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THE STEREOCHEMISTRY OF THE REACTIONS OF ORGANO TRANSITION METAL COMPLEXES

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Abstract—The stereochemistry of homogeneously catalysed hydrogenation, carbonylation and decarbonylation is discussed, as well as the stereochemistry of nucleophilic and electrophilic addition to co-ordinated alkynes and dienes. Examples are presented of formation and lysis of carbon-transition metal bonds together with data relating to the steric course of these processes.

1. *General*

The very considerable recent advance in organometallic chemistry has focussed attention on the modes of reaction of a range of organo-metallic complexes in which a transition metal is σ- or π-bonded to carbon. Within organic chemistry as a whole the steric course of reactions has very generally provided critical evidence in establishing reaction mechanisms. Similar information has been accumulating for typical reactions of transition metal organo derivatives. It is the purpose of this article to summarise the stereochemical information available for some of the principal reactions encountered in the making and breaking of carbon-transition metal bonds. It is of particular interest to ascertain how far the presence of a metallic component may modify the reaction pathways to be expected on the basis of organic chemical precedents.

2. *Catalysed hydrogen addition*

A number of transition metal complexes exhibit the important and useful property of activating molecular hydrogen, and, in suitable cases, of catalysing hydrogen addition to a co-ordinated acceptor molecule such as an alkene or alkyne.[1]

The process of hydrogen activation consists in the formation of a metal hydride complex, which may arise by hydrogen addition as in (i), or by heterolysis (ii), or homolysis of the hydrogen molecule (iii).

(i) $RhCl(PPh_3)_3 + H_2 \rightleftharpoons Rh(H)_2Cl(PPh_3)_2 + PPh_3$
(ii) $RuCl_2(PPh_3)_3 + H_2 \rightleftharpoons RuH(Cl)(PPh_3)_3 + HCl$
(iii) $2Co(CN)_5^{3-} + H_2 \rightarrow 2CoH(CN)_5^{3-}$
(iv) $L_nMH + >=< \rightarrow L_nM-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-H$

(L_n = ligands)

Reaction (i) leads to a dihydrido metal complex whilst (ii) and (iii) yield monohydrido derivatives as indicated.[2]

Hydrogen transfer from the hydride to an alkene or alkyne acceptor is generally a two step process, *viz* addition of the metal hydride across the unsaturated centre in the co-ordinated alkene or alkyne as in (iv), followed by hydrogen insertion into the carbon–metal σ-bond as in (v). Where the metal forms a dihydride the second hydrogen is found amongst the ligands and may be transferred directly as in (v)(a).[3] Where the metal forms a monohydride the second hydrogen arises from reaction of the intermediate metal alkyl complex with a second molecule of hydrogen as in the example in (v)(b).[4]

(v)(a) $RhHCl(PPh_3)_2(alkyl) \rightarrow RhCl(PPh_3)_2 + alkane$
(v)(b) $RuCl(PPh_3)_2(alkyl) + H_2 \rightarrow [Ru(H)_2Cl(PPh_3)_2(alkyl)] \rightarrow RuHCl(PPh_3)_2 + alkane$

Stage (iv), i.e. addition of the metal hydride to the pre-coordinated alkene is necessarily a cis addition process. The following examples[3,5] establish that the hydrogen insertion step (v) also occurs with retention of stereochemistry at the carbon centre concerned:

Maleic acid $\xrightarrow{(i)}$ *meso*- $\left.\right\}$ 1,2-$^2H_2$- succinic
Fumaric acid $\xrightarrow{(i)}$ *dl*- $\left.\right\}$ acid

$PhC{\equiv}CPh \xrightarrow{(n)}$ *cis*- stilbene

(i) $RhCl(PPh_3)_3 + D_2$; (ii) $RuCl_2(PPh_3)_3 + H_2$

Thus the commonly observed *cis* hydrogen addition in catalysed hydrogenation arises from *cis* addition of a metal hydride followed by hydrogen insertion into a carbon–metal σ-bond with retention of stereochemistry. The apparent exceptions to *cis* addition which are occasionally encountered can generally be related to processes involving translocation of the olefinic bond.

3. *Hydroformylation*

Hydroformylation resembles hydrogenation as a catalytic process in which the second hydrogen added in hydrogenation is replaced by carbon monoxide. In hydroformylation an alkene, $RCH{:}CH_2$ is converted *via* the aldehyde RCH_2CH_2CHO, or $RCH(CHO)CH_3$ into the alcohol $RCH_2CH_2CH_2OH$ or $RCH(CH_2OH)CH_3$ by reaction with carbon monoxide and hydrogen in presence of a suitable metal carbonyl. The course of the reaction may be illustrated using dicobalt octacarbonyl which is a rather fully investigated hydroformylation catalyst.[6]

(i) $Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4$

(ii) $HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO$

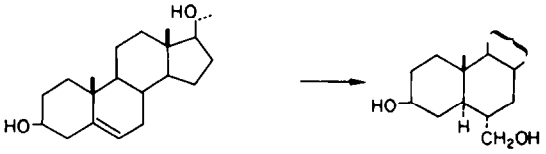
(iii) $HCo(CO)_3 + RCH{=}CH_2 \rightarrow RCH_2CH_2Co(CO)_3 + RCH(CH_3)Co(CO)_3$

(iv) $RCH_2CH_2Co(CO)_3 + CO \rightleftharpoons RCH_2CH_2Co(CO)_4 \rightleftharpoons RCH_2CH_2COCo(CO)_3$

(v) $RCH_2CH_2COCo(CO)_3 + H_2 \rightarrow RCH_2CH_2CHO + HCo(CO)_3$

(vi) $RCH_2CH_2CHO + HCo(CO)_3 + H_2 \rightarrow RCH_2CH_2CH_2OH + HCo(CO)_3$

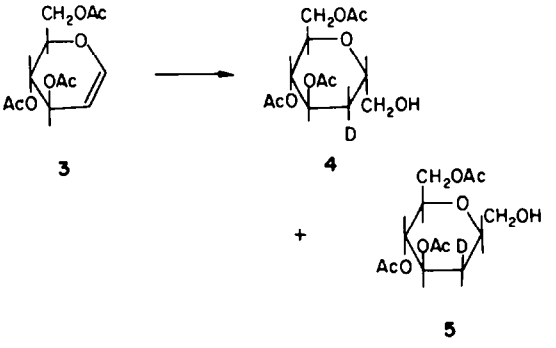
The stereochemically important steps are clearly (iii), in which the metal carbonyl hydride adds across the alkene bond, and (iv) where a carbonyl group is inserted into the metal–alkyl bond with formation of a new carbon–carbon bond. A clear indication that hydroformylation proceeds by *cis* addition of metal hydride followed by carbonyl insertion with retention of stereochemistry is provided by a number of examples. Thus pregn - 5 - en - 3β,20β - diol (1) and other similar steroids have been shown[7] to yield a 5αH, 6αCH$_2$OH derivative of the type 2 on hydroformylation using a cobalt catalyst.



1 2

Similar conclusions follow from the application of hydroformylation in the carbohydrate field.[8] By hydroformylation with dicobalt octacarbonyl in carbon monoxide and deuterium 3,4,6 - tri - O - acetyl - D - glucal (3) was shown to yield a pair of isomeric products, (4 and 5), the stereochemistry of which could be deduced from NMR proton coupling, and for 5 also by X-ray structural analysis of a derivative.

Hydrido carbonyl tris(triphenylphosphine)-rhodium is also an effective hydroformylation catalyst. The reaction sequence[9] is essentially the



3 4 5

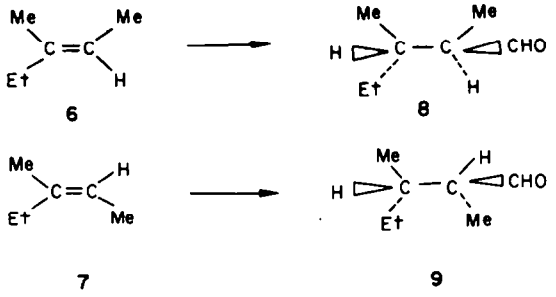
same as with hydrido cobalt carbonyl, viz:

$RhH(CO)(PPh_3)_3 + CO \rightleftharpoons RhH(CO)_2(PPh_3)_2 + PPh_3$

$RhH(CO)_2(PPh_3)_2 + RCH{=}CH_2 \rightarrow RCH_2CH_2Rh(CO)_2(PPh_3)_2 \rightleftharpoons RCH_2CH_2CORh(CO)(PPh_3)_2$

$RCH_2CH_2CORh(CO)(PPh_3)_2 + H_2 \rightarrow RCH_2CH_2CHO + RhH(CO)(PPh_3)_2$

The stereochemistry of hydroformylation with $RhH(CO)(PPh_3)_3$ has been established[10] using (E)- and (Z) - 3 - methylpent - 2 - ene, (6 and 7), which were shown to yield, respectively, *threo*-8 and *erythro* - 2,3 - dimethylpentanal (9), with only minor amounts of the alternative isomers in each case.

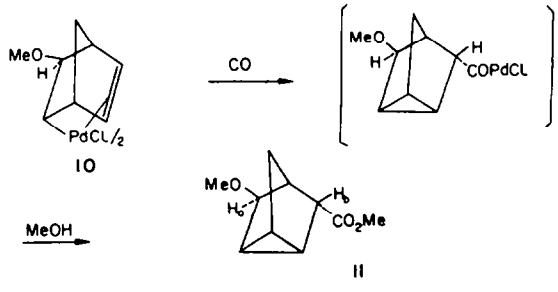


6 8

7 9

The stereochemistry of this reaction is therefore as with $HCo(CO)_3$.

The carbonyl insertion reaction is also a well known property of palladium alkyl derivatives. The stereochemistry of carbonyl insertion in this case is established[11] by the interesting transformation: **10** → **11**.



10 11

The stereochemistry of **11**, which implies carbonyl insertion with retention, could be deduced[11] from the values of δ_{H_a} and δ_{H_b}.

4. *Decarbonylation*

Carbonyl insertion into a carbon–metal bond may be shown to be reversible and suitable transition metal derivatives which are strongly bonding towards carbon monoxide effect decarbonylation of aliphatic and aromatic aldehydes.[12] The reaction sequence may be illustrated for chlorotris(triphenylphosphine)rhodium which is an effective complex for decarbonylation,[13] *viz*:

(i) $RCHO + RhCl(PPh_3)_3 \rightleftharpoons RCORh(H)(Cl)(PPh_3)_2 + PPh_3$

(ii) $RCORh(H)(Cl)(PPh_3)_2 \rightleftharpoons RRh(CO)(H)(Cl)(PPh_3)_2 \rightarrow RH + RhCl(CO)(PPh_3)_2$

The stereochemistry of the reaction was established for decarbonylation of the aldehydes **12**, **13** and **14** using $RhCl(PPh_3)_3$ in a solvent at *ca* 100°. The steric configurations of the products indicate displacement with retention of configuration in each case.[14]

12

13

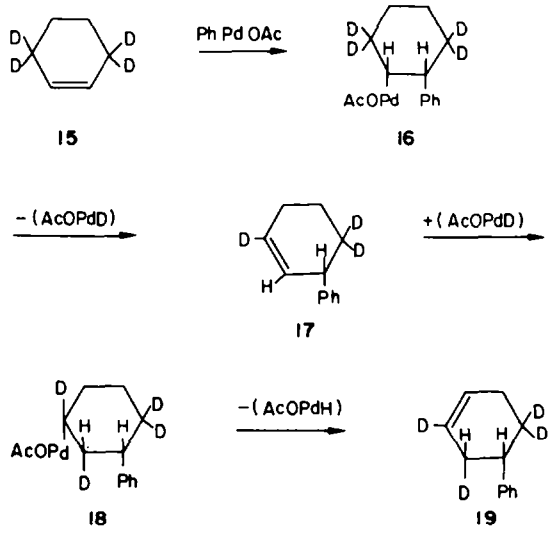
14

5. *Reaction of co-ordinated alkenes with nucleophilic addends*

In oxidative hydroxylation of olefins induced by a Pd(II) salt it is generally inferred[15] from kinetic data that in the key step hydroxyl is transferred from palladium in a process of *cis* addition, *viz*:

18 19

The addition of PhPdOAc, formed *in situ* from PhHgOAc and $Pd(OAc)_2$, to 3,3,6,6 - $^2H_4$ - cyclohexene (**15**)-has also been examined,[16] and the observed products **17** and **19** rationalised as the result of successive *cis*-addition and *cis*-elimination steps.



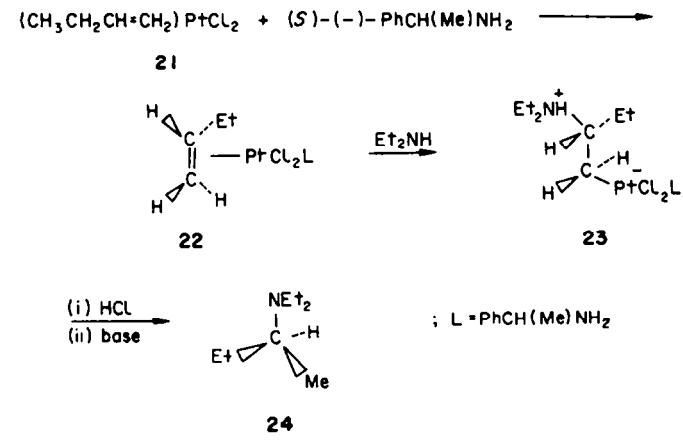
15 16 17 18 19

The mechanism in this case is tentative, but it is supported by a further example, discussed below, in which transfer of a phenyl residue from palladium to carbon by *cis* insertion is clearly established.

In these examples of transfer of hydroxyl or phenyl to carbon the transferred group is initially bonded to palladium. However, where the entering nucleophile is not first co-ordinated to the metal the alternative process of *trans* addition is encountered. This appears to be the case in the reaction of 3,3,6,6 - $^2H_4$ - cyclohexene with $Pd(OAc)_2$ in acetic acid where the products have been rationalised[17] in terms of an initial *trans*-adduct **20**.

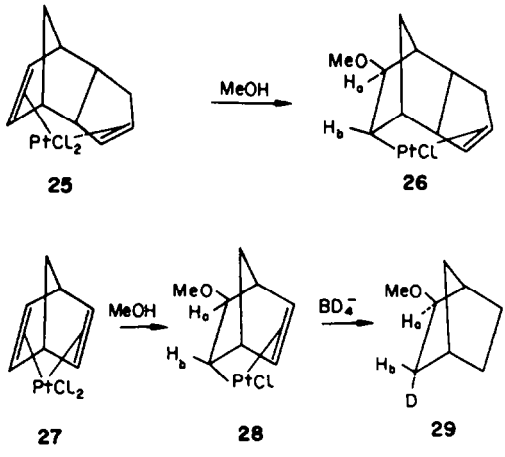
15 20

More direct evidence of a *trans* addition process is provided by the stereochemistry of addition of diethylamine to but-1-ene co-ordinated as in **22** to a $(PtCl_2\ L)$-residue where L is (*S*) - (−) - $PhCH(Me)NH_2$. The adduct **23** is found to undergo acid hydrolysis of the carbon–platinum bond with the release of the hydrochloride of (*S*) - (+) - 2 - butyl diethyl amine **24**.



The complex **22** having been crystallised to optical purity and its structure and configuration having been established from X-ray analysis and the CD-spectrum, the configuration of the amine **24** indicates that the diethylamino residue enters from the side of **22** remote from platinum.[18]

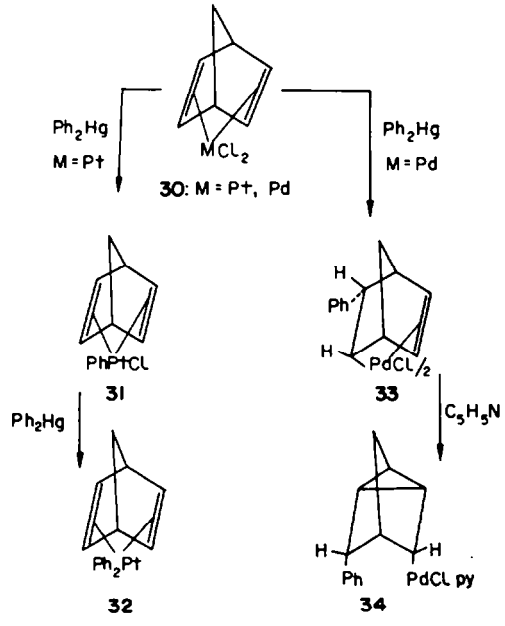
The same *trans* addition process is encountered also in the reaction of the $PtCl_2$- derivatives of cyclopentadiene dimer **25** or of bicyclo [2,2,1]heptadiene **27** with methanol.[19]



The *exo*-orientation of the methoxy addend in **26** and **28** was deduced from δ_{H_a}, δ_{H_b}, $J_{H_aH_b}$ values and for **28** was confirmed by X-ray analysis.[20]

The value of $J_{H_aH_b}$ in **29** the product of reduction of **28** with sodium borodeuteride confirmed the *exo*-orientation of the methoxy group.[19] The stereochemistry of **29** also incidentally establishes that hydrogenolysis of a palladium–carbon bond occurs with retention of stereochemistry at carbon.

It was at one time suggested[21] that the rigid molecular geometry of diene complexes such as **25** or **27** imposes a constraint which is responsible for the preferred *trans* addition of methanol, or other addends. However, it is now clear that complexes such as **25** or **27** are not exceptional. The determining factor is whether the addend enters from the medium or is first co-ordinated to the complexing metal. Persuasive evidence is provided by a comparison of the reaction of the norbornadiene complex **30** of $PtCl_2$ and $PdCl_2$ with diphenyl mercury.[22]



Whereas the platinum complex undergoes phenyl displacement of chlorine at the metal giving **31** and **32**, with the palladium complex the phenyl group is transferred to carbon, and X-ray analysis of **33** established that the phenyl is *endo* oriented. It is reasonably argued that **33** arises by phenyl transfer from palladium in a Pd-analogue of **31**, i.e. by *cis* addition to the olefin.

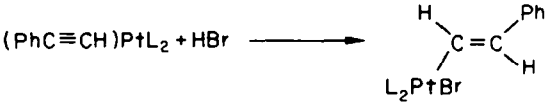
This case is therefore complementary to the examples **25** and **27** above in indicating that the steric course of addition of a nucleophile to a metal π-bonded olefin is determined by whether the addend is first complexed to the metal.

6. *Protonation of co-ordinated alkenes and alkynes*

Complexes of the type: M(alkyne)$(PPh_3)_2$, M = Pt, Pd, are found to undergo oxidative addition of a suitable acid HX, e.g. HCl, HBr, CF_3CO_2H, with protonation of the alkyne, *viz*:

$$Pt(alkyne)(PPh_3)_2 + HX \rightarrow PtX(alkenyl)(PPh_3)_2$$

The stereochemistry of addition has been determined from the value of the proton-proton coupling in the alkenyl product. Thus (phenylacetylene)$Pt(PPh_3)_2$ (**35**) with HBr gave a product recognized as the *trans* alkenyl derivative **36** from the $J_{H,H}$ value of 16·8 Hz, characteristic of coupling between *trans* related olefinic protons.

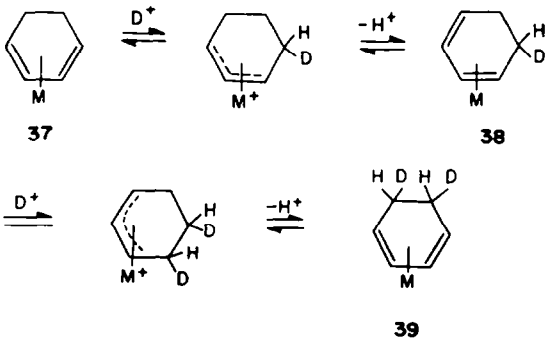


35 **36**

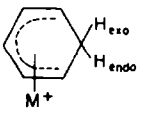
L = PPh_3

The product **36** is most directly derived by addition of a proton from the same side as the platinum and this stereochemistry follows most reasonably if the proton is first added to and then transferred from platinum.

Very similar conclusions[24] have been drawn from a study of the ^1H-^2H exchange shown by cyclohexa-1,3-diene complexes of the type **37** [M = $Fe(CO)_3$, or Rh(cp)] in CF_3CO_2D. Exchange involves a sequence of proton or deuteron addition and elimination steps:



Cyclohexadiene complexes such as **37** also undergo hydride abstraction by Ph_3CBF_4 to give a cationic complex (**40**), in which the *exo*- and *endo*-protons are distinguished both in chemical shift



40

($\delta H_{endo} > \delta H_{exo}$) and, since the ring system is non-planar also in their coupling with adjacent protons. The ^2H-derivative (**39**) on treatment with Ph_3CBF_4, yields a cationic complex in which the signal characteristic of the *endo* proton is absent, i.e. the deuteron incorporated in the sequence **37** ⇌ **38** ⇌ **39** must be *endo* oriented. Thus proton exchange is stereospecific, and the *endo*-orientation is most easily rationalised if transfer occurs *via* proton addition to the co-ordinating metal residue, M. Support for this conclusion comes from the observation of a typical high field metal hydride signal in the product of protonation of **37**, M = Ir(cp).

It also appears that hydride abstraction by Ph_3C^+ occurs stereospecifically from the *exo*-side of the ring. Hydride addition in reduction of the cationic complex **40** to the diene derivative **37** also occurs from the *exo*-side; reduction of **40** by means of $NaBD_4$ followed by ^1H-^2H exchange gave a product retaining deuterium.

7. *Formation of, and displacements at carbon transition metal bonds*

The well known oxidative addition reaction of chlorocarbonylbis(triphenylphosphine)iridium (**41**) has been examined[25] as a means of determining the stereochemistry of halogen displacement by iridium.

$$IrCl(CO)L_2 + RX \rightarrow RIrX(Cl)(CO)L_2$$
41 **42**

RX = alkyl halide; L = PR_3

Using (−)-ethyl 2-bromopropanoate, $[\alpha]_D - 6{\cdot}0°$ with **41**, (L = PPh_2Me) gave a (−)-adduct **42**, (R = CH_3CHCO_2Et, X = Br, L = PPh_3Me), which with bromine in tetrahydrofuran reformed (−)-ethyl 2-bromopropanoate, $[\alpha]_D - 4°$. Thus formation and rupture of the carbon iridium bond show appreciable stereospecificity.

It was shown in parallel experiments that $Ir(SCN)(CO)(PPh_3)_2$ with methyl iodide in methylene chloride containing an excess of $(C_4H_9)_4\overset{+}{N}\ \overset{-}{SCN}$ gives $MeIrI(SCN)(CO)(PPh_3)_2$, i.e. the added $\overset{-}{SCN}$ ion fails to compete with iodide for co-ordination to iridium. It was argued therefore that I^- ion is not released in the displacement, but that iridium is inserted into the CH_3–I bond in a concerted fashion. This would indicate halogen displacement with retention of stereochemistry at carbon, and by implication, retention also in the

subsequent lysis of the carbon-iridium bond with bromine.

This conclusion has not, however, been sustained by the results of other similar studies, which indicate metal displacement at a carbon–halogen bond with inversion of stereochemistry. However, if **41** (L = PPh_2Me) with (−)-$CH_3CHBrCO_2C_2H_5$ reacts with inversion of stereochemistry, it is necessary to establish a mechanism for reaction of **42** (R = $CH_3CHCO_2C_2H_5$, X = Br) with bromine with inversion in order to account for the reformation of (−)-$CH_3CHBrCO_2C_2H_5$. Evidence bearing on this problem is derived from a study[26] of the reaction of (−) - 1 - methylheptyl bromide $[\alpha]_D - 29°$ **43** with bis(glyoximato) (pyridine) cobalt (I) **44**. This gave a complex, (+) - (1 - methyl heptyl)bis (glyoximato) (pyridine) cobalt(III), **45**, $[\alpha]_D$ *ca* + 50°, which with bromine in acetic acid reformed (−) - 1 - methyl heptyl bromide, $[\alpha]_D - 20°$.

$$\underset{\mathbf{44}}{[Co(dmg)_2(py)]^-} + \underset{\mathbf{43}}{CH_3(CH_2)_5CH(CH_3)Br} \rightarrow$$

$$\underset{\mathbf{45}}{[CH_3(CH_2)_5CHCH_3]Co(dmg)_2(py)}$$

The overall retention of stereochemistry in this sequence reproduces the entirely similar result from reaction of (−)-ethyl bromopropanoate with $Ir(CO)(Cl)(PPh_2Me)_2$. However, it was noted that in the reaction of **45** with bromine the 1-methylheptyl bromide product is accompanied by release of oct-1-ene and oct-2-ene which are isolated as their dibromo-derivatives. This observation has led to the hypothesis that bromine may react not with the carbon–cobalt bond, but oxidatively with cobalt resulting in release of the 1-methyl heptyl residue as a carbenium ion. This ion may react rapidly with Br^- as it is released, i.e. preferentially from the rear with inversion of stereochemistry, or lose H^+ leading to octenes and the observed dibromo-products. Some support for this hypothesis is provided by an examination[27] of the oxidation of the (benzyl)cobalt complex **46** with $IrCl_6^{2-}$ leading to an intermediate cationic complex **47** which releases a benzyl cationic residue to be captured by suitable anions in solution.

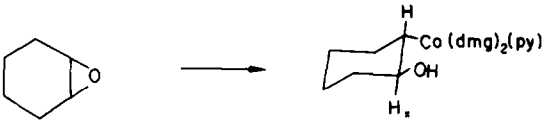
$$\underset{\mathbf{46}}{(PhCH_2)Co(dmg)_2(H_2O)} + IrCl_6^{2-} \rightarrow$$

$$IrCl_6^{3-} + \underset{\mathbf{47}}{[(PhCH_2)Co(dmg)_2(H_2O)]^+} \xrightarrow{X^-}$$

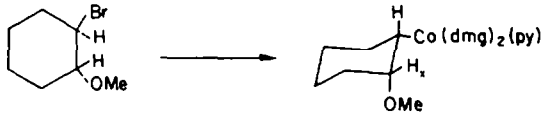
$$PhCH_2X,\ X = Cl^-,\ Br^-,\ I^-.$$

It is not clear how far these results may be made the basis of any generalisation. However, the findings for iridium (I) and cobalt (I) displacement of halogen are important in establishing a significantly stereospecific process, and further data indicating inversion in displacement by $[Co(dmg)_2(py)]^-$ are set out below.

Cyclohexene oxide (**48**) and *trans* - 1 - bromo - 2 - methoxy cyclohexane (**49**) were found[28] to give bis(glyoximato) (pyridine)cobalt derivatives **50** and **51**. The stereochemistry of **50** and **51** was deduced



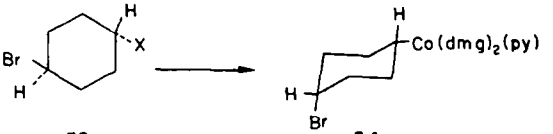
48 **50**



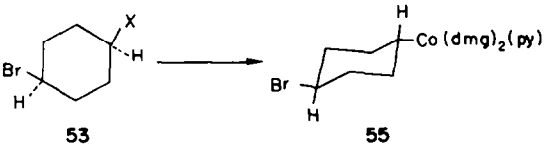
49 **51**

from the appearance of the nmr signal for H_X as a broad multiplet and a broadened singlet respectively. This pattern is most easily rationalised as resulting from displacement with inversion as indicated. However, there was evidence for a small amount of a second component accompanying the complex **51** which may indicate a contribution from a second mode of reaction.

Displacement with inversion[30] of stereochemistry appeared also to be the pattern for the analogous reactions of the 1,4-disubstituted cyclohexanes **52** and **53**.



52 **54**

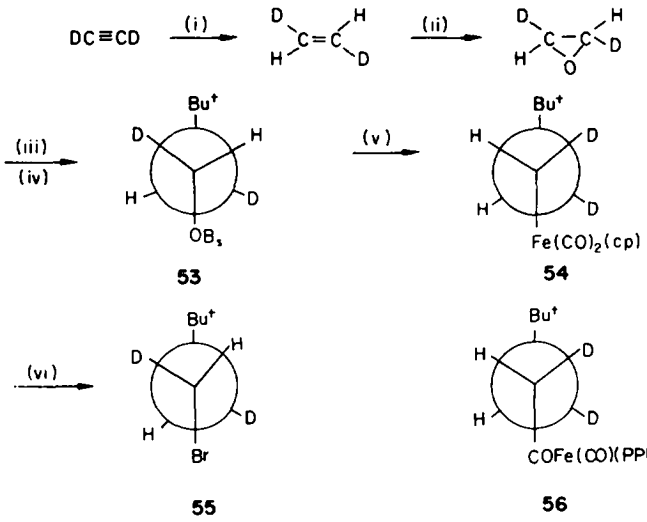


53 **55**

X = Br, OTs

The stereochemistry of **54** and **55** was based on NMR comparisons with similarly substituted cyclohexanes of known stereochemistry.

These conclusions regarding displacements by a cobalt anionic complex are supported by similar studies[29] using $NaFe(CO)_2(cp)$ in displacement of the *p*-bromobenzene sulphonyl group from the *erythro*-$^2H_2$-ester (**53**) the synthesis of which is indicated.



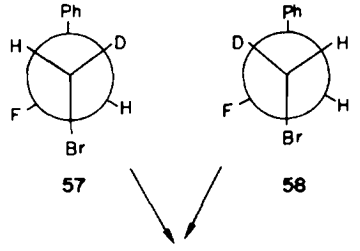
53 54 55 56

(i) $CrCl_2$, (ii) Cl_2, $Ca(OH)_2$, (iii) LiBu^t, (iv) LiBu, *p*-$BrC_6H_4SO_2Cl$, (v) $NaFe(CO)_2(cp)$ in THF, (vi) Br_2 in $CDCl_3$.

The conclusion that displacement of a *p*-bromobenzene sulphonyl group (OBs) and lysis of the carbon–iron bond both occur with inversion follows from the $J_{H,H}$ values for **54** and **55** of ~4·5 and ~13 Hz respectively in the ^{2}H-decoupled NMR spectra. The validity of these assignments is supported by the conclusion on NMR evidence that carbonylation of **54** yields **56**, i.e. with retention of stereochemistry, in agreement with the precedents noted above.

There are therefore a substantial number of instances which indicate a stereospecific pathway for displacement of halogen from carbon by metal complex reagents, and on present evidence this appears to take place generally with inversion. However, discordant results have been reported[30] for displacement of bromine from *threo*- **57** and *erythro* - 1 - ^{2}H - 1 - bromo - 2 - fluoro - 2 - phenylethane **58** by $Ir(CO)(Cl)(PMe_3)_2$. Both isomers were found to lead to the same product **59**, characterised as a mixture of isomers by the appearance of two superimposed groups of signals, namely a doublet of doublets and a doublet of multiplets in both the ^{1}H- and ^{19}F-NMR spectra. Moreover, there was also evidence for peroxide catalysis of the reaction and retardation by radical scavengers.

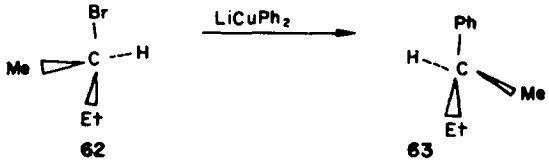
The two isomeric 1 - bromo - 2 - fluoro - cyclohexanes (**60** and **61**) were also found to give the same mixed product on reaction with $IrCl(CO)(PMe_3)_2$, and the broad conclusion must be that there is a free radical type of displacement in these instances. It is, however, worth noting that the essential difference between these non-stereospecific displacements and the stereospecific displacement by iridium in the case of (−) $CH_3CHBr\ CO_2C_2H_5$ lies only in the phosphine ligand, *viz* PMe_3 *vs* PPh_2Me.



57 58 59

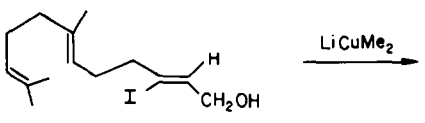
60 61

In the light of these results it is of some interest and practical importance that Li $CuMe_2$ and Li $CuPh_2$ exhibit stereospecific displacement of halogen in the cases which have been examined. (−) - (*R*) - 2 - Bromobutane (**62**) with Li $CuPh_2$ was found[31] to give (+) - (*S*) - 2 - phenyl butane (**63**), and



62 63

with an optical yield indicating a high degree of substitution with inversion. Substitution of vinylic halogen also occurs stereospecifically, but with retention, as indicated[32] by the elegant synthesis of *trans–trans*-farnesol (**65**).



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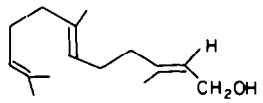

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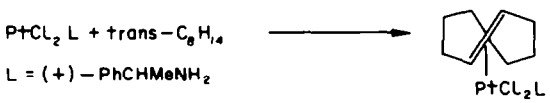
8. *Chiral ligands and induced asymmetry*

Organo-metallic complexes carrying suitable chiral ligands offer a means of effecting asymmetric syntheses. An example of this type has already been noted above in the use of (*S*) - (−) - 1 - phenylethylamine as ligand to induce asymmetric addition of diethylamine to but - 1 - ene co-ordinated to platinum. Mention may also be made of the use of (+) - 1 - phenylethylamine as ligand in the dichloroplatinum complex of *trans*-cyclo-octene (**66**) which by crystallisation led to separa-



66

tion of the diastereoisomers and resolution of *trans*-cyclo-octene which could be released[33] from the complex by means of potassium cyanide.

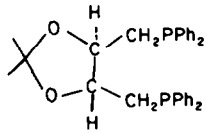
Asymmetric synthesis in the formation of a carbon–carbon bond *via* a metal complex intermediate has been realised in the case of the condensation of ethylene and cyclo-octa-1,3-diene to give 3-vinyl cyclo-oct-1-ene (**67**). This reaction

67

was effected using a complex (π-allyl) NiCl (PR_3) in combination with ethyl aluminium sesquichloride, the phosphine ligand PR_3 carrying one or more (−)-menthyl residues.[34]

Asymmetry may also be induced in homogeneously catalysed hydrogen addition using complexes bearing phosphine or other ligands as a source of a symmetry. The phosphorus may itself be the chiral centre e.g. as in the complex $RhCl_3L_3$ which was applied to catalyse the hydrogenation of α-phenylacrylic acid, or α-acylaminoacrylic acids, where L is for example (−)methylpropyl-phenylphosphine.[35]

An asymmetric phosphine ligand is, however, more conveniently available by incorporation of an asymmetric carbon residue. Two useful examples of this type are the diphosphine (**68**) derived from (+)-diethyl tartrate[36] and the neomenthyl diphenyl phosphine[37] (**69**).



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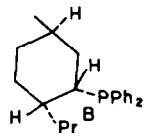

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The diphosphine (**68**) was used[36] in the synthesis of a rhodium complex (**70**) which may be applied to the synthesis of e.g. (*R*)-N-acetylphenyl alanine (**72**) in an optical yield of 72% by hydrogenation of α-acetamido cinnamic acid (**71**).

68 + $[Rh(C_8H_{14})_2Cl]_2 \rightarrow$ Rh(PP)Cl,
70

PP = **68**

71 **72**

The neomenthyl diphenyl phosphine (**69**) was similarly employed[37] combined as the rhodium complex $Rh(P)_3Cl$, P = **69** to effect hydrogenation of β-methyl cinnamic acid to give (+)-3-phenyl butanoic acid in an optical yield of 61%. However, equally successful asymmetric hydrogenation at a rhodium complex has also been reported using various optically active amides, e.g. (+)-PhCHMeN-CHO as the asymmetric ligand.[38]

A point of interest arising from these studies is that in the catalytic process the centre of asymmetry is in **68** and in the amide PhCHMeNHCHO separated by five atoms, and in **69** by four atoms from the site of hydrogen transfer.

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