Opportunities in homogeneous catalysis

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<u>Abstract</u> – An account is given of part of our exploratory journey through
homogeneous catalysis, aimed at finding potential applications of homo-
geneous catalysis in the synthesis of (large-scale) industrial chemicals.
The intimate interplay between the neutral ligands and associated anions
in electrophilic, cationic transition metal complex catalysts, determining
the catalyst activity and selectivity in a variety of reactions, has been
chosen as the theme of this presentation. To illustrate this theme, we
report a variety of findings, made in our study of reactions such as the
carbonylation of olefins, hydroformylation of formaldehyde and olefins,
reductive carbonylation of nitro-aromatic compounds and olefin
dimerization.

INTRODUCTION

The "Golden Age" of innovation in the large-scale industrial application of homogeneous
catalysis lasted about a quarter of a century and ended in the second half of the 1970s.
Despite the relatively low level of innovation in the past decade, we believe that the pros-
pects for industrial application of homogeneous catalysis in the future are excellent. This
optimistic view is based on the observation of several factors which present major chal-
lenges to the chemical industry:

* <u>environmental</u> <u>considerations</u> not only require the development of new, ecologically sound
products, but also the development of new, less environmentally demanding processes for a
variety of existing products;

* <u>changes</u> to <u>new</u> <u>feedstocks</u> necessitated by future limitations in the availability of cheap
petroleum-based resources; although still abundantly available now, it is predicted that the
cost of these resources will again escalate by the end of the century. Processes starting
from synthesis gas (CO/H_2) will have a considerable advantage because this feedstock can be
produced from coal or organic refuse;

* <u>considerable</u> <u>growth</u> <u>in</u> <u>demand</u> for specialty, "effect" chemicals, i.e. chemicals or poly-
mers with special optical, electronic or other properties, and fine chemicals such as
pharmaceuticals and agrochemicals.

These factors will certainly require new technologies to be developed, and in view of the
long lead time involved in developing a new process and/or a new product, it is now the time
to uncover and explore these new technologies, for the production of both new and existing
chemicals. We expect that organometallic chemistry and homogeneous catalysis will be at the
heart of many of the new developments to come.

In this paper we give an account of part of our exploratory journey through homogeneous
catalysis, undertaken with the aim and hope to uncover potential applications in the synthe-
sis of (large-scale) industrial chemicals. In the course of these studies we became fascina-
ted by the potentials of electrophilic, cationic transition-metal complex catalysts. In par-
ticular, the intimate interplay between ligands and accompanying anions observed in deter-
mining their (re)activity towards a variety of substrates and the selectivity of a variety
of reactions they catalyse, has intrigued us. We have chosen this aspect as the theme of
this paper.

EXPERIMENTAL

The experiments were carried out in 250-ml Hastelloy C, magnetically stirred autoclaves
using standard techniques. Products were analysed by conventional GLC and/or NMR techniques.

Averaged reaction rates were calculated on the basis of amounts of product and reaction time (0.30-5 h). Molar selectivities are based on the amounts of product formed and starting material converted. Catalyst precursors (e.g. Pd(OAc)$_2$, ligands etc.), reactants, solvents and other chemicals were all used as commercially available and were generally of p.a. quality.

HYDROFORMYLATION OF FORMALDEHYDE

An extensive study of the direct synthesis of ethylene glycol from syngas has been carried out by several research groups (ref.1). This synthesis is characterized by severe reaction conditions, a relatively low selectivity to ethylene glycol and very high catalyst costs.

As an alternative approach we have considered the Rh-catalysed hydroformylation of formaldehyde as part of a three-step, indirect process to ethylene glycol:

$$CH_3OH \quad \longleftrightarrow \quad CH_2=O \; + \; H_2 \tag{1}$$

$$CH_2=O \; + \; CO \; + \; H_2 \quad \longrightarrow \; HO-CH_2-C(O)-H \tag{2}$$

$$HO-CH_2-C(O)-H \quad + \; H_2 \; \longrightarrow \; HO-CH_2-CH_2-OH \tag{3}$$

For the present purpose we will only discuss the catalysis of reaction (2). The reaction is catalysed by Rh-based homogeneous catalysts under mild conditions. Using Rh(acac)(CO)$_2$ as catalyst precursor in the presence of phosphines, we found that hydroformylation is co-catalysed by protonic acids, i.e. both rate and selectivity strongly depend on the type of ligand and acid used. Some typical examples are shown in Table 1.

TABLE 1. Hydroformylation of Formaldehyde[a]

$$CH_2=O + CO + H_2 \longrightarrow HO-CH_2-C\overset{\displaystyle O}{\underset{\displaystyle H}{\big\backslash}}$$
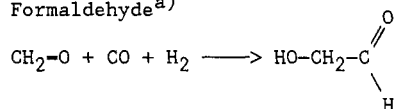
	Ligand (mmol)	Acid promoter (mmol)	Temperature (°C)	Formaldehyde [e] conversion rate (mol/(mol Rh.h))	Selectivity to glycol aldehyde [f] (%)
1	PPh$_3$ [b] (2)	–	85	60	36
2	ditto	p-toluenesulphonic acid (4)	85	150	98
3	ditto	CH$_3$COOH (45)	85	300	70
4	PBu$_3$ [c] (2)	ditto	80	400	20
5	P(PhpCl)$_3$ [d] 2.5	–	80	< 30	< 60
6	ditto	CH$_3$COOH (90)	80	270	94
7	ditto	CH$_3$O-CH$_2$COOH (20)	80	300	98

a) Catalyst precursor: 0.5 mmol Rh(acac)(CO)$_2$; 50 ml dimethylacetamide as solvent, 7.5 g formaldehyde as paraformaldehyde intake, CO/H$_2$ = 1, 60 bar (constant pressure).

b) PPh$_3$ = triphenylphosphine

c) PBu$_3$ = tributylphosphine

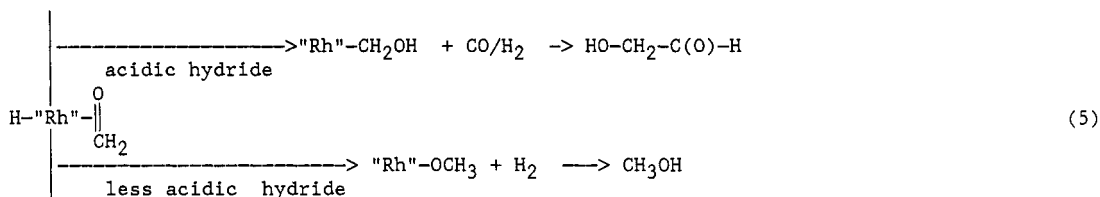d) P(Ph pCl)$_3$ = tris(p-chlorophenyl)phosphine

e) rate averaged over first hour

f) selectivity = $\dfrac{\text{mol glycol aldehyde}}{\text{mol CH}_3\text{OH} + \text{mol glycol aldehyde}}$ x 100 %

First of all, experiments 1 and 5 show the low activity and selectivity observed for reaction (2) when only phosphines and no acids are used. A strong acid (e.g. p-toluene-sulphonic acid) raises the selectivity to almost 100 %, while at the same time the reaction rate increases considerably. A weak acid, such as a carboxylic acid, further increases the reaction rate, but at the cost of selectivity (cf. experiments 2 and 3). Replacing triphenylphosphine by the more basic tributylphosphine further reduces the selectivity, i.e. the main reaction appears to be hydrogenation of formaldehyde (experiment 4). By contrast, when phosphines less basic than triphenylphosphine, such as tris(p-chlorophenyl)phosphine, are combined with weakly acidic anion donors, both a high activity and a high selectivity are observed (experiments 6 and 7).

To explain these observations we hypothesize that cationic hydrido–Rh complexes are the actual catalyst species, generated via:

$$Rh(acac)(CO)_2 + 2\ HX(acid) + n\ L(igand) \longrightarrow Acetylacetone \tag{4}$$

$$+\ H\text{--}Rh(L)_n(X)_2\ +\ 2\ CO$$
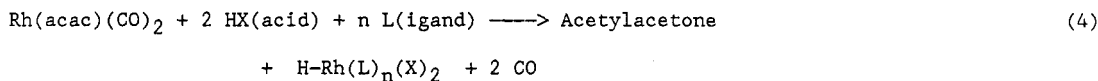
The crucial factor governing the selectivity in formaldehyde hydroformylation, we believe to be the <u>acidity</u> of the rhodium hydride:

$$
\begin{array}{l}
\rule[1ex]{0pt}{0pt}\text{---------------------}\!>\text{"Rh"--}CH_2OH\ +\ CO/H_2\ \rightarrow\ HO\text{--}CH_2\text{--}C(O)\text{--}H \\
\qquad\text{acidic hydride} \\
\qquad\quad O \\
H\text{--"Rh"--}\!\parallel \\
\qquad\ CH_2 \\
\text{------------------}\!\!\longrightarrow\ \text{"Rh"--}OCH_3\ +\ H_2\ \longrightarrow\ CH_3OH \\
\qquad\text{less acidic hydride}
\end{array}
\tag{5}
$$

The acidity of the hydride, in turn, is determined by the ligand/anion combination in the catalytic complex. We can now make it plausible that relatively basic phosphines – because they generate a larger electron density on Rh – will lead to less acidic Rh–hydride species and a low selectivity for hydroformylation. By combination with anions (X) of high electron affinity (such as non-coordinating tosylate anions) the electron density on Rh can be reduced, thus leading to a more acidic rhodium hydride and to a higher selectivity for formaldehyde hydroformylation.

When using more strongly electron-donating, coordinating anions, such as methoxyacetate and acetate, the required acidity of rhodium hydride can only be obtained by combination with strongly electron-accepting phosphines, such as tris(p-chlorophenyl)phosphine. It thus appears that fine tuning of the electrophilic properties of the cationic Rh centre in the catalyst species, brought about by a proper choice of their ligand and anion constituents, allows one to carefully control catalyst activity and selectivity.

In the next sections we will demonstrate the key role of electrophilicity of cationic Pd^{2+} in bringing forth a highly specific activation of a variety of substrates such as olefins, carbon monoxide and nitro compounds and thus in allowing them to react under very mild reaction conditions.

CARBONYLATION OF OLEFINS

Catalysts for the carbonylation of olefins:

$$R^= +\ CO\ +\ HOR'\ \longrightarrow\ R\text{--}C(O)\text{--}OR' \tag{6}$$
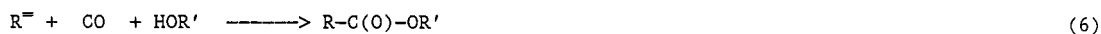
in which R'= H, alkyl, aryl or acetyl, can be generated by combining a cationic Pd^{2+} source, e.g. as a carboxylate, with a relatively large molar excess of monodentate phosphines (L) and a strong protonic acid (HX). It is believed that catalysts of the type "L_nPdX_2" are generated via:

$$Pd(OAc)_2\ +\ L\ +\ HX(excess)\ \longrightarrow\ \text{"}L_nPdX_2\text{"}\ +\ 2HOAc \tag{7}$$
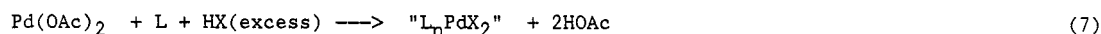
As an interesting application of reaction (6) we discuss the synthesis of <u>vinyl</u> <u>esters</u>, which can occur when HOR' is replaced by an enolizable ketone, e.g. acetone, as hydroxy reactant:

$$C_2^= +\ CO\ +\ CH_3\text{--}C(O)\text{--}CH_3\ \longrightarrow\ C_2\text{--}C(O)\text{--}O\text{--}C(CH_3)\!=\!CH_2 \tag{8}$$
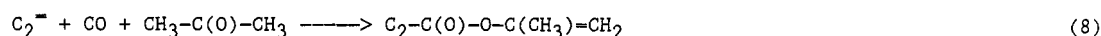
This reaction proceeds rapidly to its thermodynamic equilibrium (~ 30 % conversion of acetone) with a selectivity > 95 % (at 110 °C, $P_{CO} = P_{C_2^=} = 20$ bar), when catalysed by a Pd(OAc)$_2$/ triphenylphosphine/ p-toluenesulphonic acid (e.g. 1/30/20) catalyst. It demonstrates that the very low stationary enol concentration is sufficient and also that keto <—> enol interconversion is fast enough for the reaction to proceed effectively. Replacing the acid component by one containing more coordinating anions, e.g. phenylphosphonic acid, results in relatively slow reaction rates yielding, instead of the product of reaction (8), mainly vinyl ethyl ketone via:

$$2 \; C_2^= + \; CO \quad \text{————>} \quad CH_2=CH-C(O)-CH_2-CH_3 \tag{9}$$

The very nature of this product implies catalysis of reaction (9) by "XPd-H" species (cycle A in Figure 1), in contrast to catalysis by "XPd-carbo-alkoxy" species (cycle B in Figure 1), which we consider the most probable catalytic pathway for reaction (8).
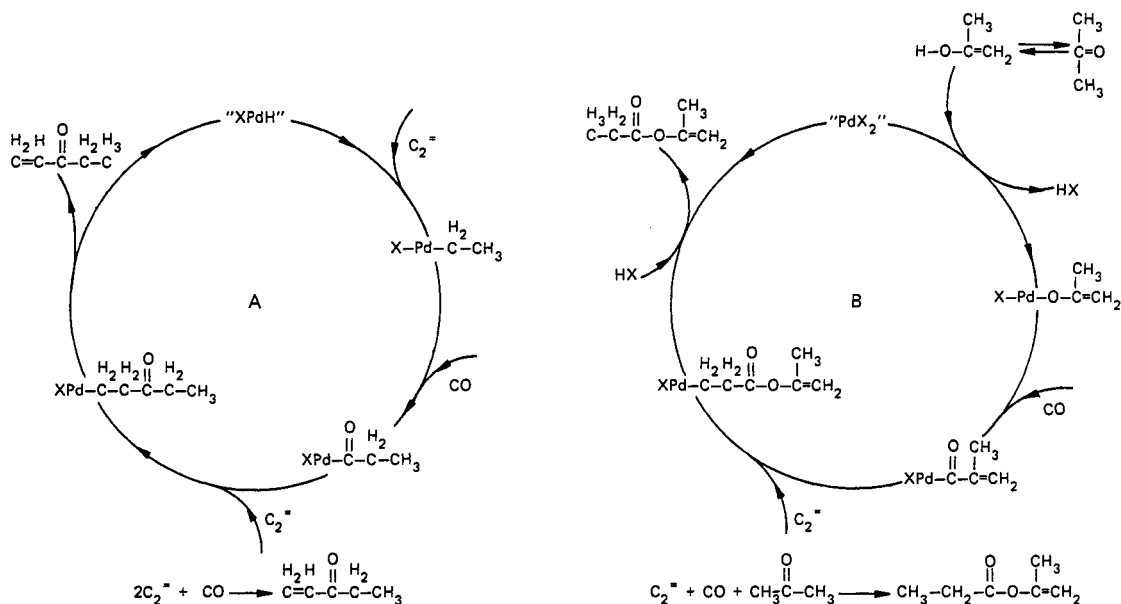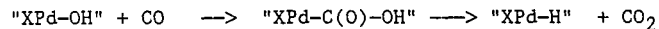

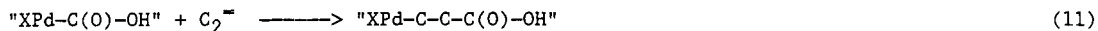FIG. 1: CATALYTIC OLEFIN–CARBONYLATION CYCLES
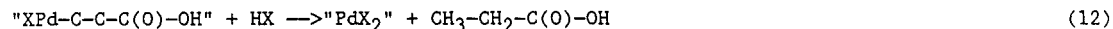
A: "Pd–H" CYCLE   B: "Pd–CARBO–ALKOXY" CYCLE

The generation of the initial "XPd-H" species most probably proceeds in situ by a partial water gas shift reaction:

$$\text{"PdX}_2\text{"} \; + \; H_2O \quad \text{————>} \quad \text{"XPd-OH"} + HX \tag{10}$$

$$\text{"XPd-OH"} + CO \quad \text{—>} \quad \text{"XPd-C(O)-OH"} \; \text{——>} \; \text{"XPd-H"} \; + CO_2$$

Apparently, generation of cationic "XPd-H" species is favoured when X is a more strongly coordinating anion. When X is a weakly coordinating anion, the intermediate "XPd-C(O)-OH" is sufficiently electrophilic to activate ethene and to force it rapidly to react:

$$\text{"XPd-C(O)-OH"} + C_2^= \quad \text{————>} \quad \text{"XPd-C-C-C(O)-OH"} \tag{11}$$

followed by:

$$\text{"XPd-C-C-C(O)-OH"} + HX \; \text{—>"PdX}_2\text{"} + CH_3-CH_2-C(O)-OH \tag{12}$$

Thus any trace of water is rapidly and catalytically converted to propionic acid, of which indeed traces are observed under these conditions.

HYDROFORMULATION OF OLEFINS

Having shown that cationic "XPd-H" species can play a role in the catalysis of reaction (10) we will now discuss our attempts to find catalysts of this type which are active in the

hydroformylation of olefins. We hypothesize that in this case "XPd-H" species could be generated by reaction with H_2 via:

$$\text{"PdX}_2\text{"} + H_2 \longrightarrow \text{"XPd-H"} + HX \tag{13}$$

and which, supposedly, can then take part in a hydroformylation catalytic cycle (ref. 2).

However, no active catalysts can be generated using a monophosphine in combination with a variety of anions ranging from coordinating to non-coordinating types. More satisfying results are obtained when the monosphosphine is replaced by chelating 2-4-carbon-atom-bridged diphosphines. For one particular example, bis(diphenylphosphino)propane, we demonstrate in Table 2 the peculiar effects brought about by the anion choice. Apparently, intermediately strong coordinating anions are required; in particular with trifluoroacetic acid as the anion source good results are obtained. Experiments 5 and 6 show that with these catalysts it is also possible to convert octenes containing internal olefinic bonds to linear aldehydes with a selectivity of ~ 67 %. It can thus be concluded that olefin isomerization takes place concurrently with hydroformylation and that hydroformylation of terminal olefinic bonds takes place at a rate that is 4 to 5 times faster than that of olefinic bonds located at internal positions.
To our knowledge these catalyst systems present the first examples of good activity Pd-based olefin hydroformylation catalysts.

TABLE 2. Hydroformulation of Octenes[a]

$$C_8^= + CO + H_2 \longrightarrow C_8 - C\overset{\displaystyle O}{\underset{\displaystyle H}{\diagdown}}$$
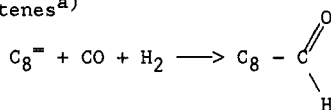
Exp. No.	Ligand (mmol)	Anion source (mmol)	Tempe-rature (°C)	Octene (ml)	Conversion rate[c] (mol olefin/ (mol Pd.h))	Sel. to alde-hyde[d] (%)	Linea-rity[e] of product (%)
1	$(Ph)_2P-(CH_2)_3P(Ph)_2$[b] 0.3	p-toluene-sulphonic acid (2)	125	octene-1 (20)	< 10	–	–
2	ditto	phenylphosphonic acid (1)	125	ditto	40	97	62.4
3	ditto	CF_3COOH (2)	125	ditto	120	97	74.6
4	ditto	ditto	140	ditto	300	92	66.7
5	ditto	ditto	125	internal octenes (20)	30 [f]	97	66.5
6	ditto	ditto	145	ditto	100	85 [g]	65.9

a) Catalyst precursor: 0.1 mmol $Pd(OAc)_2$, 50 ml diglyme as reaction solvent; CO/H_2 - 1; P - 60 bar

b) Ph - phenyl

c) conversion rate averaged over 5 h reaction time

d) selectivity to aldehydes = $\dfrac{\text{mol aldehydes}}{\text{mol aldehydes + mol alcohol + mol alkane}}$ x 100 %

e) linearity of product = $\dfrac{\text{mol n-aldehydes}}{\text{mol n-aldehydes + mol branched aldehydes}}$ x 100 %

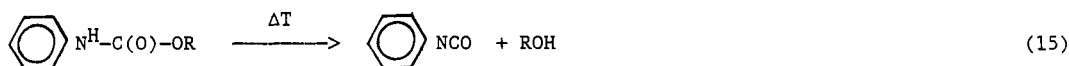f) diphenyl ether as reaction solvent

g) methyl benzoate as reaction solvent; 12 % alcohol, 3 % alkane selectivity

REDUCTIVE CARBONYLATION OF NITROAROMATIC COMPOUNDS

A potentially attractive route to isocyanates proceeds via the synthesis of carbamates:

$$\text{Ph–}NO_2 + 3\ CO + ROH \longrightarrow \text{Ph–}N^H\text{–C(O)–OR} + 2\ CO_2 \tag{14}$$
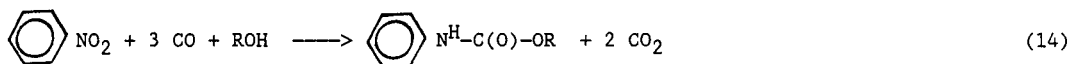
followed by pyrolysis of the carbamate:

$$\text{Ph–}N^H\text{–C(O)–OR} \xrightarrow{\ \Delta T\ } \text{Ph–}NCO + ROH \tag{15}$$

We will discuss some of our results obtained in the catalysis of reaction (14) by homoge-
neous cationic Pd catalysts, with ROH=CH_3OH.
Irrespective of the anion type used a low activity and selectivity are obtained, under the
desired mild reaction conditions, when monodentate ligands such as phosphines and pyridines
are used in the catalyst complex. However, the results summarized in Table 3 show that very
active and selective catalysts can be generated when chelating bidentate ligands are
employed.
The intimate interplay between the ligand and anion of the catalyst is again quite
remarkable. For optimal results it is required that biphosphines are combined with a weak
acid anion source, i.e. those containing coordinating anions; by far the best results are
obtained by combining bipyridyl-type ligands with strong acid anion sources i.e. those con-
taining weakly or non-coordinating anions. The anions can also be provided in the form of
their salts, e.g. as copper tosylate (experiment 7). In separate experiments we have also
demonstrated that pre-synthesized complexes e.g.
        Pd(1,10-phenanthroline)$_2$(tosylate)$_2$
as catalyst precursor, and in the presence of some excess of ligand, are as effective as the
three-component catalyst systems shown in Table 3. The delicately balanced electrophilicity
of the catalyst complex, required to effectively catalyse reaction (14), can apparently be
achieved in two ways: on the one hand, by applying "hard"-base electron-donating ligands,
such as phenanthroline, combined with anions having relatively strong electron affinity,
i.e. non-coordinating or weakly coordinating anions. On the other hand, similar electro-
philic properties can result by applying "soft"-base ligands, having the relatively strong
ability to accept d-electron density from Pd^{2+}, such as diphosphines, in combination with
anions having the possibility of covalent coordination (e.g. carboxylate anions) to Pd^{2+} as
a means to adjust its electrophilicity. Of course, these considerations can remain only
qualitative as long as many details about the mechanism are unknown.
The electrophilicity of intermediate complexes will be determined not only by ligand and
anion but also by the reactants which take part in intermediate complexes of the catalytic
cycle. In searching for these effects we found an interesting application when methanol in
reaction (14) was replaced by an aromatic amide:
  A   Pd(OAc)$_2$/2,2'-bipyridyl/Cu(tosylate)$_2$ catalyst
allows the very efficient synthesis of acylureas, e.g.:

$$\text{Ph–}NO_2 + 3CO + H_2N\text{–C(O)–Ph} \longrightarrow \text{Ph–}N^H\text{–C(O)–}N^H\text{–C(O)–Ph} + 2CO_2 \tag{16}$$
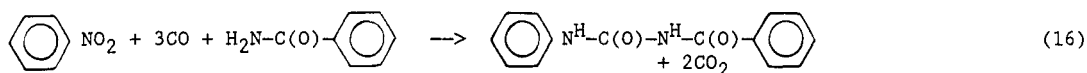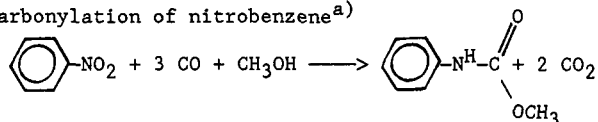
Acylurea yields of 90 % (both on nitro compound and on amide) can be obtained under mild
reaction conditions similar to those applied for reaction (14).

In the chemistry discussed so far, carbon monoxide is essential as reactant (and is there-
fore also present as catalyst ligand); in what follows, we will show an example of the use
of cationic metal catalysts in olefin activation in the absence of carbon monoxide.

DIMERIZATION OF OLEFINS

Some of the active carbonylation catalysts of the type discussed above appear to turn into
active olefin dimerization catalysts when applied to olefin substrates in the absence of
carbon monoxide.

Some typical experimental results are summarized in Table 4. Examples 1 and 2 show the use
of monodentate phosphine-based, three-component (L+Pd(OAc)$_2$+HX) catalysts; the effect of the
anion, weakly coordinating tosylate vs strongly coordinating chloride, on the dimerization
rate is noteworthy. A much higher ethene dimerization activity is displayed by catalysts
containing chelating diphosphines, i.e. both by those generated in situ from the three

TABLE 3.   Reductive carbonylation of nitrobenzene[a]

$$\text{C}_6\text{H}_5-\text{NO}_2 + 3\ \text{CO} + \text{CH}_3\text{OH} \longrightarrow \text{C}_6\text{H}_5-\text{N}^H-\overset{O}{\underset{OCH_3}{C}} + 2\ \text{CO}_2$$

Exp. No.	Ligand (mmol)	Anion source[b] (mmol)	Reaction rate[c] (mol nitrobenzene/ (mol Pd.h))	Selectivity[d] (%)
1	$(Ph)_2P-(CH_2)_3P(Ph)_2$ 1.5	TBA (16)	500	95
2	ditto	p-toluene-sulphonic acid (1)	100	60
3	ditto	HCl (1)	150	80
4	1,10-phenanthroline (1.5)	TBA (16)	700	90
5	ditto	p-toluene-sulphonic acid (1)	> 1600[e]	96
6	ditto	phenylphosphonic acid (1)	1000	95
7	ditto	Cu(tosylate)$_2$ (0.5)	> 1600[e]	98

a) Catalyst precursor: 0.033 mmol Pd(OAc)$_2$; 7.5 ml nitrobenzene in 50 ml methanol; T = 135 °C, P = .60 bar

b) TBA = 2,4,6 trimethylbenzoic acid

c) Reaction rate averaged over 1-5 reaction period

d) Selectivity based on nitrobenzene; main by-products: azo- and azoxybenzene

e) conversion of nitrobenzene = 100 %

components, Pd(OAc)$_2$, diphosphine and acid, and by pre-synthesized neutral complexes (experiments 3 and 4). The latter observation is in strong contrast to results obtained with neutral complexes based on monophosphines, e.g. (P(Ph)$_3$)$_2$Pd(tosylate)$_2$, which, in the presence of olefins and alcohols or water, decompose via a Wacker-type reduction to Pd metal and do not display any significant dimerization activity in protic solvents. In aprotic solvents, however, only a mediocre activity is observed, similar to that of analogous complexes reported by Sen et al. (ref. 3).

Protic solvents, such as alcohols or even water, are essential to efficient dimerization catalysis by cationic Pd complexes. We take this as an indication that anion-cation separation in the catalyst complex is a prerequisite for the underlying catalysis and thus underlines the importance of non-coordinating or weakly coordinating anions.

Although the diphosphine-based catalysts display a high activity for ethene dimerization they are hardly capable of catalysing propene dimerization (experiment 5). A solution to this problem is to choose bipyridyl-type ligands: experiments 6-8 show, for example, that 1,10-phenanthroline-based catalysts - the ones that proved so effective in the reductive carbonylation of nitro compounds (Table 3) - whether those generated in situ or the pre-
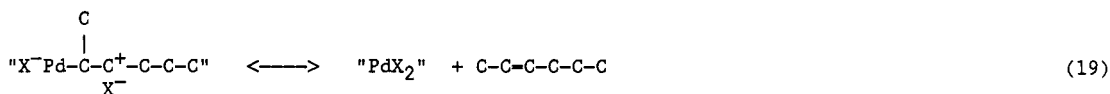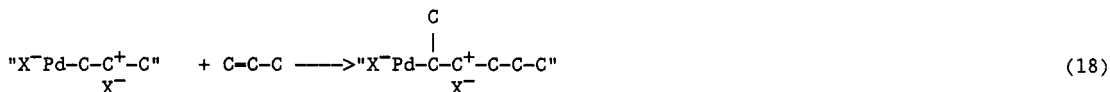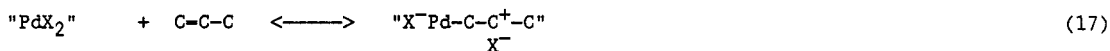
TABLE 4. Dimerisation of olefins[a]

$$C_n^= \longrightarrow C_{2n}^=$$
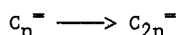
Exp. No.	Ligand (mmol)	Anion source (mmol)	Olefin	Temperature ($^\circ$C)	Conv. rate (mol/ (mol Pd.h))	Selectivity to dimer (%)
1	P(Ph)$_3$ (3)	p-toluenesulphonic acid (2)	C$_2^=$ (40 bar)	95	200	98 (C$_4^=$)
2	ditto	Hydrochloric acid (2)	ditto	95	30	98 (C$_4^=$)
3	Ph$_2$P-(CH$_2$)$_3$P(Ph)$_2$ (0.15)	p-toluenesulphonic acid (2)	ditto	95	6000	98 (C$_4^=$)
4	0.1 Pd(Ph$_2$P-(CH$_2$)$_3$PPh$_2$)(tosylate)$_2$ [b]		ditto	95	6000	98 (C$_4^=$)
5	ditto		C$_3^=$ (40 ml)	95	< 30	–
6	1,10-phenanthroline (0.2)	ditto (1)	C$_2^=$ (40 bar)	90	7500	93 (C$_4^=$) 7 (C$_6^=$)
7	0.5 Pd(1,10-phenanthroline)$_2$(tosylate)$_2$ [b]		C$_2^=$ (40 bar)	70	7000	90 (C$_4^=$) 6 (C$_6^=$) 3 (C$_8^=$)
8	ditto		C$_3^=$ (50 ml)	75	1250	94 (C$_6^=$) (linearity 60%!) 6 (C$_9^=$)

a) Catalyst precursor: 0.1 mmol Pd(OAc)$_2$, reaction solvent 50 ml methanol
b) Complexes synthesized by adding phosphine ligand in 1:1 ratio, or, 1,10-phenanthroline
   ligand in 2:1 ratio to Pd(tosylate)$_2$ in methanol as solvent at room temperature;
   complexes isolated by cold filtration.

synthesized neutral complexes, have a high activity not only for ethene but also for propene
dimerization (oligomerization). Of the propene dimers and trimers, 60 and 25 %, respective-
ly, are linear.

The following catalytic cycle for olefin dimerization by cationic "PdX$_2$" complexes can be
envisaged:

$$\text{"PdX}_2\text{"} \quad + \quad \text{C=C-C} \quad \longleftrightarrow \quad \text{"X}^-\text{Pd-C-C}^+\text{-C"} \qquad\qquad (17)$$
$$\text{X}^-$$

$$\text{"X}^-\text{Pd-C-C}^+\text{-C"} \quad + \text{ C=C-C } \longrightarrow \text{"X}^-\text{Pd-}\overset{\overset{\textstyle C}{|}}{C}\text{-C}^+\text{-C-C-C"} \qquad\qquad (18)$$
$$\text{X}^- \qquad\qquad\qquad\qquad\qquad \text{X}^-$$

$$\text{"X}^-\text{Pd-}\overset{\overset{\textstyle C}{|}}{C}\text{-C}^+\text{-C-C-C"} \quad \longleftrightarrow \quad \text{"PdX}_2\text{"} \quad + \text{ C-C=C-C-C-C} \qquad\qquad (19)$$
$$\text{X}^-$$

Such a proposed mechanism does not invoke the intermediacy of Pd-hydrido species (in a con-
ventional Ziegler-type catalytic cycle), but emphasizes the electrophilic properties of the
catalyst complex.

Whatever the mechanism, the results once again demonstrate the versatility of cationic L_nPdX_2 complexes in catalysing a variety of reactions between a variety of substrates, with their key property, electrophilicity, being governed and tunable by the choice of ligand and anion constituents.

CONCLUDING REMARKS

We have given an impression of our exploratory journey through part of homogeneous cata-
lysis. The emphasis has been placed on the phenomenology of the discovery of catalyst
systems for a variety of reactions, rather than on mechanistic considerations and explana-
tions. The experimental results lead to the construction of working hypotheses which are
then used as direction indicators for the next experiments. The results of these experiments
lead to elimination or reconstruction of hypotheses from which new experiments follow, etc.
Of course, hypotheses do not necessarily represent the physical truth nor does their vali-
dity require a full proof in advance; we simply use them as long as the results fit with
expectations based upon them. It is our experience that those hypotheses which in hindsight
proved to be false have been extremely valuable in directing the research to areas of origi-
nally unforeseen opportunities; having a wrong hypothesis is by far better than having no
hypothesis at all!
The leading hypothesis which has directed the underlying research concerns the tuning of the
electrophilicity of cationic transition metal complexes used as homogeneous catalysts for a
variety of reactions. It has been amply demonstrated that the choice of both the ligand and
anion constituents in these catalysts is crucial to their (re)activity and the selectivity
of reactions they catalyse.

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