The Platinum Metals in Organic Syntheses

ORGANOMETALLIC COMPLEXES AS PREPARATIVE REAGENTS

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The synthesis of organic molecules is of growing importance to the chemical industry but conventional methods are becoming increasingly inadequate. Transition metal complexes, in particular those of the platinum metals, provide routes in synthetic chemistry to many useful and interesting compounds. Here the principles involved are explained and a number of the reactions are described.

It is now apparent that the application of transition-metal organometallic compounds to the synthesis of organic molecules is one of the most powerful preparative tools available to the chemist. This article is an attempt to present some of the current ideas concerning the structure and reactivity of such organometallic complexes of the platinum metals and to apply them to the preparation of organics.

To date much of the emphasis has been placed on complexes of iron and consequently some of the principles are explained by reference to that metal but there is growing interest in the platinum metals, which have already proved their versatility in so many fields of chemistry. In no way is this a rigorous and complete exposition but it is hoped that an introduction to these ideas will serve to indicate the synthetic potential of reactions involving organometallic reagents.

Coordination

In synthetic reactions involving metal ions, activation of simple molecules such as H_2, CO, olefins, acetylenes, aromatic species and many other compounds takes place through coordination. This act of coordination has a number of effects.

Change in Reactivity

The act of coordination alters the electron distribution within the organo group. This very often involves donation of electron density (π) from the organic molecule (e.g., as with olefins) to the metal so that electron distribution within the molecule can be extensive. When coordinated to Pd(II), for example, an olefin, normally susceptible to electrophilic attack, now reacts with nucleophiles.

$$[C_2H_4\ PdCl_3]^- : OH^- \rightarrow CH_3CHO$$

Equally important is the manner in which a change of metal can modify the reactivity of the organic within an analogous series of compounds. This is especially true for olefin complexes. Recently, Pettit extended his studies of cyclobutadiene complexes to derivatives of ruthenium, molybdenum and tungsten tricarbonyl and was able to show that, whereas $C_4H_4Ru(CO)_3$ resembles $C_4H_4Fe(CO)_3$ and behaves as a pseudo-aromatic species, the related molybdenum and tungsten complexes $C_4H_4M(CO)_3$ (M = Mo or W) did not, emphasising the importance of the metal ion within this particular system. Within this account we will in fact be concerned to a large extent with the variation in reactivity of coordinated olefins and it is perhaps pertinent at this stage to discuss the nature of the metal-olefin bond and thereby rationalise (or attempt to rationalise) the

modification in behaviour or change in metal.

The bonding of olefins to metal ions is generally considered in terms of the Chatt-Dewar-Duncanson Model. This simply views the bonding as being composed of two parts:

(a) the donation of electron density *from* the *filled* ethylene π-orbitals into an appropriate metal σ-orbital, e.g. dsp^2 in the case of four coordinate platinum(II) having a square planar configuration.
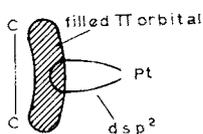

(b) back donation *from* the *filled* d-orbitals of the transition metal (e.g. dxz with Pt(II)) into the *empty* anti-bonding orbitals of the olefin.
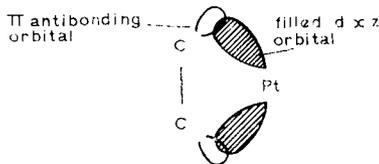

For such a metal the metal-olefin bond obviously depends upon:

(i) The metal, its electronic configuration and oxidation state;

(ii) the auxiliary ligands present; and

(iii) the olefin itself.

Consider, for example, Zeise's salt, an ethylene complex of platinum(II). Since the metal is in a relatively high oxidation state a drift of electron density away from the ethylene to the metal via the σ-bond ((a) above) would be expected. For the same reason little drift of electron density back to the olefin via the π-bond is expected to occur. Consequently the ethylene acquires a net $\delta +$ character and undergoes nucleophilic addition reactions.
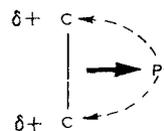
In contrast for olefin complexes of Fe(O), Ru(O), or Os(O), e.g. $C_4H_4M(CO)_3$ (M = Fe, Ru or Os), since the metal in this situation has a large degree of electron density associated with it, σ-bond formation is poor, whereas back donation would be expected to be good with the formation of a strong π-bond. In this case, the net result is electron density build-up on the olefin leading to susceptibility to electrophilic attack.
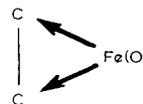

The role of auxiliary ligands or groups is also understandable under these terms. Highly electronegative ligands result in electron drift away from the metal and this is reflected in the enhancement of the activation of the olefin towards nucleophiles, whereas highly electronegative substituents on the olefin (e.g. CF_3 groups) would cause an even greater electron movement from the metal to the olefin. Many of the reactions of metal-olefin complexes may be rationalised in these simple terms. Other factors, of course, must also be considered. Often, for example, auxiliary ligands produce strong steric effects which cause modification of the reaction path.

Stabilisation of "Unstable" Organic Molecules

Perhaps one of the most dramatic aspects of this field is the stabilisation of organic molecules which do not exist in the free state. Beyond question the most notable example of this type of behaviour is cyclobutadieneiron(tricarbonyl). Cyclobutadiene has excited organic and theoretical chemists

alike for many years but prior to the work of Pettit and his co-workers no good evidence for the existence of this molecule was available. Cyclobutadieneiron-(tricarbonyl) shows many of the properties associated with aromatic systems. Thus the ring system readily undergoes electrophilic reactions (see scheme on right).
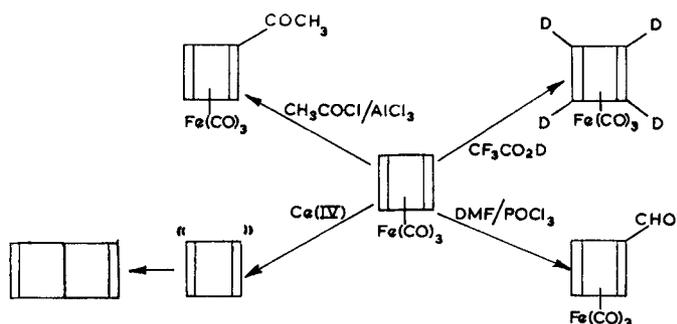

An important facet of this work is the ease with which the free organic is produced on oxidation with Ce(IV), for instance liberation of cyclobutadiene in the presence of a dienophile leads to the production of Dewar benzene derivatives. This is important since if such reactions are to have any potential synthetic use then it must be possible to remove the metal under conditions which are not too violent, such that the organic group is not decomposed.

## Stabilisation of Unusual Conformers or Tautomeric Forms

Very often the organic molecule under consideration can exist in a number of conformations or tautomeric forms. In such cases, because of the stereochemical requirements of the metal ion, the organic group may be "forced" to adopt a particular arrangement. For phenol, for example, two tautomeric forms may be written.
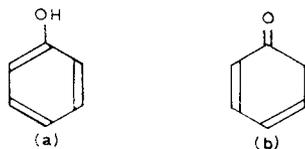

In the free state only tautomer (a) is observed. By the reaction sequence shown here (right), it is possible to isolate an iron-(tricarbonyl) derivative in which the ketonic form (b) is stabilised.
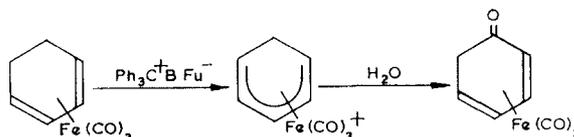
Another example is provided by cyclooctatetraene which coordinates to a variety of metal ions including Fe(O), Rh(I) and Pd(II). The conformation adopted on coordination depends entirely on the metal ions employed even though all have the same (d^8) electronic configuration. Thus with Rh(I) and Pd(II) the tub conformation is preferred whereas with Fe(O) a chair form is observed (in the solid state). (See Figs. I-III).
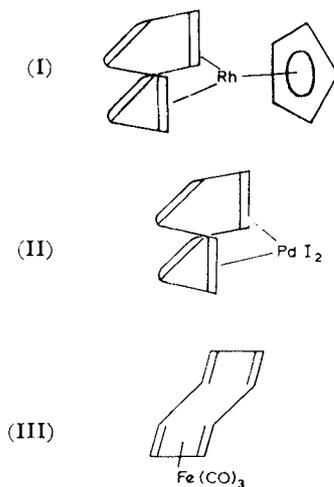
It is relevant to note that a further form of C_8H_8 has been noted for osmium complex $C_8H_8Os(CO)_3$ (See Fig. IV).

(IV)
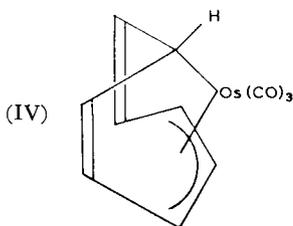
It is then possible to examine the reactivity of such *usual* modifications of the organo-group (albeit modified on coordination) (see below).

Reduction of the Reaction Course

Finally it is important that we realise the behaviour of organic groups coordinated to metal ions can be modified in rather subtle ways. Cyclooctatetraene does not undergo any of the typical aromatic reactions under the usual "organic" conditions. For example, under Friedel Crafts conditions, rather than acetylation, polymerisation occurs with only minute yields of the expected acetyl derivative. In fact the majority of the chemistry of cyclo-octatetraene is concerned with such polymerisations. However, recently it has been shown that on coordination to a $Fe(CO)_3$ or $Ru(CO)_3$ unit the reactivity of cyclo-octatetraene is modified sufficiently to allow acetylation, formylation and other electrophilic reactions to occur readily. One could consider this modification in reactivity to be subtle in the sense that the molecule is susceptible to electrophilic attack both in the free and coordinating state but that the act of co-

ordination simply redirects the course of this attack. Here the $M(CO)_3$ unit may be regarded as a protecting group.

## Some Reactions Described

Formation of Carbon-Carbon Bonds

Olefins readily undergo nucleophilic addition in the presence of Pd(II) or Pt(II) salts. The reactions of many nucleophiles have been examined but possibly those of greatest interest to us are those involving carbanions. By such reactions carbon-carbon bond formation is possible.
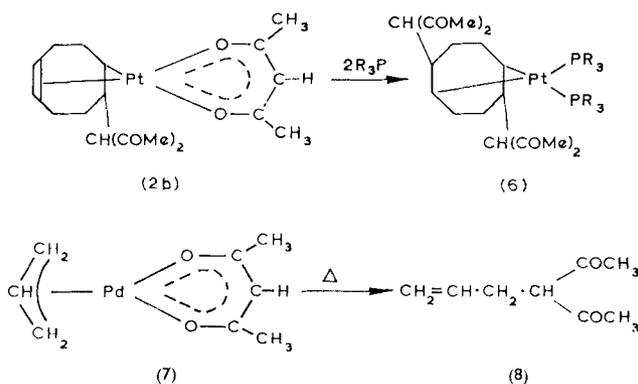
Reaction of (cyclooctა-1,5-diene)palladium dichloride or (cyclooctა-1,5-diene)platinum dichloride with the conjugate bases of malonic esters, keto-esters, or β-diketones leads to complexes (1,2) which contain a new carbon-carbon bond; e.g.
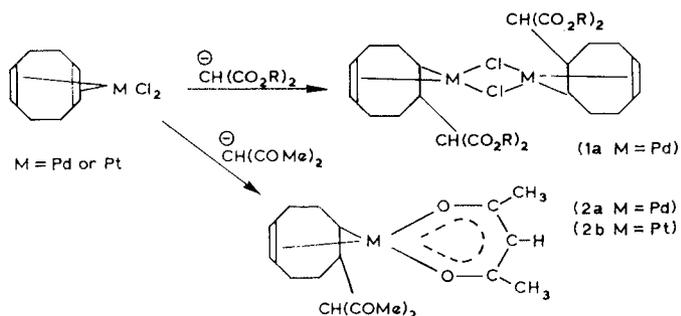
The complexes (1,2) have σ and π bonds with the metal and in certain cases undergo further transformations on treatment with base, the course of the transformation depending very much on the strength of the base employed. Treatment of (1a) with a strong
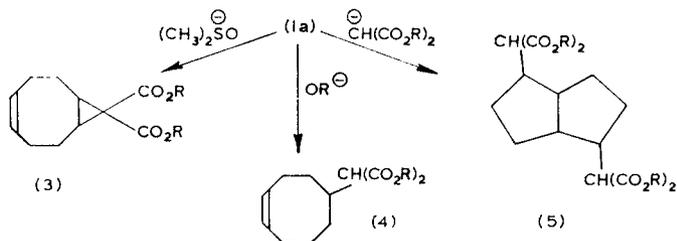
base produces a bicyclo [6, 1, o] nonene derivative (3) and palladium metal. Another molecule of malonate gives rise to a complicated reaction sequence. Attack occurs intermolecularly at the π-complexed olefinic bond and is followed by a transannular reaction of the eight membered ring to form a bicyclo [3, 3, o] octane ring system containing two malonate groups (4). In contrast, if attack of a second carbanion is encouraged by reaction with tertiary phosphine as with complex (2) a cyclooctene is the product when M = Pd, but a chelating σ-bonded cyclooctane when M = Pt (6):

Carbon-carbon bond formation is not restricted to the nucleophilic addition of carbanions to co-ordinated double bonds. It is also possible by oxidative coupling of olefinic and aromatic compounds in the presence of, for example, palladium(II) acetate.

$$ArCH=CH_2 + ArH \xrightarrow{Pd(OAc)_2} ArCH=CHAr$$
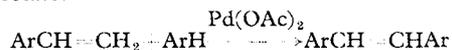
Possibly the most remarkable observation in this area is the coupling of benzene in the presence of Pd(II)/NaOAc/HOAc to produce diphenyl as shown below.
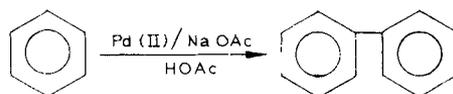

(2b)   (6)

(7)   (8)

π-Allylpalladium chloride reacts with ethyl malonate to give allyl- and diallyl malonates. Related to the behaviour discussed above is the thermal decomposition of π-allyl-palladium acetylacetonate (7) to give allylacetone (8) via ligand coupling.
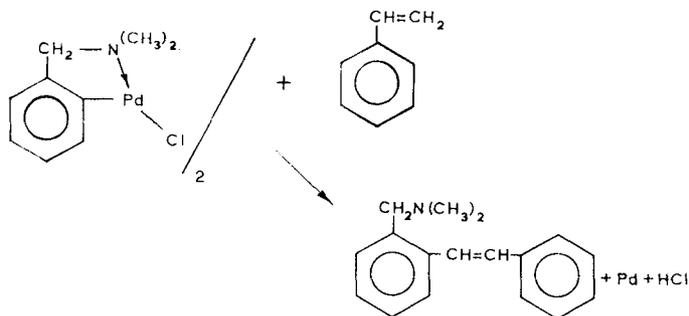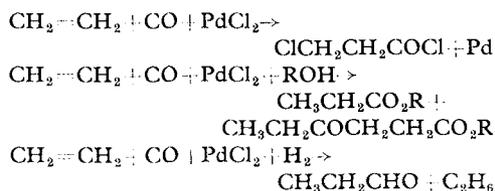

Other coupling reactions find their uses:

Whereas carbon-carbon bond formation takes place by nucleophilic addition to olefins coordinated to palladium or platinum entities, on coordination to iron, ruthenium or osmium tricarbonyls it takes place by electrophilic addition. In general this is not of particular synthetic utility since olefins themselves undergo such reactions. However, in particular cases, it is of tremendous importance. One case, that of cyclobutadiene, has been described above in some detail. Other important examples are the cyclo-octatetraene and cycloheptatriene complexes of iron or ruthenium tricarbonyl. Both

of several important industrial processes. By this means many useful and important CO-containing organics may be produced. Most important is the carbonylation of ethylene, e.g.

$$CH_2=CH_2 + CO + PdCl_2 \rightarrow$$
$$ClCH_2CH_2COCl + Pd$$
$$CH_2=CH_2 + CO + PdCl_2 + ROH \rightarrow$$
$$CH_3CH_2CO_2R +$$
$$CH_3CH_2COCH_2CH_2CO_2R$$
$$CH_2=CH_2 + CO + PdCl_2 + H_2 \rightarrow$$
$$CH_3CH_2CHO + C_2H_6$$

Such reactions have been studied extensively and are, of course, catalytic. However, carbonylation of more "exotic" organics pro-

(9)   (10)
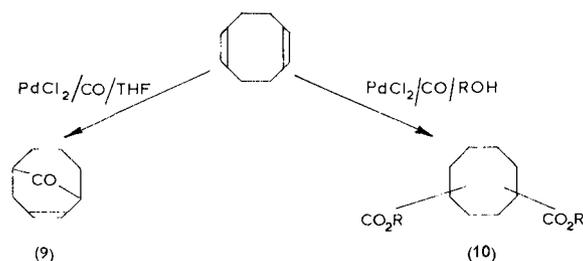
organics polymerise under normal electrophilic conditions but, on coordination, addition reactions take place efficiently,

vides a useful route to many interesting cyclic systems, e.g. (9) and (10)

Carbonylation of π-allylic derivatives provides a direct route to unsaturated acids, acid chlorides and esters:
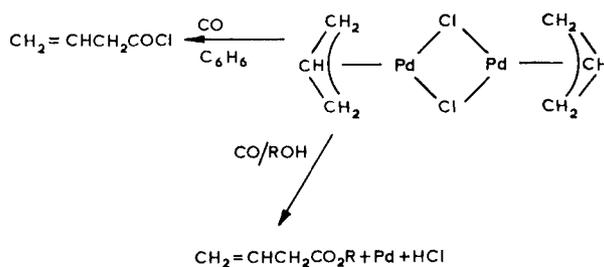
allowing a complete systematic chemistry to be built up.

Carbonylation and Decarbonylation

The carbonylation of olefins in the presence of transition metal catalysts forms the basis

The carbonylation of acetylenes also provides routes into useful organic molecules. Numerous transition metal complexes are known to be active for cyclisation or oligomerisation of acetylenic compounds. Of particular use is the employment of transition metal units to produce cyclic ketones. Here

the carbonyls of Fe, Ru or Os and various Pd derivatives are of particular note.

$$PhC \equiv CPh + CO \longrightarrow$$

$$H_3C - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} - C \equiv CH + CO \xrightarrow{C_6H_6}$$

Systems containing N may also be carbonylated by these methods.

$$+ PdCl_6^{2-}$$

$$\xrightarrow{CO/C_6H_6} \quad + Pd$$

Large Ring Chemistry

It is often of considerable use to be able to carry out specific substitution reactions on ring systems. Here metal complexes can be extremely useful. Consider the chemistry of coordinated 1,5-cyclooctadiene. Complexes of this comp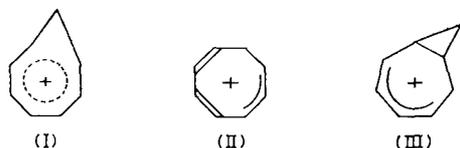ound may be formed with Fe(O), Ru(O), Os(O), Rh(I), Ir(I), Pd(II) or Pt(II). As discussed above (commencing on page 63) for the formation of carbon-carbon bonds, the complexes of palladium or platinum undergo nucleophilic addition to give complexes of the type:

$$\xrightarrow{R^{\ominus}}$$

In contrast, the analogous complexes of Rh(I), Ir(I), Fe(O), Ru(O) or Os(O), do not undergo such additions but rather electrophilic reactions of the type:

$$\xrightarrow{2Ph_3C^+} \left[\quad RhC_5H_4 \cdot CPh_3 \right]^+$$

$(Cp = C_5H_5)$

$$\xrightarrow{Ph_3C^+} \left[\quad Ru(CO)_3 \right]^+$$

In fact for M—Fe, form III is observed; for M—Ru, form II and for M—Os, a mixture of II and III. In the last case form III fairly rapidly converts to form II. Thus on simply changing from M—Fe to M—Ru or Os different tautomeric forms of $C_8H_9{}^+$ may be stabilised and their chemistry examined. Thus on reaction with nucleophilic reagents neutral bicyclic or monocyclic derivatives are obtained:
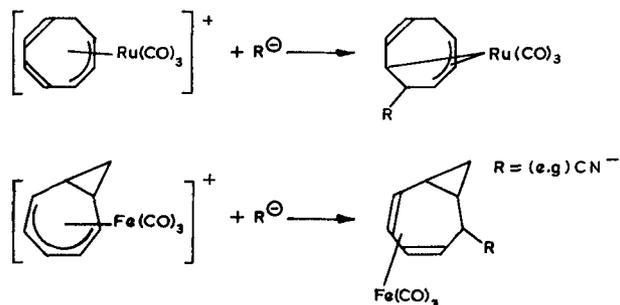
to produce allylic derivatives by H abstraction. These salts then undergo subsequent nucleophilic addition to give derivatives in which an alternative type of substitution was obtained as shown above.

Earlier we noted the ability of metal containing units to stabilise organic molecules in unusual conformations or tautomeric forms. This enjoys wide synthetic application and here we will consider the cyclooctatetraene complexes, $C_8H_8M(CO)_3$, of iron, ruthenium and osmium. All three are readily protonated by strong acids such as HBF_4, HPF_6 or CF_3CO_2H to give cationic species of general formula $C_8H_9M(CO)_3{}^+$. For the organic part of this cation a number of tautomeric forms are possible, remembering that each form must retain the ability to coordinate to the metal. Some of these tautomers are shown:

R = (e.g) CN⁻

(I)   (II)   (III)

Conclusions

In the work outlined above, examples of useful synthetic procedures involving metal ions having the d^8 configuration have been given. Many of these reactions are impossible or difficult to attain by other methods. Often these procedures are useful not only for stoichiometric reactions but also in catalysis. This is particularly the case for palladium derivatives. In the main this facet of this chemistry is poorly explored. The role of the metal and the auxiliary ligands is obviously critically important but relatively few systematic studies have yet been done.