: deuterochloroform or dichloromethane were used as solvents.

The gases (either ethylene or carbon monoxide) were passed through a solution of the complex in a NMR tube. The reaction time was correlated with the gas uptake by the results obtained gasometrically.

---

* With Miss M. Gronert and J. W. F. M. Lemmers.

IR measurements

The IR spectra were determined with a grating IR spectrophotometer Perkin–Elmer 337 E.

The reactions with carbon monoxide and ethylene were followed by the IR spectra either of the solutions or of the complexes obtained by quenching of the reaction mixture with pentane. The IR spectra of the precipitates formed were recorded as mulls.

Conductivity measurements

Conductivities were measured with a Philips Philoscope G.M. 4249 using Pt electrodes. Dichloromethane was used as solvent.

Starting materials and analyses

The syntheses of the starting materials $L_2Rh(\pi\text{-}C_3H_4\text{–}R)Cl_2$ have already been described in Part I[1].

Tris(triphenylstibine)carbonylrhodium chloride was prepared by the method of Vallarino[26,29,30].

The elemental analyses were performed by means of the usual techniques except for the metals, arsine and stibine which were analysed by (radio-active) activation techniques.

Sulfur dioxide

A solution of bis(triphenylphosphine)-π-methallylrhodium chloride (0.5 g) in 15 ml of liquid sulfur dioxide was kept at 20° for 40 h. Addition of 200 ml of pentane to the reaction mixture yielded, after evaporation of the excess sulfur dioxide, 0.46 g of bis(triphenylphosphine)(sulfur dioxide)-σ-methallylrhodium dichloride. (Found: C, 54.6; H, 4.5; Cl, 8.4; P, 6.8; Rh, 11.7; S, 4.4. $C_{40}H_{37}Cl_2O_2P_2RhS$ calcd.: C, 58.13; H, 4.39; Cl, 8.6; P, 7.80; Rh, 12.81; S, 3.88%.)

By direct introduction in the mass spectrometer SO_2 was found as the only sulfur-containing fragment.

By a similar procedure the corresponding allyl compound was obtained. (Found: C, 54.8; H, 4.56; Cl, 8.9; P, 6.8; Rh, 11.0; S, 4.4. $C_{39}H_{35}Cl_2O_2P_2RhS$ calcd.: C, 58.29; H, 4.39; Cl, 8.83; P, 7.71; Rh, 12.81; S, 3.99%.)

Ethylene

The hydrocarbon analysed in the ethylene experiments were identified by GLC technique (6 m squalane, 25% Sil-o-Cel; 55°; 0.5 atm H_2; flame ionization).

Carbon monoxide

The allyl chlorides were identified by NMR and GLC. The monovalent *trans*-$L_2(CO)RhCl$ compounds obtained from the reaction mixture appear to be identical with authentic samples.

REFERENCES

1 H. C. Volger and K. Vrieze, *J. Organometal. Chem.*, 9 (1967) 527.
2 K. Vrieze and H. C. Volger, *J. Organometal. Chem.*, 9 (1967) 537.

3 H. C. VOLGER AND K. VRIEZE, *J. Organometal. Chem.*, 6 (1966) 297.
4 J. P. BIBLER AND A. WOJCICKI, *J. Amer. Chem. Soc.*, 86 (1964) 5051; 88 (1966) 4862.
5 F. A. HARTMAN AND A. WOJCICKI, *J. Amer. Chem. Soc.*, 88 (1966) 844.
6 A. WOJCICKI, J. P. BIBLER AND F. A. HARTMAN, *Proceedings, 9th ICCC*, St. Moritz Bad, September 1966, p. 175.
7 H. S. KLEIN, *Chem. Commun.*, (1968) 377.
8 D. MEDEMA, C. F. KOHLL AND R. VAN HELDEN, to be published.
9 R. F. HECK, *J. Amer. Chem. Soc.*, 85 (1963) 1220.
10 C. S. KRAIHANZEL AND P. K. MARPLES, *J. Amer. Chem. Soc.*, 87 (1965) 5267.
11 J. TSUJI, J. KIJI, S. IMAMURA AND M. MORIKAWA, *J. Amer. Chem. Soc.*, 86 (1964) 4350.
12 M. GREEN AND D. C. WOOD, *J. Amer. Chem. Soc.*, 88 (1966) 4107.
13 J. TSUJI *et al.*, *Tetrahedron Lett.*, (1965) 3969, 4565; *J. Amer. Chem. Soc.*, 88 (1966) 3452, 4713.
14 J. BLUM, *Tetrahedron Lett.*, (1966) 1605.
15 J. CHATT AND B. L. SHAW, *J. Chem. Soc., A*, (1966) 1437.
16 J. T. MAGUE AND G. WILKINSON, *J. Chem. Soc., A*, (1966) 1736.
17 D. N. LAWSON, J. A. OSBORN AND G. WILKINSON, *J. Chem. Soc., A*, (1966) 1733.
18 R. CRAMER, *J. Amer. Chem. Soc.*, 87 (1965) 4717.
19 J. A. OSBORN, F. H. JARDINE, J. F. YOUNG AND G. WILKINSON, *J. Chem. Soc., A*, (1966) 1711.
20 L. VASKA AND S. S. BATH, *J. Amer. Chem. Soc.*, 88 (1966) 1333 and references cited therein.
21 K. VRIEZE, C. MACLEAN, P. COSSEE AND C. W. HILBERS, *Rec. Trav. Chim. Pays-Bas*, 85 (1966) 1077.
22 C. A. REILLY AND H. E. THYRET, *J. Amer. Chem. Soc.*, 89 (1967) 5144.
23 R. J. MAWBY, F. BASOLO AND R. G. PEARSON, *J. Amer. Chem. Soc.*, 86 (1964) 5043.
24 L. VASKA AND J. W. DILUZIO, *J. Amer. Chem. Soc.*, 83 (1961) 2784; 84 (1962) 679.
25 R. CRAIG TAYLOR, J. F. YOUNG AND G. WILKINSON, *Inorg. Chem.*, 5 (1966) 20.
26 W. HIEBER, H. HEUSINGER AND O. VOHLER, *Chem. Ber.*, 90 (1957) 2432.
27 J. CHATT, N. P. JOHNSON AND B. L. SHAW, *J. Chem. Soc.*, (1964) 1625.
28 L. CATTALINI, A. ORIO, R. UGO AND F. BONATI, *Chem. Commun.*, (1967) 48.
29 W. HIEBER AND V. FREY, *Chem. Ber.*, 99 (1966) 2614.
30 L. VALLARINO, *J. Chem. Soc.*, (1957) 2287.
31 M. C. BAIRD, J. T. MAQUE, J. A. OSBORN AND G. WILKINSON, *J. Chem. Soc., A*, (1967) 1347.
32 K. VRIEZE, P. COSSEE, A. P. PRAAT AND C. W. HILBERS, *J. Organometal. Chem.*, 11 (1968) 353.