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Stoichiometric and catalytic functionalization reactions of alkynes at transition metal complexes stabilized by tripodal polyphosphine ligands

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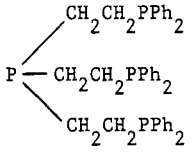
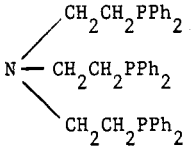
Abstract - Tripodal polyphosphine ligands react with transition metal ions to form either unsaturated fragments or, in combination with suitable coligands, highly reactive complexes. Both the fragments and the complexes appear appropriately designed to interact with ethyne and 1-alkynes. By a purposeful variation of the polyphosphine ligand, metal, coligand and reaction conditions, a great variety of organometallic and organic products can be stoichiometrically and catalytically synthesized in a highly selective manner. The use of polyphosphine ligands allows the isolation and characterization of many intermediate species not normally seen in catalysis cycles.

INTRODUCTION

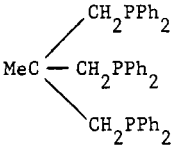
Acetylene and its derivatives undergo several, intriguing metal-assisted reactions of which no industrial use has yet been made due to their low selectivity. Our work is attempting to address this limitation by examining the use of transition metal catalysts stabilized by tripodal polyphosphine ligands such as $P(CH_2CH_2PPh_2)_3$ (PP_3), $N(CH_2CH_2PPh_2)_3$ (NP_3) and $MeC(CH_2PPh_2)_3$ (triphos). These ligands combine the well-known polyphosphine advantages (ref. 1) with a rigorous and unique control on the stereochemistry of the resulting complexes (ref. 2). By this control, polyphosphine metal species can induce highly selective transformations of ethyne and of 1-alkynes. Some of these reactions are described, with selected examples, in the following sections.



PP_3



NP_3



triphos

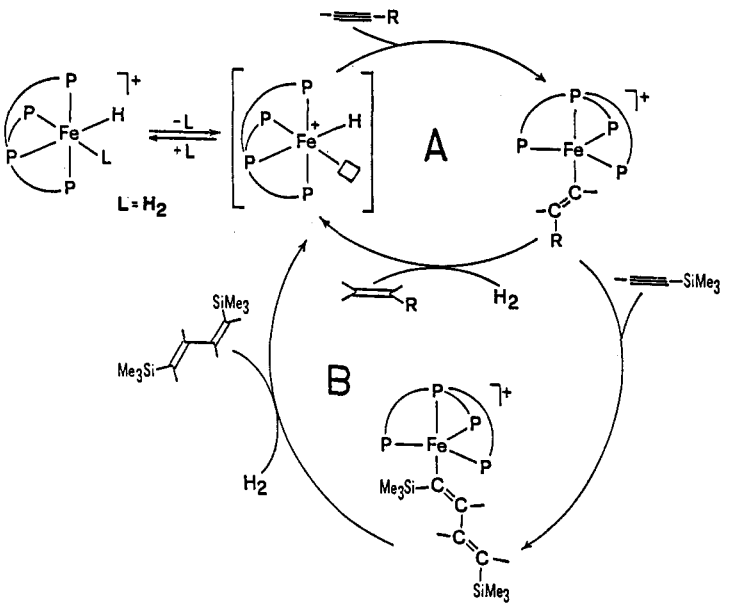
SELECTIVE HYDROGENATION OF 1-ALKYNES TO ALKENES

It is well known that in alkyne/alkene mixtures, the alkyne function is preferentially reduced because of its greater bonding ability with the metal center. However, in most instances, once the alkyne is consumed, the hydrogenation of alkene occurs.

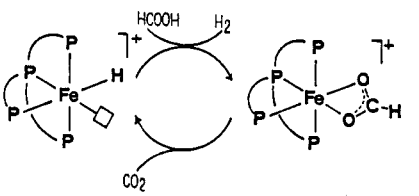
We have synthesized a couple of metal systems, namely the cis-hydride(dihydrogen) complexes $[(PP_3)M(H)(\eta^2\text{-}H_2)]BPh_4$ (M = Fe, 1 (ref. 3); Ru, 2) that catalyze the selective reduction of 1-alkynes to the corresponding alkenes with no formation of alkanes. The reactions are carried out in tetrahydrofuran under 1 atm of H_2 and exhibit turn-over numbers that increase with the temperature but do not depend on the alkyne substituent. The latter may be an alkyl, aryl, vinyl or trimethylsilyl group.

The catalysis cycles for both metal systems are similar to each other. As shown in Schemes 1 and 3, the two cycles apparently differ in the structure (and in the spin state) of the product of the primary insertion, namely the σ-alkenyl intermediates $[(PP_3)M(CH{=}CHR)]^+$. The

Scheme 1



Scheme 2

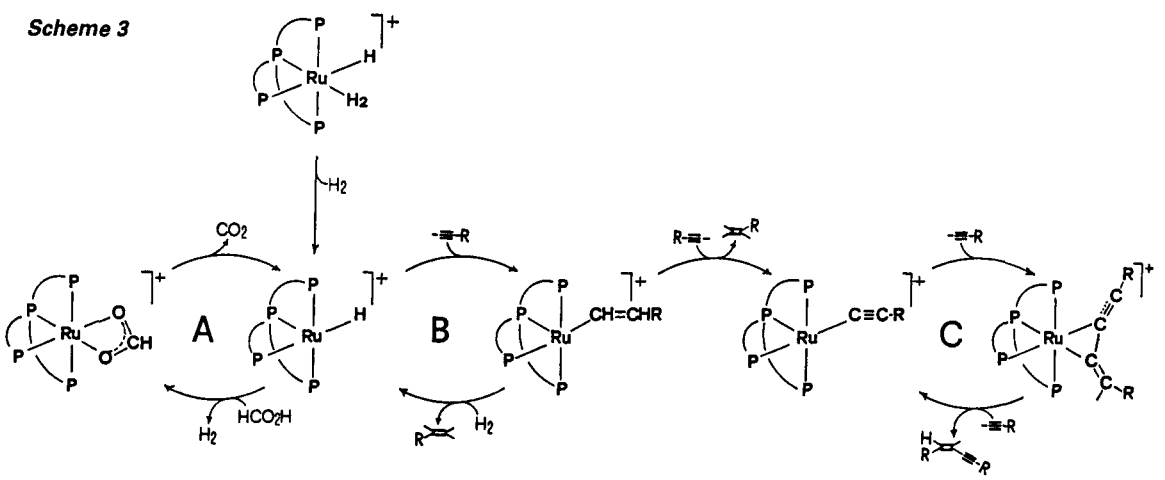


iron complexes are trigonal-bipyramidal and paramagnetic with magnetic moments corresponding to two unpaired spins (ref. 3). The trans insertion of 1-alkynes across the Fe-H bond has been determined by NMR spectroscopy on the diamagnetic carbonyl derivative $[(PP_3)Fe(CO)\{CH{=}CH(SiMe_3)\}]BPh_4$ obtained by reacting the corresponding σ-alkenyl with CO. In contrast the ruthenium complexes are diamagnetic and exhibit a distorted square-pyramidal geometry.

In both hydrogenation reactions, H_2 can be replaced with HCOOH since the precursors 1 and 2 prove efficient catalysts for the decomposition of formic acid to CO_2 and H_2 (see Schemes 2 and 3, cycle A) via η^2-formate intermediates that are isolable working under a CO_2 atmosphere.

The different structure of the iron and ruthenium σ-alkenyl intermediates strongly influences the kinetics of the hydrogenation reactions as the rate determining step is the alkyne insertion across the metal-hydrogen bond for Fe and the addition of H_2 to the alkenyl complex for Ru.

Scheme 3



REDUCTIVE DIMERIZATION OF 1-ALKYNES TO 1,4-DISUBSTITUTED BUTA-1,3-DIENES

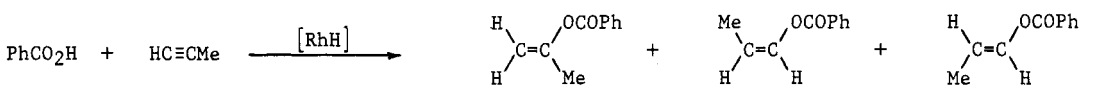
The facile loss of the dihydrogen ligand from 1 to give an unsaturated Fe(II) monohydride is the first step also for the reductive dimerization of $HC{\equiv}CSiMe_3$ to 1,4-trimethylsilyl-buta-1,3-diene. At reflux temperature in tetrahydrofuran, the formation of the latter molecule prevails over hydrogenation to vinyltrimethylsilane (rates, mol of substrate transformed per mol of catalyst per hour: 9.8 vs. 2.2) (ref. 3). The dimerization reaction to butadiene reasonably proceeds via a trigonal-bipyramidal σ-butadienyl species (Scheme 1, cycle B). In fact, a complex of the latter type is likely formed when cis-1-ethoxy-1-buten-3-yne, $HC{\equiv}CCH{=}CH(OMe)$, is reacted with 1 to give $[(PP_3)Fe\{C{\equiv}CCH{=}CH(OMe)\}]BPh_4$ as the butadiene $H_2C{=}CHCH{=}CH(OMe)$ is quantitatively liberated.

SELECTIVE DIMERIZATION OF 1-ALKYNES TO *Z*-1,4-SUBSTITUTED BUTENYNES

The ruthenium complex 2 reacts with 1-alkynes in tetrahydrofuran at reflux temperature selectively producing 1,4-disubstituted butenynes regardless of the alkyne substituent. The selectivity in the Z-isomer is 94% with turn-over numbers of ca. 100 (mol of product per mol of catalyst per hour). By a purposeful variation of the stoichiometry it is possible to characterize spectroscopically and, in most instances, to isolate the intermediates in the catalysis cycle shown in cycles B and C of Scheme 3: σ-alkenyl, σ-alkynyl and η^2-butenynyl complexes. As an example of the latter compounds, the 1,4-trimethylsilylbutenynyl derivative $[(PP_3)Ru(Me_3SiC_3CHCiMe_3)]BPh_4$ has been authenticated by an X-ray analysis. As is evident from Scheme 3, the overall geometry around ruthenium is distorted octahedral. The butenynyl ligand is bound to the metal through the central carbon atoms, one belonging to the alkene moiety (C=C bond distance 1.343(6) Å), the other to the alkyne moiety (C≡C bond distance 1.267(6) Å). The formation of the $Me_3SiC_3CHSiMe_3$ ligand reasonably proceeds by coupling of a trimethylsilylacetylene molecule with a σ-$C{\equiv}CSiMe_3$ group via a vinylidene intermediate (ref. 4). The selective formation of butenynes where the alkynyl group and the alkyne substituent are mutually cis is a consequence of the steric requirements of the tripodal tetradentate ligand, particularly of the presence of the six phenyl rings on PP_3.

REGIOSELECTIVE SYNTHESIS OF ENOL ESTERS FROM 1-ALKYNES AND CARBOXYLIC ACIDS

Enol esters are useful starting compounds in a wide range of catalytic and stoichiometric organic reactions. The most common synthetic route to enol esters is the 1:1 condensation of 1-alkynes and carboxylic acids catalyzed by transition metal complexes. One of the major problems in this procedure is given by the lack of selectivity as three isomers (G, E and Z) can in principle be obtained. This limitation can be overcome by the use of appropriately designed metal catalysts such as the trigonal-bipyramidal Rh(I) monohydrides $[(PP_3)RhH]$ (1) and $[(NP_3)RhH]$ (2) (ref. 5). As an example, these catalyze the regioselective formation of 2-(benzoyloxy)propene from the addition of benzoic acid to propyne. The reactions are catalytic under relatively mild conditions: catalyst to substrate ratio 1:100, toluene, 100 °C, 4 h.



G Z E

[RhH] = 1: G 94%, E 3%, Z 3%

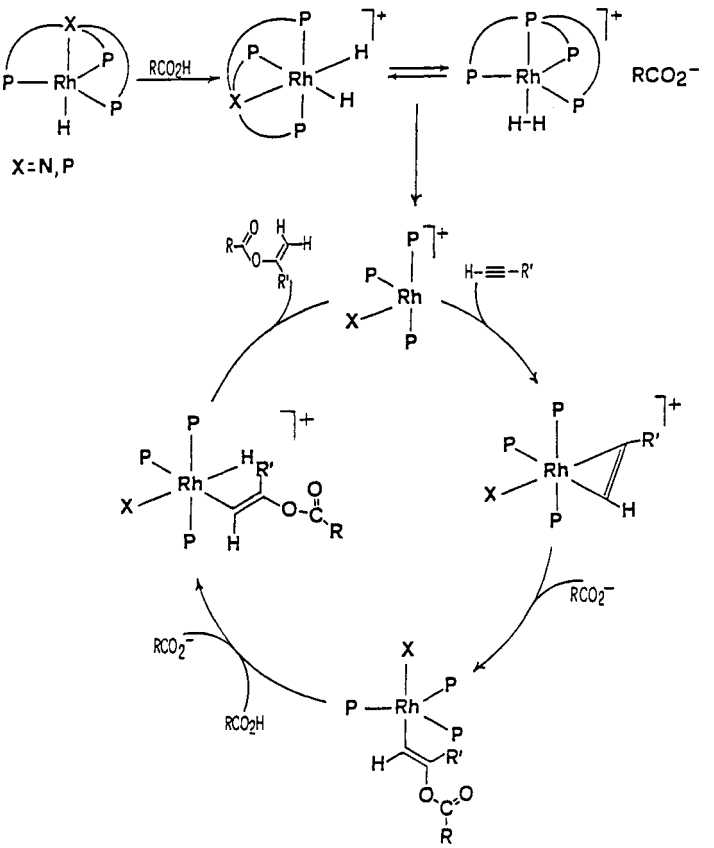
[RhH] = 2: G 92%, E 4%, Z 4%

A detailed experimental study on the reactions of 1 and 2 with carboxylic acids, 1-alkynes, or carboxylic acids/1-alkynes mixtures has allowed us to propose the cycle shown in Scheme 4 to account for the present synthesis of 2-(benzoyloxy)propyne. This involves the Rh(I) monohydrides 1 and 2 as catalyst precursors and the 16-electron systems $[(L)Rh]^+$ (L = PP_3, NP_3) as real catalysts. The latter species are generated by protonation of 1 and 2 by the carboxylic acid, followed by reductive elimination of H_2. The elimination of H_2 is promoted by 1-alkynes that interact with $[(L)Rh]^+$ forming π-alkyne adducts as kinetic products (ref. 6). These can be chemically trapped by reaction with nucleophiles such as the carboxylate anion which is present in the reaction mixture. The Rh(I) σ-alkenyl complexes

that form upon attack by carboxylate at η^2-alkyne are susceptible to protonation at the metal by a second molecule of carboxylic acid. As a result, Rh(III) cis-(hydride)(alkenyl) derivatives form which undergo reductive elimination of alkene (enol esters), thus regenerating the $[(L)Rh]^+$ catalysts.

In accord with the catalysis cycle shown in Scheme 4, the chlorides $[(L)RhCl]$ (L = PP_3, NP_3) do not catalyze the formation of enol esters from carboxylic acids and 1-alkynes. In fact, although the Rh(I) chlorides are protonated by carboxylic acids, the resulting Rh(III) cis-(hydride) chlorides are quite stable with respect to the reductive elimination of HCl and, therefore, do not generate the 16-electron fragments $[(L)Rh]^+$. In contrast, the methyl derivatives $[(L)RhMe]$, although less efficient than hydrides 1 and 2, prove catalyst precursors for the synthesis of enol esters. The higher activity of the hydrides as compared to the methyl derivatives is ascribed to the occurrence of an induction period (ref. 5).

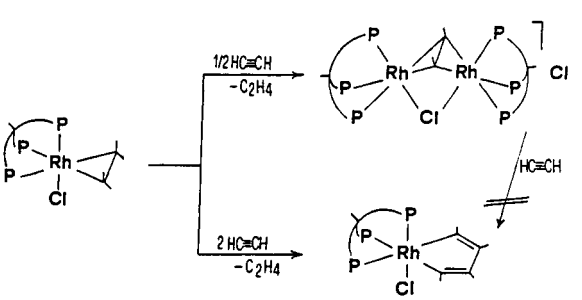
Scheme 4



CATALYTIC AND STOICHIOMETRIC FUNCTIONALIZATION REACTIONS OF ETHYNE

Depending on the metal to ethyne ratio, the reaction of $[(triphos)RhCl(C_2H_4)]$ (ref. 2) in tetrahydrofuran with ethyne forms either the binuclear complex $[(triphos)Rh(\mu\text{-}Cl)(\mu\text{-}\eta^2,\eta^2\text{-}C_2H_2)Rh(triphos)]Cl$ (3), or the mononuclear rhodacyclopentadiene complex $[(triphos)RhCl(\eta^2\text{-}C_4H_4]$ (4) (Scheme 5).

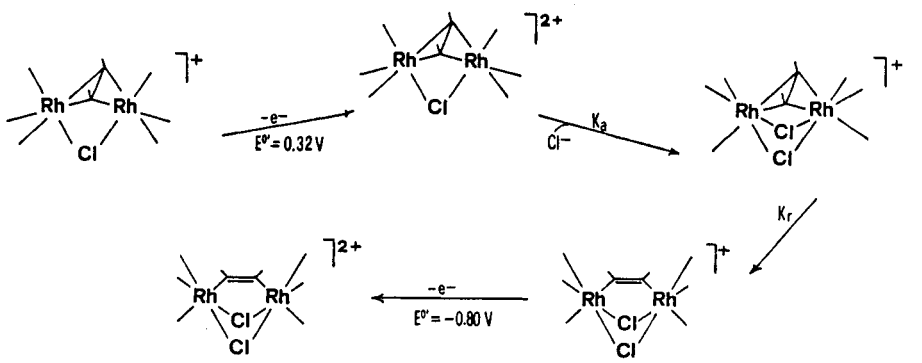
Scheme 5



The crystal structure of the binuclear complex has been determined by X-ray methods. In the complex cation, a chloride ligand and an ethyne molecule bridge two (triphos)Rh fragments with a Rh-Rh separation corresponding to no formal metal-metal bond. The acetylene ligand is positioned in the "perpendicular" mode and formally serves as a four-electron donor.

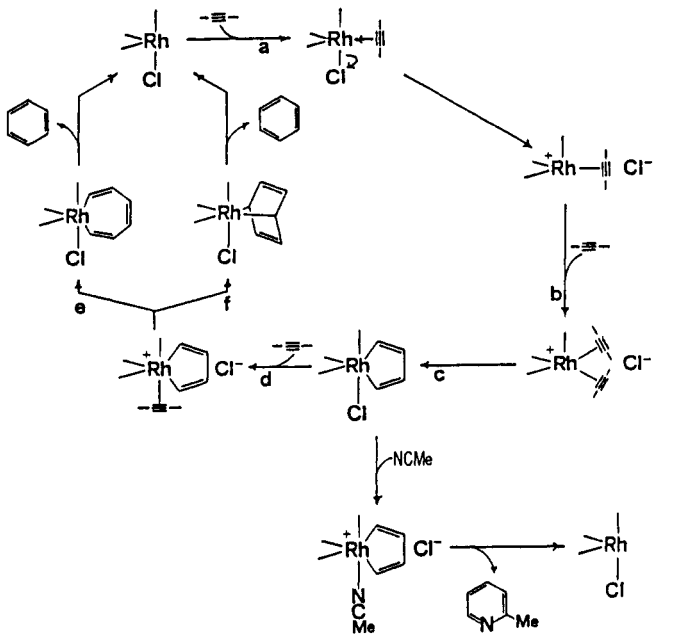
Complex 3 undergoes single-stepped two-electron oxidation by chemical or electrochemical methods converting to the "parallel" derivative $[(triphos)Rh(\mu\text{-}Cl)_2(\mu,\eta^1,\eta^1\text{-}C_2H_2)Rh\text{-}(triphos)]^{2+}$ (5) which can be isolated as ClO_4^- or PF_6^- salt. The reaction is reversible as 3 is regenerated from 5 by two one-electron reduction steps. Electrochemical studies have shown that the 3 → 5 conversion proceeds via an EC_aC_rE mechanism where E = electron transfer, C_a = addition of chloride and C_r = stereochemical rearrangement (Scheme 6).

Scheme 6



On the basis of spectroscopic data, complex 4 is assigned a structure where rhodium is octahedrally coordinated by triphos, by a chloride ligand and by the two terminal carbons of a C_4H_4 diene moiety. In contrast to 3 or 5 which are dead-ends for catalytic functionalization reactions of ethyne, the rhodacyclopentadiene compound catalyzes under very mild conditions the cyclotrimerization of ethyne to benzene as well as the cocyclization of ethyne with acetonitrile to give 2-picoline (Scheme 7).

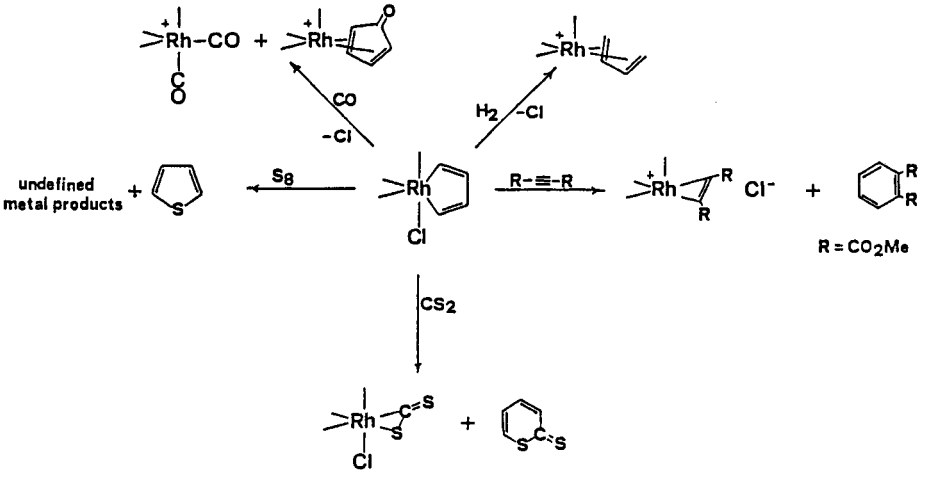
Scheme 7



From our studies it is concluded that both the cyclotrimerization and cocylization reactions require creation of a free site at rhodium. Such a condition is satisfied by the decoordination of the chloride (Scheme 7). In addition to the catalytic reactions above reported, the rhodacyclopentadiene complex undergoes several stoichiometric transformations to give a variety of heterocyclic compounds containing the C_4H_4 diene moiety. Dimethyl phthalate, dithiopyrone and thiophene are obtained by reaction of 4 with dimethyl acetylenedicarboxylate, carbon disulphide and cyclooctasulphur, respectively (Scheme 8). Interestingly,

carbon monoxide reacts with 4 yielding a rare example of unsubstituted cyclopentadienone ligand bonded to rhodium via the midpoints of the diolefinic double bonds. Finally, 4 reacts with dihydrogen under very mild conditions (room temperature, 1 atm of H_2) converting to the η^4-butadiene derivative $[(triphos)Rh(\eta^4\text{-}C_4H_4)]BPh_4$ (Scheme 8).

Scheme 8



CONCLUDING REMARKS

The use of tripodal polyphosphine ligands to prepare transition metal catalysts for reactions involving ethyne or 1-alkynes is an area in its initial stages of investigation. However, it is clear from our work that this approach has great potential for the development of highly selective reactions.

From our results it is apparent that tripodal polyphosphine metal complexes are often less efficient in terms of turn-over numbers than comparable systems with monodentate phosphines. However, our compounds can allow the isolation and characterization of many intermediate species not normally seen in reactions assisted by monodentate ligands.

Acknowledgements

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