

SYNTHESIS, STRUCTURE AND REACTIONS OF CHELATE METAL-OLEFIN COMPLEXES

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ABSTRACT

The results of a series of investigations of the behaviour of potential olefin-phosphine and olefin-arsine chelate groups with transition metals are presented. After a brief discussion of the nature of the metal-olefin bond the various types of reaction which are shown by C=C double bonds which are in close proximity with or are coordinated to a transition metal atom are summarized. The *coordination*, *isomerization* and *oxidation* reactions of ortho-chelate ligands with transition metals are then discussed. Some interesting intramolecular re-arrangements which are analogous with organic Wagner-Meerwein re-arrangements are discussed.

INTRODUCTION AND SCOPE

The object of this lecture is to attempt to bring together some recent advances in the chemistry of transition metal complexes containing chelate groups in which there is one σ donor atom (charged or uncharged) and one or more olefin groups suitably located for possible coordination with the metal atom. Their synthesis, structure and reactions will be discussed. In particular, the action of halogens on those complexes which contain double bonds coordinated to, or in close proximity with, metal atoms will be considered in some detail.

Of the many fundamental questions concerning the metal-carbon bond in transition metal complexes the following are of special interest:

1. What properties of the metal atom (formal charge thereon, electron configuration, nature of other ligands attached thereto, etc.) determine whether stable metal olefin bonds can be formed?
2. What is the effect of substituents in the olefin group on the stability of the metal-olefin bond.
3. What properties of the metal atom and the carbon ligand decide the stability of metal-carbon σ bonds?
4. What factors determine the ease of change-over from metal-olefin to metal-carbon (σ) type bonds when reaction occurs with other reagents?

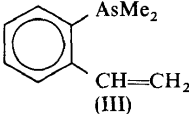
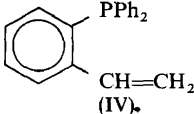
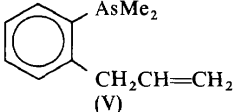
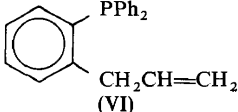
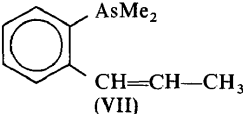
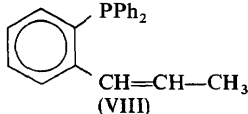
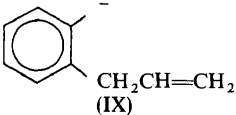
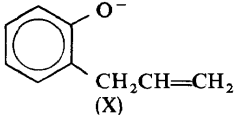
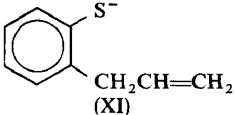
To help answer some of these questions, we started, some years ago, to prepare a series of potential chelating olefin ligands containing at least one strong σ donor located geometrically so as to enable the double bond to be capable of being oriented in the appropriate position for coordination. This

chelate effect was expected to enable one to stabilize olefin complexes of those metals for which unchelated mono-olefin derivatives were either unknown or unstable.

TYPES OF CHELATING OLEFIN LIGANDS

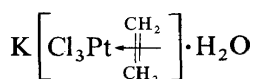
Ligands have been prepared in which one, two and three olefin groups are present in addition to one donor group charged or uncharged. The best σ donors are polarizable atoms such as tertiary arsine or phosphine atoms; also charged atoms such as RO^- , RS^- and R_3C^- are convenient. Tervalent nitrogen has been used but in general is not as convenient for the later transition metals as the more polarizable ligands. The bidentate chelate groups studied in these investigations are given in *Table 1*.

Table 1. Olefin chelate groups studied

| | | | | |
|--------------------|---|-------|--|--------|
| | (I) $(CH_3)_2AsCH_2CH_2CH_2CH=CH_2$ | | (II) $Ph_2PCH_2CH_2CH_2CH=CH_2$ | |
| <i>o</i> -styryl |  | (III) |  | (IV) |
| <i>o</i> -allyl |  | (V) |  | (VI) |
| <i>o</i> -propenyl |  | (VII) |  | (VIII) |
| charged |  | (IX) |  | (X) |
| | | |  | (XI) |

NATURE OF THE METAL-OLEFIN BOND

The simplest and best known metal-olefin complex is Zeise's salt



first reported in 1827. The stereochemistry of attachment of the C_2H_4 group

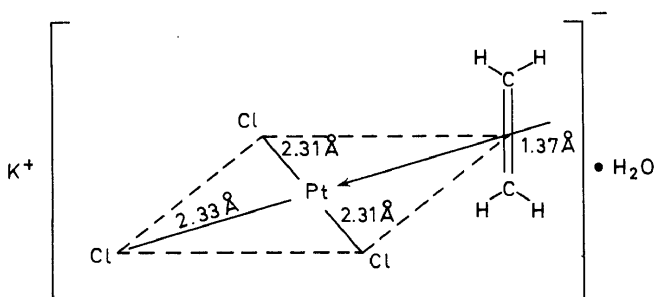


Figure 1. Structure of Zeise's salt (Owston *et al.*, 1970). The C=C bond is inclined at an angle of $84^\circ \pm 1^\circ$ to the vertical plane. It is tilted in towards the Pt atom and the centre of the C=C bond is 0.20 \AA above the plane of Pt.

in this compound was first determined by x-ray investigation¹ in 1955. A more detailed structure by Owston² and his collaborators is shown in Figure 7. The Chatt–Dewar–Duncanson³ model of the bonding has received widespread acceptance; it explains the main features of the structure and the observed physical properties such as infra-red and p.m.r. spectra. In essence, as shown in Figure 2, it assumes a donation of π electron density of

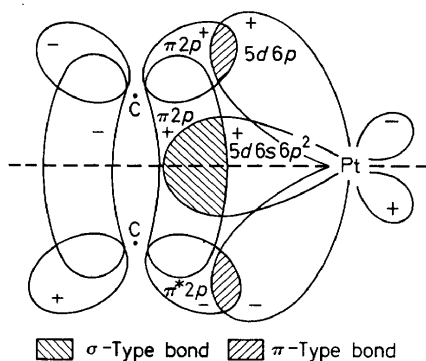


Figure 2

the C=C bond into one of the $5d\ 6s\ 6p^2$ (σ) orbitals of the platinum with a synergistic return of electron density by the Pt(II) atom to the olefin by overlap of the (filled) d_{xy} orbital of the metal atom with the (empty) anti-bonding p^* orbitals of the two carbon atoms. Loss of π electron density from the double bond is expected to weaken the C=C bond and hence decrease its stretching frequency (1623 cm^{-1} in the free ligand); the addition of electron density to the anti-bonding orbitals of the two carbon atoms has the same effect. The size of the decrease in the C=C stretching frequency upon coordination depends on many factors, e.g. the nature of the metal; the groups attached to the two carbon atoms, and the other ligands attached to the platinum atom; Grogan and Nakamoto⁴ have reported the data in Table 2; they suggest that although the decrease in the C=C stretching

frequency is widely used as a measure of strength of coordination of the olefin to the metal atom, the metal-olefin stretching frequency (or better still the force constant thereof) would be a better measure of strength of attachment. Although most investigators have assumed that the change in

Table 2. The C=C and Pt-olefin stretching frequencies of mono-olefin Pt(II) in cm^{-1} complexes

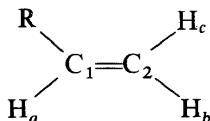
| Complex | $\nu_{(\text{C}=\text{C})}$ Free olefin | $\nu_{(\text{C}=\text{C})}$ Coordinated olefin | $\Delta\nu$ | ν for metal-olefin |
|--|---|--|-------------|---------------------------|
| $\text{K}[(\text{C}_2\text{H}_4)\text{PtCl}_3] \cdot \text{H}_2\text{O}$ | 1623 | 1526 | 97 | 407 |
| $\text{K}[(\text{C}_2\text{D}_4)\text{PtCl}_3] \cdot \text{H}_2\text{O}$ | 1515 | 1428 | 87 | 387 |
| $\text{K}[(\text{C}_2\text{H}_4)\text{PtBr}_3] \cdot \text{H}_2\text{O}$ | 1623 | 1511 | 112 | 395 |
| $\text{K}[(\text{C}_3\text{H}_6)\text{PtCl}_3]$ | 1649 | 1505 | 144 | 393 |
| $\text{K}[(\textit{trans}\text{-C}_4\text{H}_8)\text{PtCl}_3]$ | 1681 | 1522 | 159 | 387 |
| $\text{K}[(\textit{cis}\text{-C}_4\text{H}_8)\text{PtCl}_3]$ | 1672 | 1505 | 167 | 405 |

the (alleged) C=C stretch is a good first order measure of strength of bonding, Hiraishi⁵ and co-workers have questioned the use of this criterion. It is claimed that the C=C stretching frequency is mixed with a CH_2 scissoring mode and they have studied the C_2D_4 complexes to obtain support for their suggestion. It is proposed that whereas the 1520 cm^{-1} band in the C_2H_4 complex is due mainly to the CH_2 scissoring, a band at 1243 cm^{-1} is due to C—C stretching; on deuteration a new band at 1353 cm^{-1} is considered to arise from C—C stretching and the 962 cm^{-1} band is assumed to arise from CD_2 scissoring. Hiraishi and his collaborators assign the bands at 405 cm^{-1} and 493 cm^{-1} to symmetric and anti-symmetric Pt—C stretching and like Grogan and Nakamoto regard these bands as a better indication of the strength of the Pt-olefin bonding. More work seems to be necessary on partially substituted olefin-platinum complexes before the assignments of the C=C stretch and CH_2 scissoring can be regarded as final. At least it can be said that there is a band observed about 1520 cm^{-1} and the difference in frequency between this and the free ligand C=C stretch at $\sim 1623 \text{ cm}^{-1}$ is empirically a rough criterion of the strength of the olefin-platinum bond and will be used as such here, with the reservations indicated above.

The use of Pt—Cl frequencies as a measure of Pt-olefin bond strength is less satisfactory since the Pt—Cl frequency is relatively insensitive to the nature of the olefin; neither deuteration nor the replacement of ethylene by another olefin has much effect upon the Pt—Cl stretching frequency.

Studies of the n.m.r. spectra of the protons in C_2H_4 provide some information concerning the nature of the metal olefin bond. Thus it has been shown⁶ that the increase in magnetic shielding felt by the olefinic protons when coordinated to platinum(II) decreases in the order ethylene > propene > *cis*-2-butene > styrene. The observed net increase in shielding seems to suggest that in the coordinate bond the π component is more significant than the σ component in the attachment to the metal atom.

It is considered that the inductive effect of the $-\text{CH}_3$ group in propene and in *cis*-2-butene and the conjugative effect of the phenyl group in styrene renders the anti-bonding p_π^* orbitals of the olefin less able to overlap effectively with the (filled) t_{2g} orbital on the Pt(II) atom. Studies of proton shielding in complexes of the mono-substituted olefin indicate that the Pt atom is



closer to C_2 than to C_1 . This is attributed to electron release by R causing π -electron density drift towards C_2 . Also a larger coupling between the Pt atom and H_b as compared with H_c suggest an orientation of the olefin so that H_b is closer to the Pt atom. It is assumed that this may be due to steric effects arising from R.

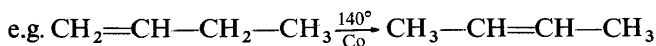
Certain general points concerning the nature of the metal-olefin bond emerge from a consideration of the stability of the known complexes of simple olefins. First, they are formed only by transition metal atoms, and especially with those in which there are one or more filled d orbitals available for donation to the p_π^* orbitals of the carbon atom. Secondly, they usually become more stable as one descends a vertical transition metal triad, e.g. Pt(II) > Pd(II) > Ni(II). [In the next triad, however, Ag(I) appears to be a better olefin acceptor than Cu(I) or Au(I)]. Thirdly, as the oxidation state of a metal atom increases, ease of complex formation with olefin decreases; thus Pt(II) forms many olefin complexes whereas none of Pt(IV) are known. Fourthly, replacement of the hydrogen atoms C_2H_4 by electron releasing (e.g. CH_3) or electron attracting (e.g. $-\text{F}$ or $-\text{CN}$) groups tends to diminish complex formation. It is difficult here to disentangle three factors: steric effects arising from bulky substituents; enhanced donation of π electrons of the C_2H_4 into the σ bond orbitals of the metal atom by introducing electron releasing groups [e.g. as in $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$]; and enhanced attraction of d_e electrons of the metal into the p_π^* (anti-bonding) orbitals of the carbon atoms arising from the presence of electron attracting groups ($-\text{F}$ or $-\text{CN}$) on the carbon atom.

REACTIONS OF SIMPLE AND CHELATING OLEFIN LIGANDS

Before discussing the reactions of complexes containing the chelate groups in which we are specially interested, it is of interest to summarize the wide variety of reactions of simple olefins which are brought about by metals or metal compounds⁷.

These include:

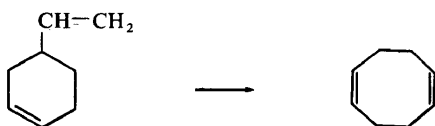
(i) Double bond isomerization (without skeletal change)



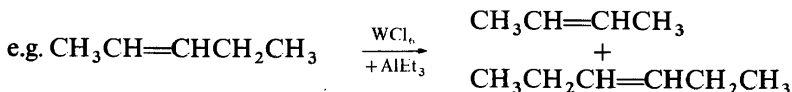
(ii) Isomerization with skeletal change

e.g. the conversion of 4-vinyl cyclohexene to 1,5-cyclo-octadiene with a Pd^{2+} catalyst

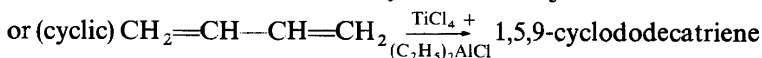
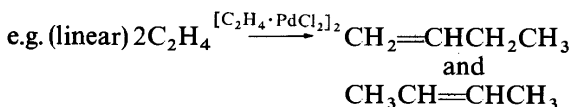
viz.



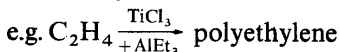
(iii) Disproportionation



(iv) Oligomerization



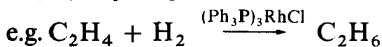
(v) Polymerization



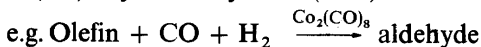
(vi) Olefin insertion



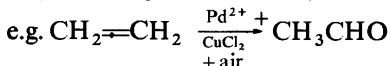
(vii) Hydrogenation



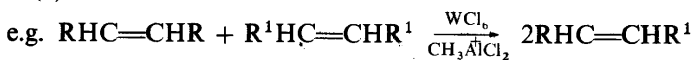
(viii) Hydroformylation (Oxo)



(ix) Catalytic oxidation (Wacker)



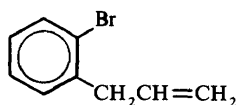
(x) Transmutation



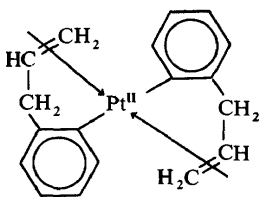
With the ligands (i) to (xi) the following types of reaction have been observed.

Coordination

Although this is a trivial type of reaction, reference is made to it to indicate the methods of synthesis used with the ligands employed. For the uncharged ligands (i) to (vii) the usual procedure is the replacement of another ligand already attached to the metal by each of the coordinating centres. Thus Cl^- is displaced from $[\text{PtCl}_4]^{2-}$ and CO from $\text{Mo}(\text{CO})_6$.⁸ A similar procedure is adopted with (ix) and (x) but in the case of (xi)⁹ one treats anhydrous platinumous chloride suspended in benzene with the Grignard reagent formed from

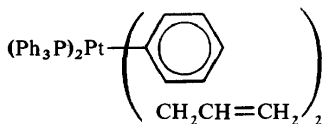


The yellow product of this reaction contains no chlorine; it melts at 186°C and analytical, infra-red and molecular weight data support the assignment of structure (XII)*



(XII)

The original $\text{C}=\text{C}$ band in *o*-bromoallyl benzene at 1635 cm^{-1} disappears and is replaced by a single band at 1532 cm^{-1} indicating that both olefin groups are coordinated. Treatment of (XII) with Ph_3P displaces both double bonds forming



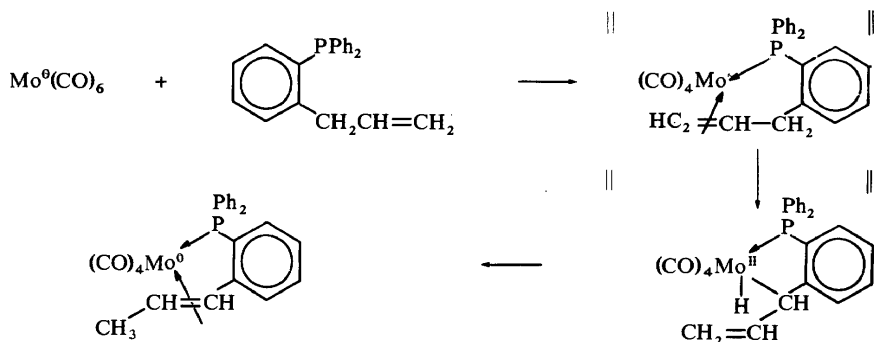
the $\text{C}=\text{C}$ frequency at 1635 cm^{-1} being once more observed. However, if anhydrous HCl be passed into a solution of (XII) in benzene, *bis*-allylbenzene dichloro platinum(II) is formed from which allylbenzene can be obtained by treatment with triphenyl-phosphine.

Surprisingly we find that *o*-allylphenol will form a *bis*-chelate compound with $\text{Pt}(\text{II})$ but *o*-allyl-thiophenol forms a hexamer with no coordinated double bonds.

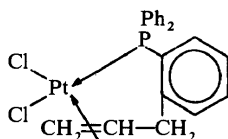
Isomerization

Treatment of the *o*-allylphosphine chelate (VI) with the hexacarbonyls of Cr, Mo and W (or better with the tetracarbonyl norbornadiene derivative) yields a tetracarbonyl metal complex in which the chelate is attached as the *cis*-propenyl-phosphine chelate group¹⁰. This isomerization takes place even in benzene solution and hence appears not to involve acid-base catalysis. A mechanism involving a π -allyl intermediate has also been postulated for such isomerization reactions. Such a mechanism here would require that the Group VI metal exceed the 18 election rule in the reaction intermediate. We suggest therefore that the following reaction path may be followed:

* Note added in proof. The electric dipole moment of (XII) indicates a *cis*-configuration.



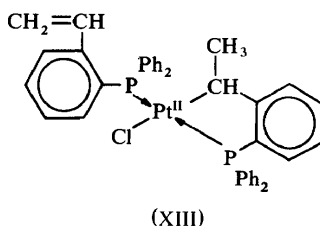
This involves a seven-coordinate hydride of Mo(II); derivatives of this type are in fact well known, e.g. $\text{C}_5\text{H}_5(\text{CO})_3\text{MoH}$. It is interesting to note that the same allyl \rightarrow propenyl isomerization does not occur with Pt(II), the product of coordination being



Although the reason may be simply because less vigorous conditions are required for this reaction, it may be significant that an isomerization by the above mechanism would require in this case the formation of a monohydride of Pt(IV) and compounds of this type appear to be unknown.

Olefin insertion reactions

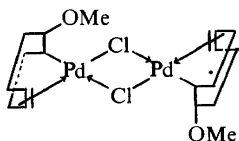
As with simple olefins, insertion reactions are observed with certain of these chelate groups. Thus if one treats *trans*-(Ph_3P)₂PtCl(H) with the *o*-styryl phosphine (IV) both triphenylphosphine groups are displaced and a compound is formed in which there is no Pt—H stretching frequency¹¹. Owing to the low solubility of the product it is difficult to assign the structure using p.m.r. with certainty but since a CH_3 group appears to be present we assign structure (XIII) to this compound



Insertion reactions of this type are, of course, well known with simple olefins but the use of chelate compounds enables one to isolate more stable products, facilitating investigations of the course of the reaction.

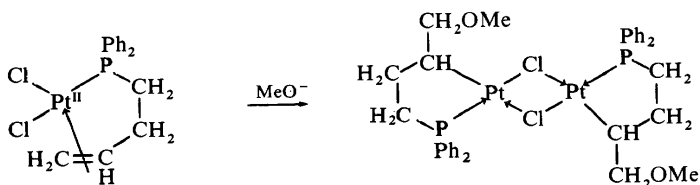
Nucleophilic attack forming metal-carbon σ bonds

Several investigators¹¹ have studied the reactions of coordinated dienes with a variety of nucleophiles, such as MeO^- , NR_2^- , the malonate ion, the acetylacetonate ion etc. For example, 1,5-cyclo-octadiene palladous chloride reacts with MeO^- to yield a halogen bridged dimer in which only one double bond is coordinated, the other becoming saturated forming one Pd—C and one C—OMe bond as in (XIV)¹².



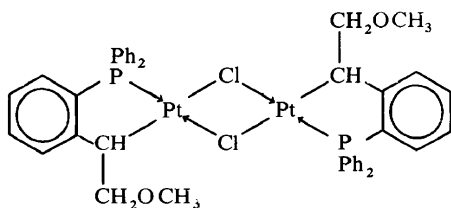
(XIV)

Hewertson and Taylor¹³ have observed a similar reaction with the chelate group $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ coordinated to Pt(II) forming (XV).



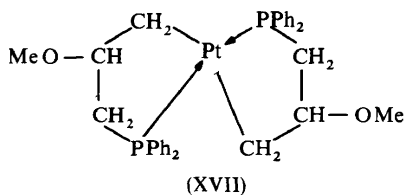
(XV)

A similar reaction occurs with the chelated *o*-vinyl phosphine chelate Pt(II) complex forming (XVI).



(XVI)

Reactions with nucleophiles are not restricted to coordinated olefins as shown by Hewertson and Taylor¹³. By treating the compound $\text{Cl}_2\text{Pt}(\text{PPh}_2-\text{CH}_2\text{CH}=\text{CH}_2)_2$ with the methoxide ion the interesting ring compound (XVII) is obtained.

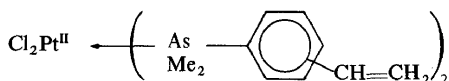


The nucleophilic reactions discussed above do not involve an oxidation of the metal atom, a halide ion being lost for each metal-carbon (σ) bond formed. We now discuss reactions in which both oxidation of the metal atom and metal-carbon (σ) bond formation occur.

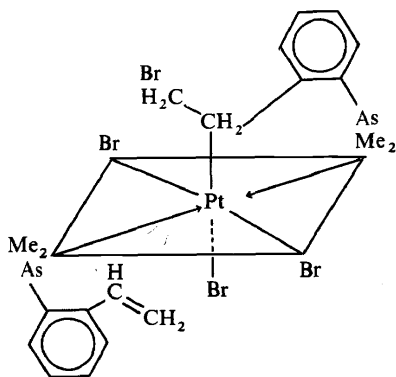
Oxidative reactions with oxidation of the metal and metal-carbon (σ) bond formation

Bidentate chelate groups with an uncoordinated olefin group

Some years ago⁸ we studied the oxidation of complexes of the type



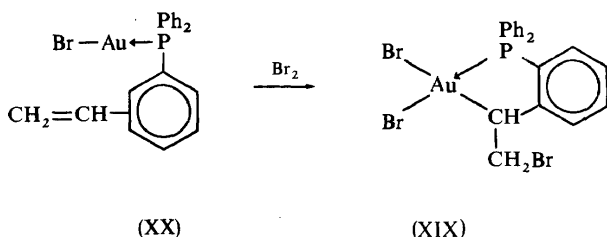
where the styryl group was in a *meta* or a *para* position. It was observed that the Pt^{II} complex reacts with three moles of bromine; the first mole oxidizes the Pt^{II} to a tetrabromo Pt^{IV} -bis-arsine complex. The second two moles then saturate successively the two double bonds. An entirely different reaction occurs, however, with the *ortho* styryl ligand. One mole of bromine causes saturation of one double bond as well as causing oxidation of the Pt^{II} to Pt^{IV} . In the product of the reaction (XVIII), discussed below, the Pt^{IV} atom is attached to the α carbon atom. Similar oxidative reactions



(XVIII)

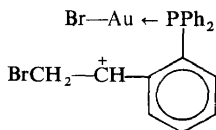
are shown by the Au^{I} bromo complexes of *o*-styryl phosphine, yielding (XIX).

SYNTHESIS, STRUCTURE AND REACTIONS OF COMPLEXES



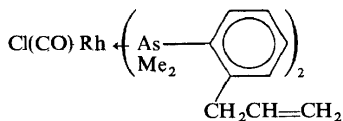
A crystal structure determination has been carried out on (XIX)¹⁴. This confirms the evidence from p.m.r. spectra that the gold atom is attached to the α carbon atom of the original styryl group.

The mechanism of the bromination reaction has not been finally established but we favour a mechanism in which the terminal carbon atom of the $-\text{CH}=\text{CH}_2$ is attacked by the positive pole of a $\text{Br}-\text{Br}$ dipole; a synchronous mechanism could then enable the negative pole to become attached to the Pt atom. Alternatively, ionization might occur, forming an intermediate of the type



the Br^- ion then attaching itself to the gold atom followed by an intramolecular nucleophilic attack of the Au^- atom on the $-\text{CH}^+-$ group. A similar mechanism would explain why in the allyl-Pt complex the Pt atom becomes attached to the β carbon atom as observed from p.m.r. studies.

These investigations have been extended to other transition metals. Complexes of Pd(II) appear to behave in the same way as those of Pt(II) on oxidation with bromine but the product, presumably containing a Pd(IV)-C(σ) bond, is much more reactive and stable products could not be isolated. The derivatives of Rh(I), however, have been studied in some detail¹⁵. Treatment of $(\text{Ph}_3\text{P})_2(\text{CO})\text{RhCl}$ with the *o*-allyl arsine ligand (V) yields the compound



This is a very convenient complex for investigation because the CO stretching frequency is diagnostic of the oxidation state of the Rh atom. [It appears at $\sim 1950\text{ cm}^{-1}$ in Rh(I) complexes and at $\sim 2050\text{ cm}^{-1}$ in Rh(III) derivatives]. Chlorination of the Rh(I) complex results first in conversion to and Rh(III) complex with a Rh-C(σ) bond; a second mole of chlorine saturates the remaining double bond and a third mole causes fission of the

Rh—C bond as shown in the sequence of reactions in *Figure 3*. Similar reactions occur with univalent iridium but the products are less soluble and hence are not easy to purify.

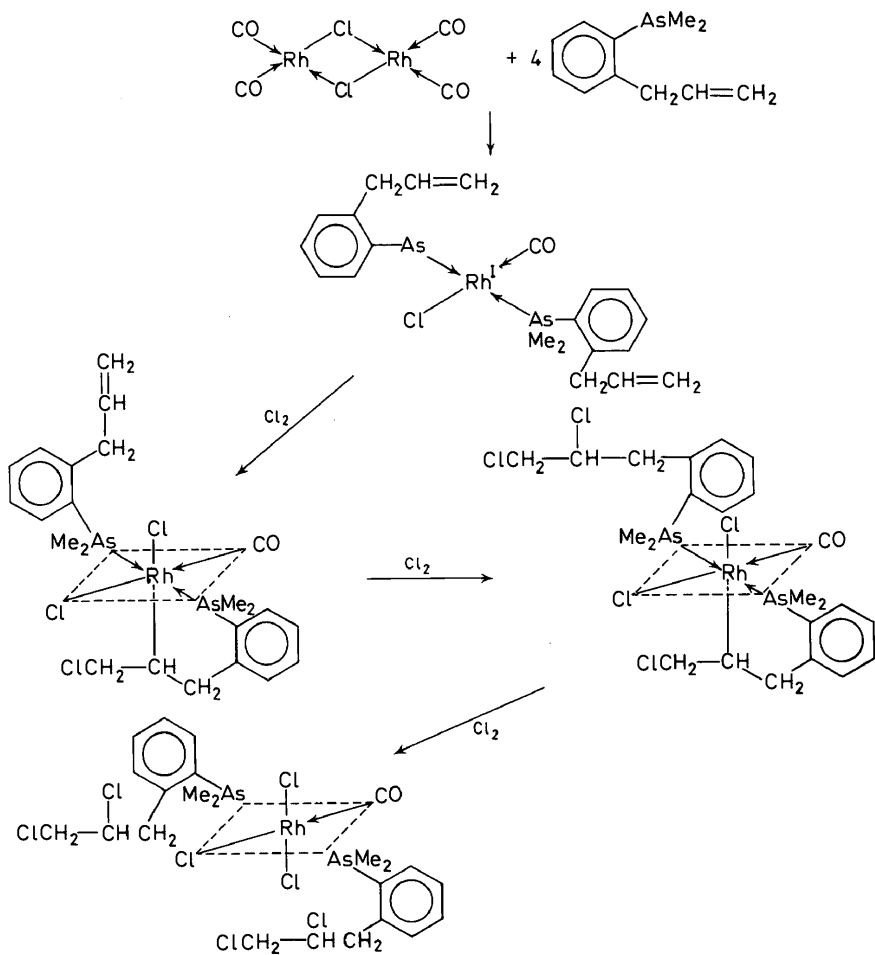
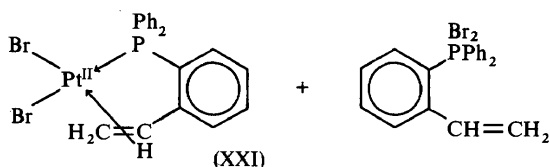
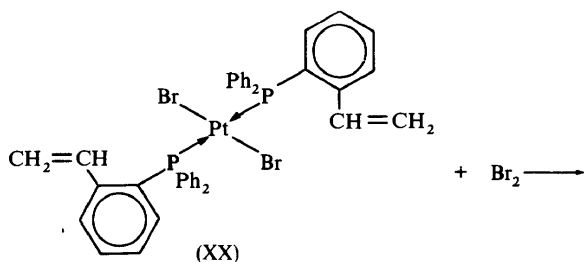
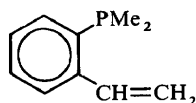


Figure 3. Chlorination of *o*-allyl-arsine rhodium(I) complexes.

The behaviour of the *o*-styryl phosphine platinum complexes is in contrast with the behaviour of the *o*-allyl arsine and *o*-styryl-arsine derivatives. If one treats the platinous complex (XX) with bromine, no oxidation of the Pt(II) atom occurs but one mole of the *o*-styryl phosphine ligand is oxidized, yielding the chelated derivative (XXI);

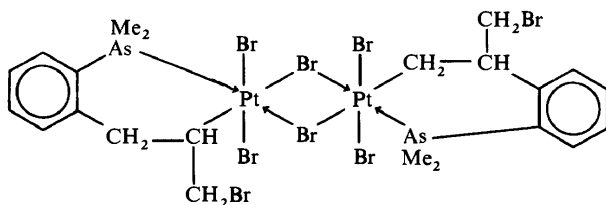
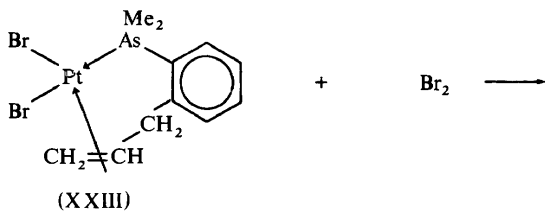


We believe that this unexpected result is due to steric effects arising from the bulky nature of the two phenyl groups attached to the phosphorus atom. But until one has studied the behaviour of the corresponding complexes of the ligand (XXII) one cannot rule out the possibility that it is caused by the more facile oxidation of the Pt—P bond.



Chelated complexes with coordinated olefin groups

Using the *o*-allyl-arsine chelate group (V) we have also studied the oxidation of chelate complexes of the type (XXIII).

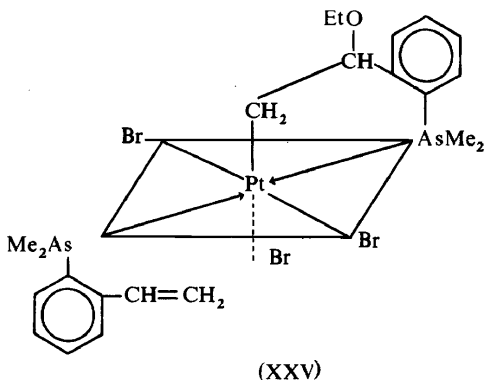


Similar oxidative reactions leading to the formation of Pt—C(σ) bonds take place but since the resulting Pt(IV) atom would be five-coordinate dimeric complexes (XXIV) are isolated.

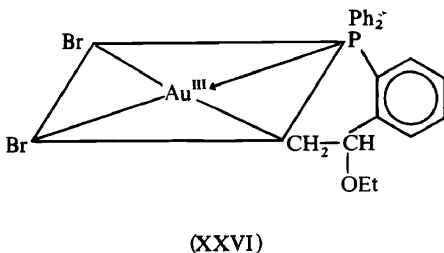
Similar dimeric compounds are obtained using chelated *o*-styryl-arsine and phosphine complexes.

Wagner–Meerwein rearrangements

A very interesting and unexpected series of reactions occur when one treats the Pt(IV) complexes of types (XVIII) or (XIX) with ethanol or methanol. The terminal Br attached to the —CH—CH₂ group is readily lost but the —OEt (or —OMe) group which replaces it is then found to be attached to the α carbon atom. Thus (XVIII) on treatment with ethanol yields the compound (XXV)



Similarly the Au(III) complex (XIX) (See p 137) yields (XXVI)



One can regard these reactions as examples of the Wagner–Meerwein rearrangement in which the Pt(IV) or Au(III) atom becomes part of a three centre intermediate as shown in *Figure 4*.

In the process of addition the OEt group attaches itself to the α carbon atom whilst the Au(III) atom becomes attached to the β carbon atom forming a six-membered ring.

In retrospect the behaviour of Au(III) and Pt(IV) in simulating quadrivalent carbon can be understood if one bears in mind that both atoms have electro-

SYNTHESIS, STRUCTURE AND REACTIONS OF COMPLEXES

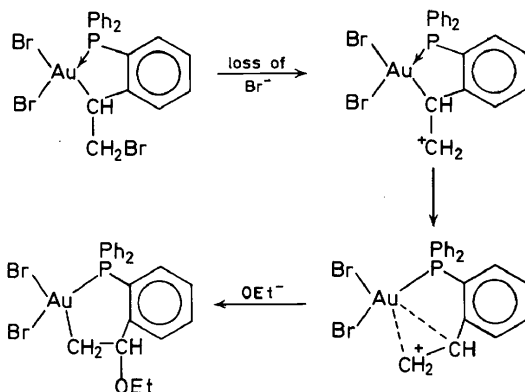


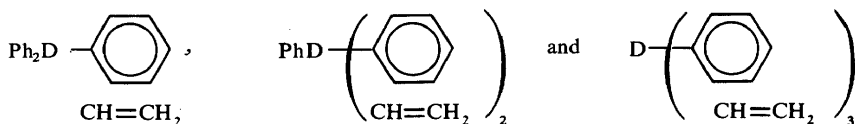
Figure 4. Wagner-Meerwein rearrangement with an Au(III) complex.

negativities similar to carbon (~ 2.5) and form metal-carbon σ bonds which are both strong and relatively unreactive.

CHELATE GROUPS CONTAINING MORE THAN ONE DOUBLE BOND

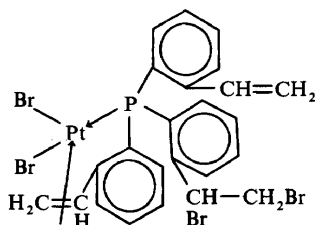
Considerable interest has developed recently in metal complexes in which more than olefin group is attached to the metal atom. Complexes with two double bonds are well known; the double bonds may be unconjugated as in the 1,5-cyclooctadiene rhodium monochloride dimer or conjugated as in butadiene tricarbonyl iron(0). Similarly three unconjugated double bonds are coordinated to the metal atom in the Ni^0 derivative of 1,5,9-cyclododecatriene whilst three conjugated double bonds are attached in chromium(0) dibenzene.

We have been comparing the ligands



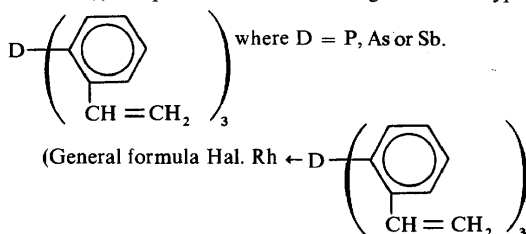
where D is a Group V (P, As Sb) donor¹⁶. This enables us to investigate the lability of the olefin group more readily than is the case with the complexes of simple olefins such as C_2H_4 as studied by van der Ent and van Soest in compounds such as $\text{IrCl}(\text{C}_2\text{H}_4)_4$. We have investigated the *tris-o*-styryl phosphorus, arsenic and stibine complexes of both Pt(II) and Rh(I) halides in some detail. In the former one obtains chelate complexes in which only *one* double bond is coordinated. In the solid state the infra-red spectrum shows two different $-\text{CH}=\text{CH}_2$ groups but in solution the p.m.r. spectrum indicates that all *three* $\text{CH}=\text{CH}_2$ groups are equivalent. These can be interpreted to mean that the three $\text{CH}=\text{CH}_2$ groups are rapidly exchanging with

the Pt(II) atom. Oxidation of this complex with bromine yields, surprisingly, the compound



Since the double bond of the styrene is attacked so much less readily than the Pt(II) atom or the coordinated double bond we believe that we have a case of Pt(II) catalysed bromination of the double bond.

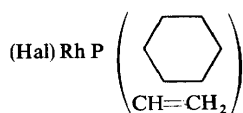
Table 3. Rhodium(I) complexes of the tri-olefin ligands of the type



| Donor atom D | Halogen | Colour | M.pt | i.r. in 1260 cm ⁻¹ region |
|--------------|---------|-------------|------------|--------------------------------------|
| P | Cl* | cream | 282°C | 1269 cm ⁻¹ |
| | Br* | pale yellow | 277°C | 1267 cm ⁻¹ |
| | I* | yellow | 236°C | 1267 cm ⁻¹ |
| As | Cl* | yellow | 239°C | 1270 cm ⁻¹ |
| | Br* | yellow | 244°C | 1270 cm ⁻¹ |
| | I | dark red | 190°C | 1252 cm ⁻¹ |
| Sb | Cl | brown | } unstable | |
| | Br | brown | | |
| | I | brown red | | |

- All complexes non-electrolytes in acetone and partly dissociated in methanol.
- Compounds marked * are monomeric.
- P.m.r. of compounds marked *: $\alpha \sim 3.75 \tau$; *cis*- $\beta \sim 5.5 \tau$; *trans*- $\beta \sim 6.6 \tau$; coupling constants; $J_{(cis)} \sim 9.0$ Hz; $J_{(trans)} \sim 165$ Hz.

The corresponding rhodium(I) complexes are shown in Table 3. Although the structure of the complex



has not yet been determined in detail preliminary x-ray studies indicate¹⁷ that all three double bonds are coordinated with C_3 symmetry as shown in Figure 5.

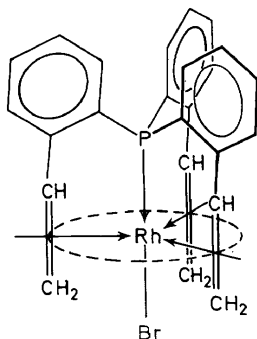
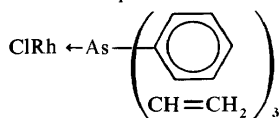


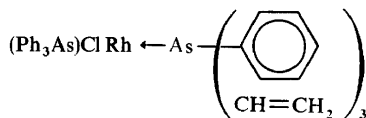
Figure 5. Proposed structure of $[\text{RhBr} \cdot \text{P}(\text{o-styryl})_3]$.
[Reproduced from *Chem. Commun.* 488 (1970) by permission.]

It is of interest to compare this structure with that of the compound $\text{ClRh} \leftarrow \text{P}(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_3$ which is also five-coordinate but in which the three double bonds are believed to be perpendicular to the axis of the trigonal bipyramid, lying in the trigonal plane.

When the five-coordinate complex



is treated with triphenylarsine, one double bond is displaced to form



but since only one $-\text{CH}=\text{CH}_2$ group is observed in the p.m.r. spectrum it is assumed that rapid exchange of the three double bonds is again taking place. The specific effect of the σ donor is illustrated by the fact that whereas the arsenic derivative reacts with AsPh_3 , the phosphine derivative does not.

CONCLUSION

A wide variety of reactions of polyolefin chelate groups has been discussed. These ligands display the expected capacity for stabilizing complexes containing several coordinated olefin groups and facilitate the study of reactions involving both replacement and oxidative reactions. Work done so far in the field suggests that the subject has a most promising future in fundamental

* Note added in proof. The $\text{CH}=\text{CH}_2$ groups are in fact inclined at an angle to the horizontal plane.

research and, perhaps, important implications for a better understanding of catalytic processes used in applied chemistry.

REFERENCES

- ¹ J. A. Wunderlich and D. P. Mellor, *J. Chem. Soc.* 2519 (1960).
- ² P. G. Owston, personal communication (1970).
- ³ M. J. S. Dewar, *Bull. Soc. Chim. France*, 18, C79 (1951);
J. Chatt and L. A. Duncanson, *J. Chem. Soc.* 2939 (1953).
- ⁴ M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.* **88**, 5454 (1966).
- ⁵ J. Hiraishi, *Spectrochim. Acta*, **25A**, 749 (1969);
J. Hiraishi, D. Finseth and F. A. Miller, *Spectrochim. Acta*, **25A**, 1657 (1969).
- ⁶ M. L. Maddox, S. L. Stafford and H. D. Kaesz, *Adv. Organometal. Chem.* **3**, 1 (1965);
H. P. Fritz, K. E. Schwarzhaus and D. Sellman, *J. Organometal. Chem.* **6**, 551 (1966).
- ⁷ For a more detailed discussion including mechanism, see R. Ugo, *Chim. e Industr.*, **51**, 1319 (1969);
F. R. Hartley, *Chem. Rev.* **57**, 799 (1970).
- ⁸ R. S. Nyholm, in 'Colloques Internationaux du Centre National de la Recherche Scientifique', p 254, Paris (1970) for survey.
See also: M. A. Bennett, H. W. Kowenhoven, J. Lewis and R. S. Nyholm, *J. Chem. Soc.* 4570 (1964);
M. A. Bennett, J. Chatt, J. Lewis, R. F. Long and R. S. Nyholm, *J. Chem. Soc. A*, 501 (1967);
M. A. Bennett, W. R. Kneen and R. S. Nyholm, *Inorg. Chem.* **7**, 552 (1968);
M. A. Bennett, W. R. Kneen and R. S. Nyholm, *Inorg. Chem.* **7**, 556 (1968);
L. V. Interrante, M. A. Bennett and R. S. Nyholm, *Inorg. Chem.* **5**, 2212 (1966);
L. V. Interrante and G. V. Nelson, *Inorg. Chem.* **7**, 2059 (1968).
- ⁹ M. Aresta and R. S. Nyholm, unpublished observations (1970).
- ¹⁰ L. V. Interrante, M. A. Bennett and R. S. Nyholm, *Inorg. Chem.* **5**, 2212 (1966);
H. Luth, M. R. Truter and A. Robson, *J. Chem. Soc. A*, 28 (1969).
- ¹¹ J. Chatt, L. M. Vallarino and L. M. Venanzi, *J. Chem. Soc.* 2496 and 3413 (1957).
See also: B. F. G. Johnson, J. Lewis and M. S. Subramanium, *J. Chem. Soc. A*, 1993 (1968) and
F. R. Hartley, ref. 7, p 817.
- ¹² P. R. Brookes and R. S. Nyholm, *Chem. Commun.* 169 (1970).
- ¹³ W. Hewertson and I. C. Taylor, *Chem. Commun.* 428 (1970).
- ¹⁴ R. Mason and A. Towl, unpublished (1970).
- ¹⁵ M. A. Bennett, S. Gruber and R. S. Nyholm, unpublished observations (1969).
- ¹⁶ D. I. Hall and R. S. Nyholm, *Chem. Commun.* 488 (1970).
- ¹⁷ M. R. Truter, personal communication (1970).