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Tripodal polyphosphine ligands control selectivity of organometallic reactions

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CONTENTS

A. INTRODUCTION

The development of the field of organometallic chemistry is largely driven by the prospect of using metal complexes as catalysts for the selective transformation of organic compounds. Selectivity is needed to produce pure products in high yields. In fact, the formation of by-products not only impacts on the economics of a process but, most importantly, provides environmental constraints.

Our work attempts to address the question of selectivity in the transformation of organic molecules by examining the use of transition metal complexes stabilized by tripodal polyphosphine ligands. Some of these ligands are shown in Chart 1.

The coordination chemistry of polyphosphines has been investigated widely over the past three decades by several research groups, particularly by those led by Sacconi [1], Meek [2] and Venanzi [3]. It is now apparent that polyphosphine ligands exhibit several advantages over comparable monodentate phosphines, includ-

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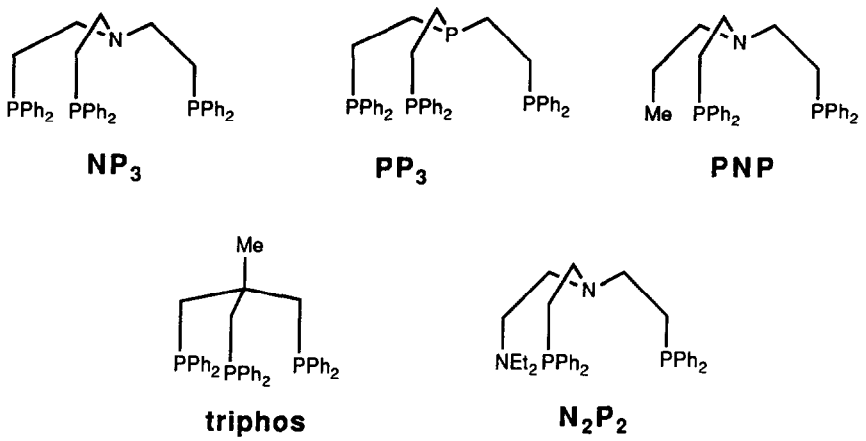


Chart 1.

ing: excellent bonding ability, strong *trans* influence, formation of stable complexes in a variety of metal oxidation states, adaptability to many different coordination numbers, increased nucleophilicity of the coordinated metal centres, rigorous control on the stereochemistry and stoichiometry of the resulting complexes. Using tripodal polyphosphines, we have found that a variety of homogeneous reactions are catalyzed in a selective way. Some transformations of relevant organic molecules, assisted by tripodal polyphosphine metal complexes, are:

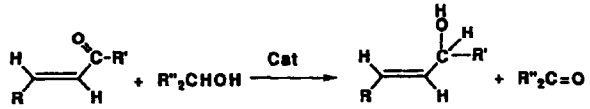
(i) selective hydrogenation of 1-alkynes to alkenes [4],
(ii) hydroformylation of alkenes to either branched or linear aldehydes [5],
(iii) acetalization of aldehydes and ketones [6],
(iv) selective homo-coupling and cross-coupling of 1-alkynes to Z-butenynes [7],
(v) selective synthesis of (G)-enol esters from 1-alkynes and carboxylic acids [8],
(vi) selective reduction of α,β-unsaturated ketones to allylic alcohols [9],
(vii) reduction of organic nitriles to amines [10],
(viii) linear and cyclic oligomerization of alkynes [11],
(ix) co-cyclization of ethyne and nitriles to give 2-substituted pyridines [11(c)],
(x) oxidation of primary alcohols to carboxylic acids [12],
(xi) selective oxidation of catechols to *o*-quinones [13],
(xii) intra- and extra-diol cleavage of catechols [13,14],
(xiii) disproportionation of acyclic ketones to carboxylate ions and ethers [9(b)],
(xiv) isomerization reactions of olefins [4(d),15], and
(xv) functionalization reactions of alkynes [11(c)].

In this article, the *tripodal polyphosphine-control element* will be developed essentially through examples from the author's own work, as applied particularly to chemo-, regio- or stereoselective transformations of 1-alkynes and ketones.

B. CATALYTIC REACTIONS

(i) Chemoselective reduction of α,β-unsaturated ketones to allylic alcohols

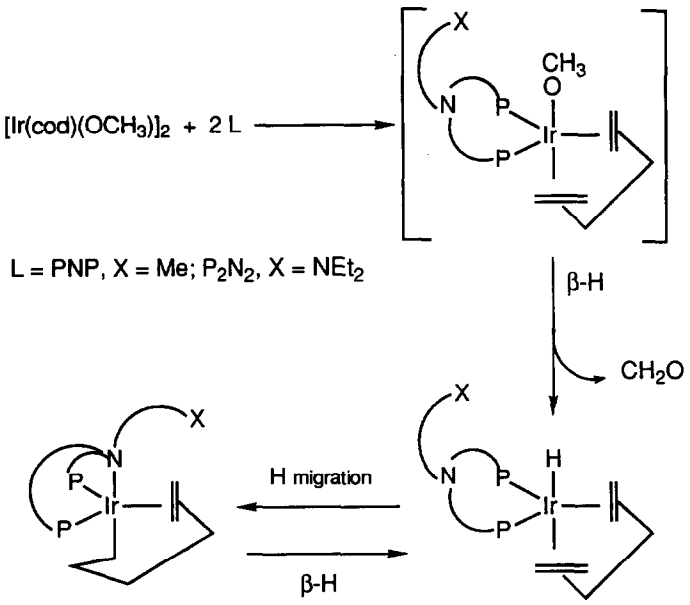
The cyclooctenyl iridium complexes [(PNP)Ir(σ,η^2-C_8H_{13})] (**1**) and [(P_2N_2)Ir(σ, η^2-C_8H_{13})] (**2**) are efficient catalyst precursors for the chemoselective hydrogen-transfer reduction of α,β-unsaturated ketones to allylic alcohols [9(a)] (eqn. (1)).



(1)

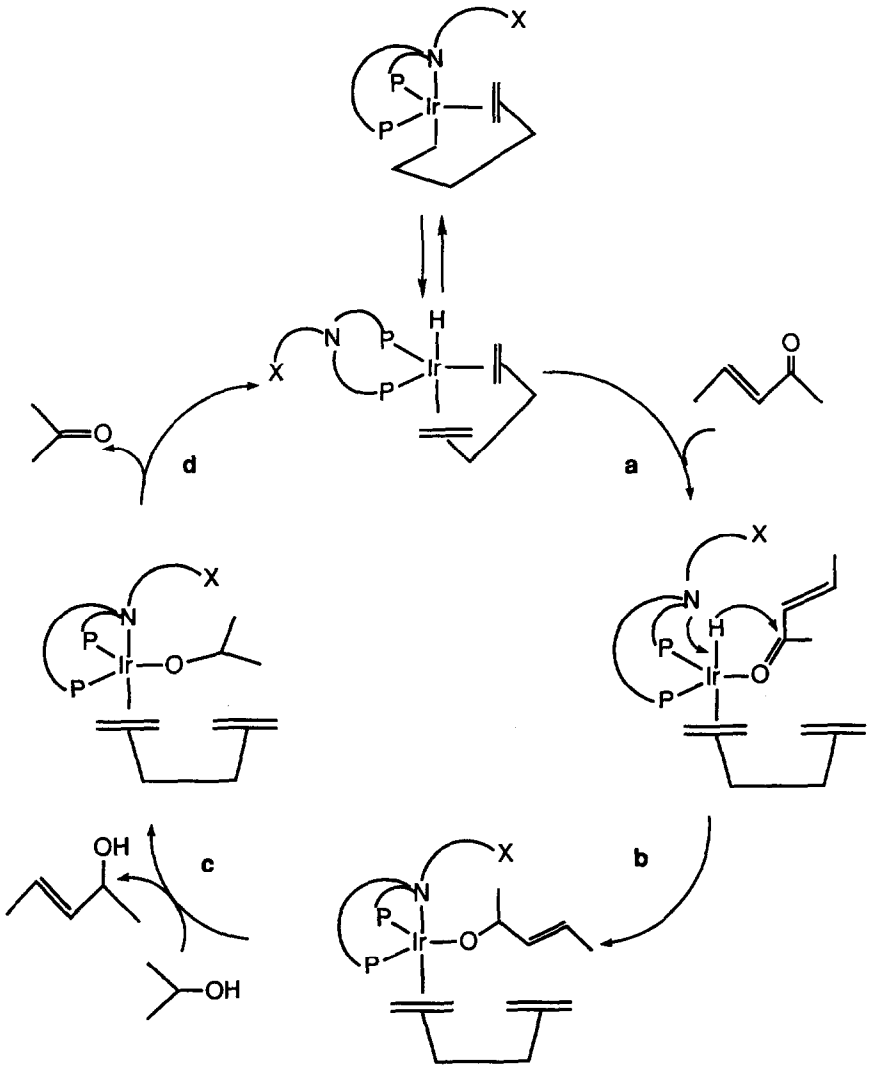
Compounds **1** and **2** have been prepared by reacting the polydentate ligands with the dimer $[Ir(cod)(OCH_3)]_2$ in tetrahydrofuran (cod = cycloocta-1,5-diene) (Scheme 1).

As shown in Scheme 1, the σ,η^2-cyclooctenyl complexes in solution are in equilibrium with the hydrides [(L)Ir(H)(cod)] (L = PNP (**3**); P_2N_2 (**4**)) via a β-H elimination/hydride migration process. The equilibrium concentrations of the hydrido complexes which contain η^2(P,P)-PNP and -P_2N_2 ligands increase with the temperature. From the determination of the equilibrium constants at different temperatures by ^{31}P NMR integration, the thermodynamic functions (ΔG^0, ΔH^0, ΔS^0) for the **1**↔**3** and **2**↔**4** interconversions have been calculated. The thermodynamic data indicate



Scheme 1.

that the conversion of the N_2P_2 complex **2** to the corresponding hydride is slightly favoured over that of the PNP derivative. This point is rather important in connection with the catalytic activity of the two complexes. In fact, **1** and **2** are quite effective in catalyzing the reduction of PhCH=CH(COMe) to PhCH=CH(CH_2OH) via hydrogen transfer from propan-2-ol or cyclopentanol. The proposed catalysis cycle is illustrated in Scheme 2. This involves the active participation as catalysts of the hydrido species which interacts with the unsaturated ketone. The ketone approaches the metal, displacing one olefinic end of cod (step **a**). At this point, the selective



Scheme 2.

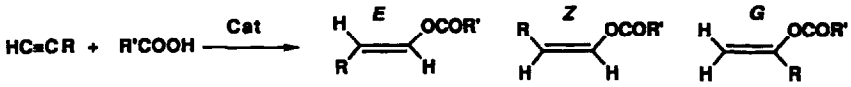
transfer of hydride to the carbonyl group occurs to give an alkoxy complex, a path that may be promoted by intramolecular coordination of the free nitrogen donor to the metal (step **b**). The alkoxy complex reacts with the secondary alcohol in excess to give the allylic alcohol and a new alkoxy complex (step **c**), which finally regenerates the hydrido catalyst via a β-H elimination process (step **d**).

By finely tuning the reaction conditions, turnover frequencies and selectivities up to 14.000 (mol of product per mol of catalyst per hour) and 80%, respectively, have been obtained. In keeping with the thermodynamically easier conversion to the hydrido derivative, the P_2N_2 complex proves more active than the PNP.

A crucial point to explain the effectiveness of **1** and **2** in the catalytic reaction is believed to be the ability of the *hybrid* polydentate PNP and P_2N_2 ligands to readily fasten/unfasten a nitrogen donor to/from the metal at different steps of the catalysis cycle. Indeed, the substitution of phosphorus for nitrogen as it occurs in the related σ,η^2-cyclooctenyl complex of triphos generates a species, [(triphos)Ir(σ,η^2-C_8H_{13})], which is totally inactive for the chemoselective reduction of benzylideneacetone [9(a)]. This fact has been related to the lesser tendency of the (triphos)Ir system to undergo a ligand "arm-off" process (step d in Scheme 2).

(ii) Regioselective synthesis of (G)-enol esters from 1-alkynes and carboxylic acids

The addition of carboxylic acids to 1-alkynes to give enol esters can be promoted by transition metal complexes (eqn. 2).

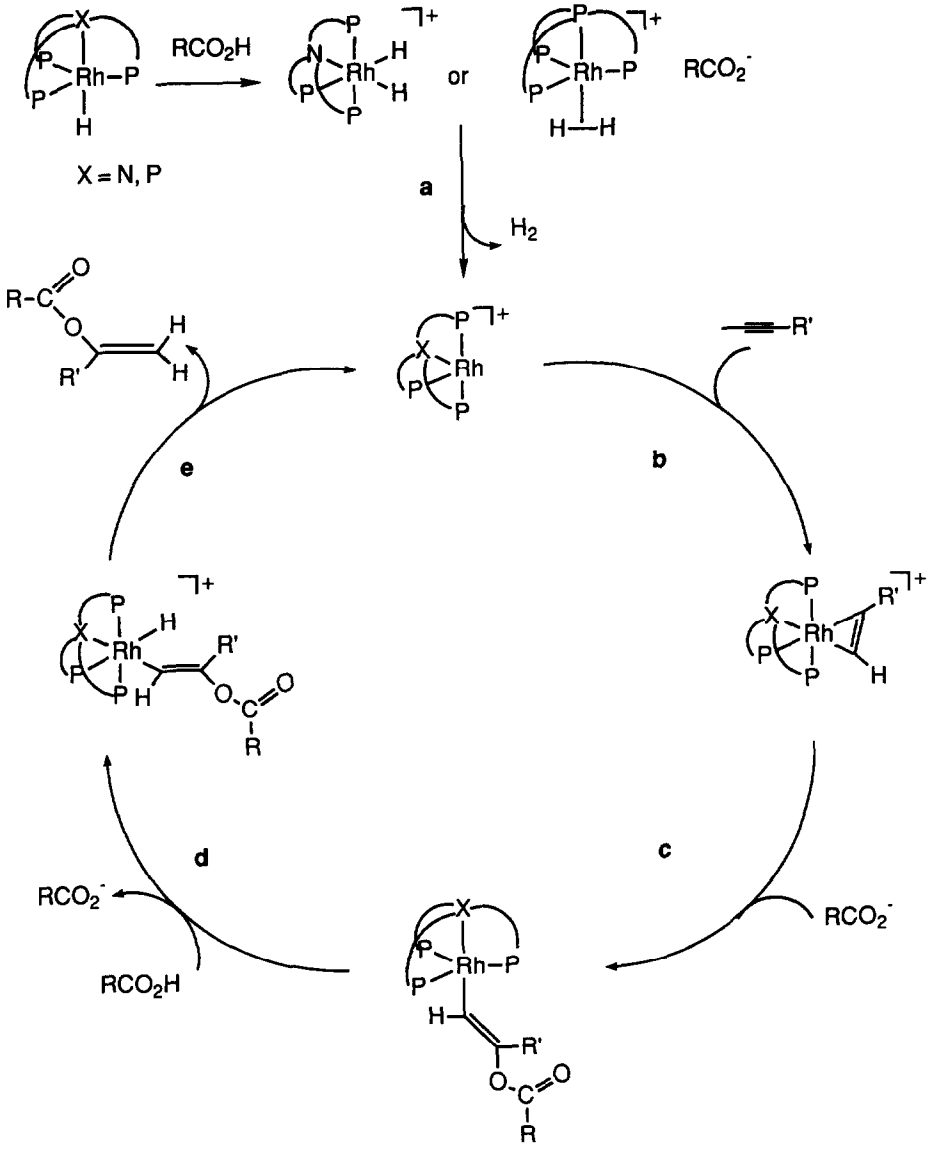


(2)

Besides acting as catalysts, metal complexes have the potential to drive the reaction to the selective formation of any one of the three possible G, E and Z isomers. A case in point is represented by the Rh(I) monohydrides [(PP_3)RhH] (**3**) and [(NP_3)RhH] (**4**) with the tripodal tetradentate ligands NP_3 and PP_3 [16]. Compounds **3** and **4** have been found to catalyze the regioselective formation of (G)-(benzoyloxy)propene from benzoic acid and propyne under mild conditions and with selectivities up to 94% [8].

The catalysis cycle is illustrated in Scheme 3.

The Rh complexes enter the cycle as the 16-electron fragments $[(L)Rh]^+$ (L= PP_3, NP_3) obtainable in a two-step reaction from the monohydrides [16]. The first step is the protonation of the monohydrides by the carboxylic acid to give either a classical, octahedral Rh(III) dihydride with NP_3 or a non-classical Rh(I) dihydrogen complex with PP_3 [17]. From both compounds, the elimination of H_2 readily occurs by interaction with the 1-alkyne, which forms π-alkyne adducts (step **b**). The latter compounds undergo nucleophilic attack by the carboxylate ion at the substituted carbon atom of the coordinated alkyne to give trigonal-bipyramidal Rh(I) σ-alkenyl species (step **c**). As in the monohydride precursors, the Rh(I) metal centre in the



Scheme 3.

σ-alkenyl complexes is highly basic and can be protonated by a carboxylic acid molecule. As a result, octahedral Rh(III) *cis*-hydride(alkenyl) complexes are formed (step **d**) which, finally, regenerate the 16-electron catalyst via reductive elimination of an enol ester molecule (step **e**).

As one may readily infer from inspection of Scheme 3, it is proposed that the tripodal ligands play a determinant role in the cycle due to their ability to favour

interconversion between C_{2v} and C_{3v} symmetries of the [(L)Rh] system. Such a structural exchange allows easier occurrence of sequences of reductive elimination and oxidative addition paths at rhodium.

The regioselective synthesis of (G)-(benzoyloxy)propene from propyne and benzoic acid is catalyzed also by the σ-methyl derivative [(PP_3)RhMe] [8]. Like the related monohydride complexes, the σ-methyl compound is a precursor to the 16-electron catalyst $[(PP_3)Rh]^+$ through an identical protonation/reductive elimination path (in this case methane is reductively eliminated). The lesser catalytic effectiveness of the σ-methyl complex has been attributed to the occurrence of an induction period occasioned by the fact that the protonation of the methyl complex by benzoic acid is less fast than that of the monohydride complexes.

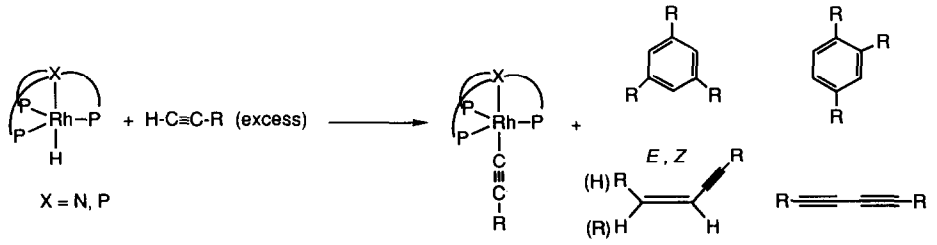
(iii) Stereoselective dimerization of 1-alkynes to (Z)-butenynes

In the absence of carboxylic acids, the Rh(I) monohydrides [(L)RhH] ($L = NP_3$, PP_3) react with 1-alkynes under catalytic conditions, yielding mixtures of various oligomerization products and σ-alkynyl complexes as termination products [11(a)] (Scheme 4).

In line with the catalytic cycle, which has been proposed to involve sequences of insertion/C–H oxidative addition steps [11(a)], both the conversion and the selectivity of such reactions depend on the nature of the 1-alkyne substituent as it controls both the type of insertion (*cis*, *trans*, *gem*) and the acidity of the terminal alkyne C–H bond. In particular, electron-withdrawing substituents favour cyclotrimerization over linear dimerization. As an example, under identical conditions, the NP_3 hydride converts $HC{\equiv}CCO_2Et$ to a mixture of 1,3,5- (40%) and 1,2,4-tricarbethoxy benzene (48%) almost quantitatively, whereas HC≡CPh is partially converted (80%) to a mixture of 1,3,5- (3%) and 1,2,4-triphenylbenzene (7%), 1,4-diphenylbut-3-ene-1-yne (33%) (E and Z isomers) and, 1,4-diphenylbutadiyne (30%).

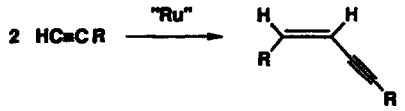
The substitution of cobalt for rhodium, i.e. by using [(PP_3)CoH] as catalyst, does not appreciably modify the conversion or the product composition [11(b)].

Much better results have been obtained by using the two Ru(II) complexes $[(PP_3)Ru(H)(\eta^2\text{-}H_2)]BPh_4$ and $[(PP_3)Ru(H)(N_2)]BPh_4$ [18]. Indeed, both com-



Scheme 4.

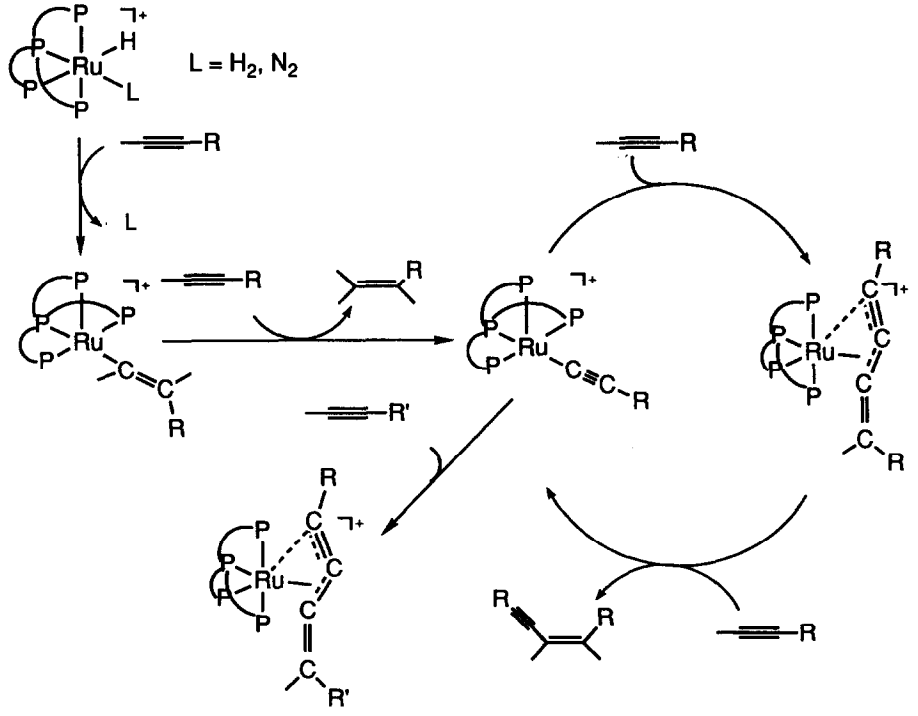
pounds have been found to catalyze the stereoselective formation of butenynes from 1-alkynes (eqn. (3)) with conversions and selectivities in the Z isomers in up to 95% yield [7].



(3)

A detailed experimental study on the reactions of the ruthenium complexes with $HC{\equiv}CSiMe_3$ and $HC{\equiv}CPh$ has allowed the determination of the catalytic cycle shown in Scheme 5. This involves displacement of the weakly bound H_2 and N_2 ligands by the 1-alkyne, followed by alkyne *trans* insertion into the Ru–H bond. As a result, a σ-alkenyl complex forms which, by treatment with a second alkyne molecule, transforms into a σ-alkynyl derivative, while free alkene is liberated. Reaction with a third 1-alkyne molecule gives a η^3-butenynyl complex, which finally reacts with a fourth 1-alkyne molecule, restoring the σ-alkynyl compound and generating the (Z)-1,4-disubstituted enyne.

The isolation and characterization of all of the complexes shown in Scheme 5, including a single-crystal X-ray analysis on the η^3-butenynyl complex, and a cross-



Scheme 5.

coupling reaction with a $HC{\equiv}CSiMe_3/HC{\equiv}C{-}n\text{-}C_5H_{11}$ mixture have provided valuable information on the mechanism of the dimerization reaction [7]. In particular, the following points have been established:

(i) 1-alkynes react with the σ-alkynyl catalysts, undergoing a 1,2-H shift at the metal to give vinylidene(alkynyl) intermediates [19];

(ii) the butenynyl ligands form via C–C bond formation between the α-carbons of cis vinylidene and alkynyl ligands (such a reaction is most likely the rate-determining step); and

(iii) the butenynyl ligand is anchored to the metal by using three carbon atoms. One carbon, namely that of the alkynyl moiety, is less strongly bound [2.485(2) Å] than the other two [2.234(3) and 2.144(3) Å] and can be displaced by an incoming 1-alkyne molecule.

The selective formation of (Z)-enynes has been interpreted in terms of steric factors. In particular, the six phenyl substituents on the phosphorus donors of PP_3 are believed to force the cis arrangement of the two 1-alkyne substituents.

C. STOICHIOMETRIC REACTIONS

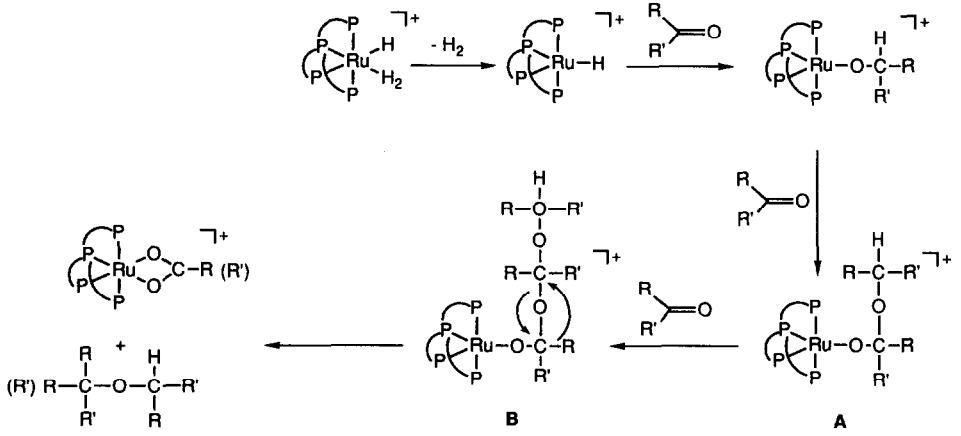
(i) Disproportionation reactions of acyclic ketones to carboxylate ions and ethers

Of the many tripodal polyphosphine metal complexes so far tested in homogeneous catalytic reactions, the Ru(II) η^2-H_2 compound $[(PP_3)Ru(H)(H_2)]BPh_4$ is the one showing the greatest versatility. In fact, besides promoting the stereoselective dimerization of 1-alkynes to (Z)-butenynes [7], this ruthenium complex has been found able to catalyze a variety of different reactions, including the selective hydrogenation of 1-alkynes to alkenes [4(b)], the chemoselective hydrogen-transfer reduction of α,β-unsaturated ketones to allylic alcohols [9(b)], and the hydrosilylation of alkynes [10(b)].

A relevant stoichiometric reaction uniquely assisted by $[(PP_3)Ru(H)(H_2)]BPh_4$ is the disproportionation of acyclic ketones to carboxylate ions and ethers [15]. The ruthenium complex reacts in tetrahydrofuran at room temperature with acyclic ketones such as acetone, diethyl ketone, ethyl methyl ketone, or acetophenone, producing asymmetric ethers and transforming into η^2(O,O)-carboxylato derivatives of the general formula $[(PP_3)Ru(O_2CR)]BPh_4$ (R = Me, Et, Ph) (eqn. (4)). No reaction occurs with cyclic ketones such as cyclopentanone.

$$2[(PP_3)Ru(H)(H_2)]^+ + 6RR'C{=}O \rightarrow 2H_2 + [(PP_3)Ru(O_2CR)]^+ + [(PP_3)Ru(O_2CR')]^+ + R_2R'COCH(R)R' + R'_2RCOCH(R)R' \quad (4)$$

The proposed reaction mechanism is illustrated in Scheme 6. All the steps preceding the formation of intermediate A are well established as they also enter the



Scheme 6.

catalytic cycle of the reduction of α,β-unsaturated ketones catalyzed by the same complex [9(b)].

The existence of the key intermediate **A** has indirectly been established by the reactions of the starting Ru complex with an excess of aldehydes such as MeCHO and EtCHO. As a result, the stoichiometric formation of the corresponding η^2(O,O)-carboxylato compounds $[(PP_3)Ru(O_2CR)]BPh_4$ (R = Me, Et) and of the symmetric ethers RCH_2OCH_2R occurs, but appreciable amounts of the esters $RC(O)OCH_2R$ are also formed. Just the catalytic production of these esters (Tishchenko-type reaction [20]) suggests the intermediacy of intermediate **A**, which is appropriately designed to undergo a β-H elimination path (Scheme 7).

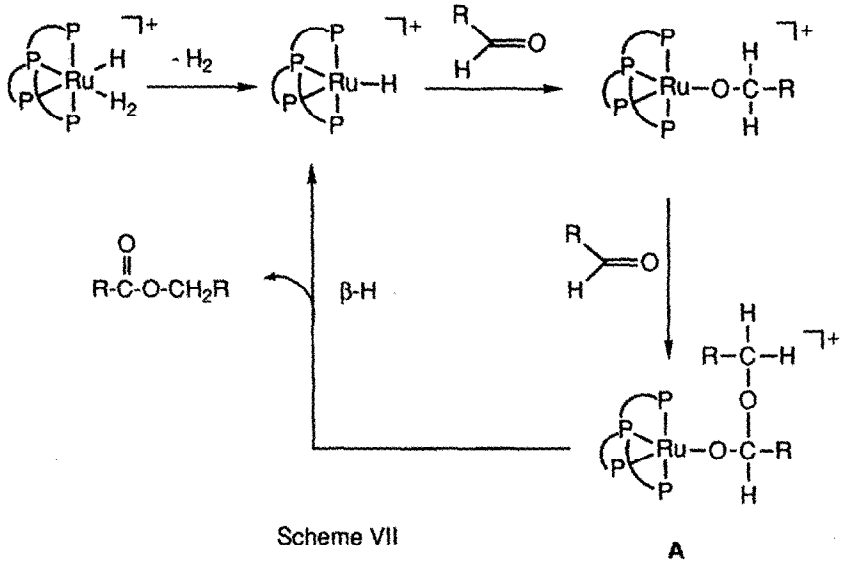
Returning to Scheme 6, intermediates of type **A** can react with a ketone molecule to give ruthenium products of type **B**, which finally decompose to the stable η^2-carboxylato complexes and ethers.

(ii) Oxidation of primary alcohols to carboxylic acids

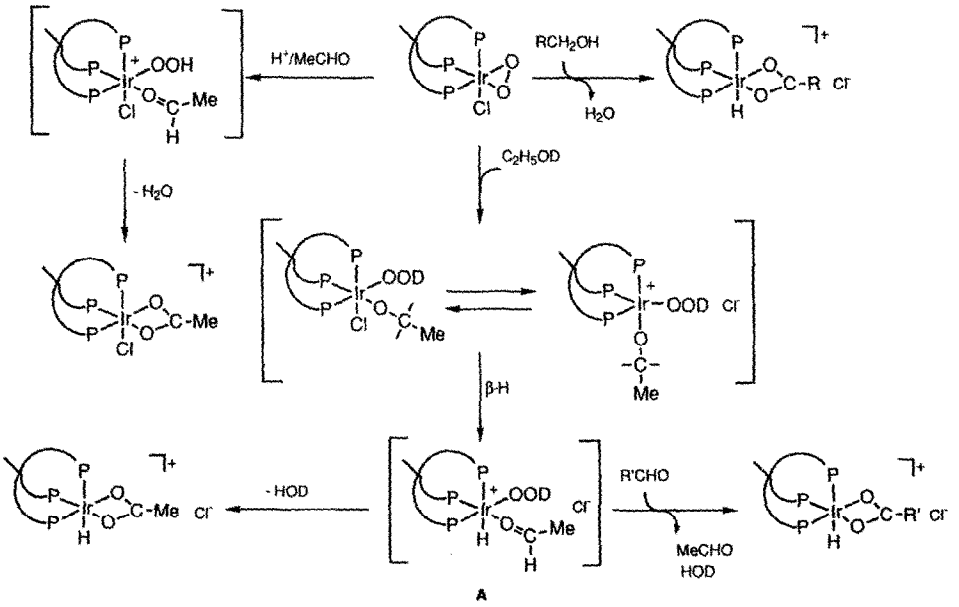
The selective oxidation of primary alcohols to carboxylic acids via dioxygen metal complexes is a reaction of which only two examples are known [12,21]. One of the two examples involves the participation of the peroxo complex [(triphos)Ir-Cl(O_2)] obtained by bubbling O_2 through a solution of [(triphos)IrCl(C_2H_4)] [12] (Scheme 8).

The dioxygen complex readily reacts with neat primary alcohols or in CH_2Cl_2 solution with stoichiometric amounts of alcohols producing H_2O and converting to η^2(O,O)-carboxylate(hydride) complexes of the general formula [(triphos)Ir (H)(O_2CR)]Cl (R = H, Me, Pr, Bu, Ph).

By using partially (C_2H_5OD, C_2D_5OH) and fully (C_2D_5OD) deuterated ethanol, the stepwise mechanism of the oxidation reaction has been elucidated. The first



Scheme 7.



Scheme 8.

step is the protonation of one end of the nucleophilic peroxo group by ethanol. As a result, a hydroperoxo intermediate forms which is believed to contain an ethoxy ligand. Indeed, the presence of such a ligand in the metal coordination sphere has been inferred by the nature of the final product, i.e. a metal hydride. In fact, it has been demonstrated that the hydridic hydrogen comes from the CH_2 group of ethanol, reasonably by a β-H elimination path. The aldehyde so formed remains coordinated to the metal so as to be oxidized by the cis hydroperoxo group to carboxylate ions while H_2O is eliminated (both hydrogen atoms of water come from ethanol, one of the two being that bound to oxygen). The intermediacy of an aldehyde complex has unequivocally been established by the results of the reactions of the dioxygen precursor with either H^+/MeCHO or a 1:10 C_2H_5OH/RCHO (R = Pr, Bu, Ph) mixture (see Scheme 8).

(iii) Functionalization reactions of ethyne

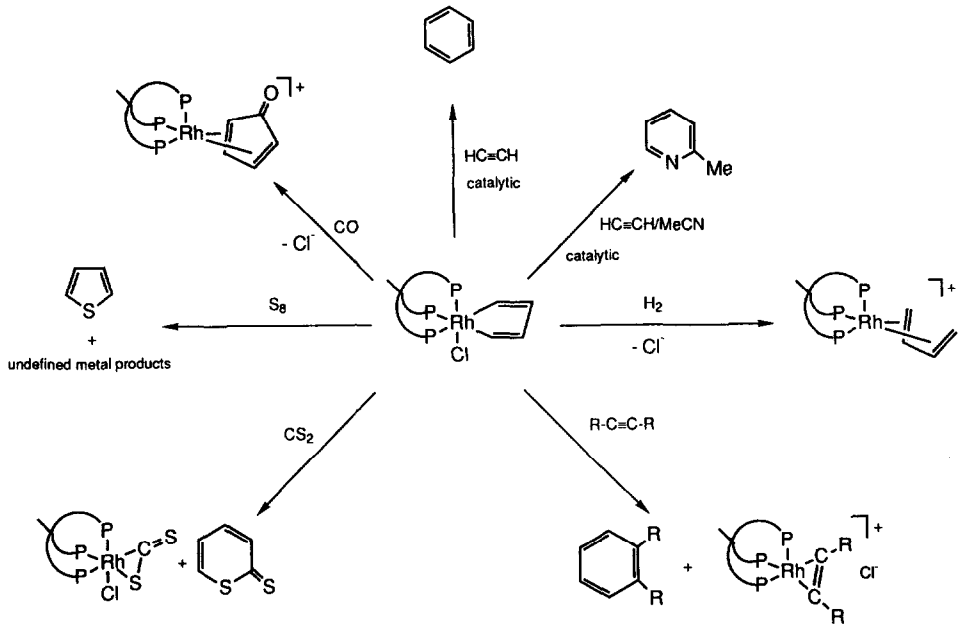
In comparison with its derivatives, ethyne is less reactive toward functionalization and exhibits a great tendency to linear and cyclic oligomerization and polymerization. In order to overcome this obstacle, several strategies have been developed for the functionalization of ethyne. A currently employed route involves the design of metal catalysts, which are able to form MC_4H_4 metallocycles [22]. The latter compounds must be sufficiently stable to be used in co-cyclization reactions with small organic and inorganic molecules.

The tripodal ligand triphos forms a stable metallocycle of this type with rhodium. The complex of formula [(triphos)RhCl(C_4H_4)] can be isolated in the solid state [11(c)]. Its reactions with a variety of small molecules, including CO, CS_2, S_8, $MeO_2CC{\equiv}CCO_2Me$, H_2, HC≡CH and HC≡CH/MeCN mixtures, have been carried out [11(c)]. The results of such reactions are summarized in Scheme 9.

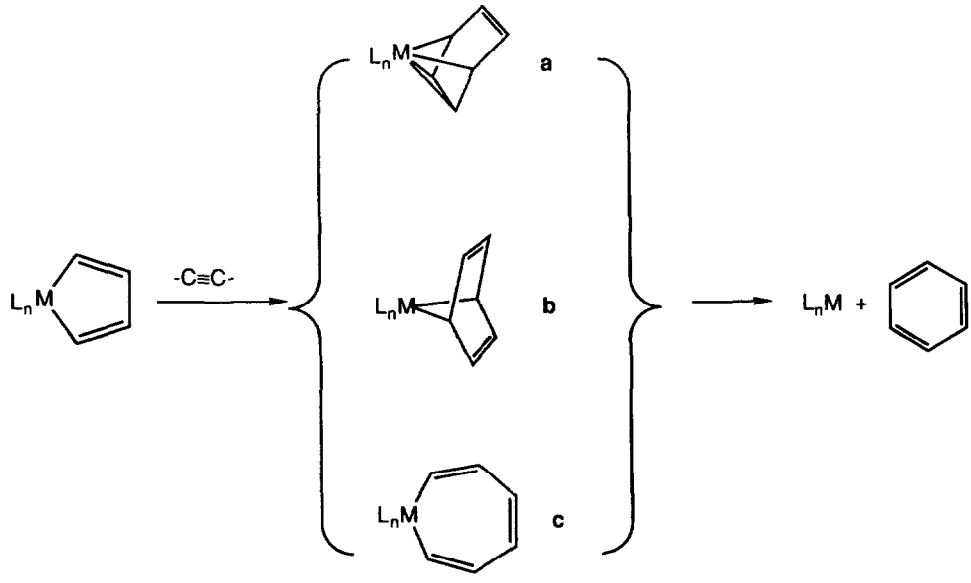
Catalytic reactions occur with HC≡CH and with HC≡CH/MeCN mixtures. Ethyne is selectively converted to benzene, while acetonitrile is incorporated into the C_4H_4 unit to give 2-methyl pyridine.

The mechanism of both transformations (Scheme 10) has recently been established through the isolation and X-ray characterization of several intermediates, including the rhodacyclopentadiene complex and an η^4-benzene complex of iridium, namely [(triphos)Ir(η^4-C_6H_6)]BPh_4 [11(d)]. It is now clear that the η^4-benzene complex mediates ethyne cyclotrimerization. In particular, the benzene ligand forms from the corresponding metallocycle, [(triphos)IrCl(C_4H_4)] [10(b)] in the presence of HC≡CH (**a**), via a concerted path and not via the commonly suggested intermediacy of either metallanorbornadiene (**b**) or metallacycloheptatriene (**c**) species [11(c),(d),22].

All of the other reactants listed above react with the rhodacyclopentadiene compound in a stoichiometric way, essentially due to the great stability of the complexes that the [(triphos)Rh]$^+$ and [(triphos)RhCl] moieties form with the



Scheme 9.



Scheme 10.

substrates. As an example, carbon monoxide is readily incorporated into the MC_4H_4 fragment to give the η^4-cyclopentadienone complex $[(triphos)Rh(C_4H_4CO)]^+$. However, since the latter compound reacts faster with CO to give the stable dicarbonyl $[(triphos)Rh(CO)_2]^+$ [5(a)] than with ethyne, no reaction with further ethyne can occur. In a similar way, carbon disulphide reacts quantitatively with the rhodacyclopentadiene complex, producing dithiopyrone and the stable η^2-CS_2 adduct $[(triphos)RhCl(CS_2)]$ [23], dimethyl acetylenedicarboxylate gives dimethyl phthalate and the π-alkyne complex $[(triphos)Rh(MeO_2CC{\equiv}CCO_2Me)]Cl$ [5(a)], and cyclooctasulphur yields thiophene and undefined sulphur-containing metal species.

An interesting reaction is observed with H_2 as the η^4-butadiene complex $[(triphos)Rh(C_4H_6)]BPh_4$ is formed quantitatively [11(c)]. Recent studies on this reaction are consistent with a mechanism involving the oxidative addition of H_2 to the metal, followed by a two-step reductive elimination process [10(b)].

D. CONCLUSIONS

Surveying the results herein presented, one may readily infer that the *tripodal polyphosphine-control element* is so effective that the combined bulk of the ligand–metal assembly and substrate, in most instances, operates to exclude alternatives so that one reaction path is specifically favoured. Obviously, the nature of the metal centre must be finely tuned, depending on the type of reaction involved. However, this is not a serious obstacle due to the capability of tripodal ligands to form stable complexes with different metals in a variety of metal oxidation states as well as their adaptability to many different coordination numbers [5(a)]. Indeed, tripodal polyphosphine ligands form stable complexes with most d-block metals, particularly with the platinum group metals, which constitute the essential ingredient in the majority of catalyst systems.

A great potential in homogeneous catalytic reactions is shown by *hybrid* polydentate ligands, namely those containing different donor atoms [8,9(a),11(a),(b)]. In fact, the *hybrid* ligands, particularly those with phosphorus and nitrogen donors, can provide free coordination sites at the metal during catalysis cycles by the alternative decoordination of either donor, depending on the electronic requirements of the metal-reactant assembly. Finally, it is worth mentioning that the use of tripodal polydentate ligands quite often allows the isolation and characterization of many intermediate species not normally observable in catalytic cycles where monodentate ligands are employed.

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