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Efficient palladium catalysts for the copolymerization of carbon monoxide with olefins to produce perfectly alternating polyketones *

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Abstract

A class of highly efficient homogeneous palladium catalyst systems has been developed for the production of perfectly alternating copolymers of carbon monoxide with ethylene. Mixtures of carbon monoxide, ethylene and propene are converted into the corresponding alternating carbon monoxide/olefin terpolymers in which C_3 units randomly replace ethylene units along the chain. The essential features of the new catalyst systems are that they are formed by the combination of an equimolar quantity of a suitable bidentate phosphine ligand with a palladium(II) species in which the counter anions are weakly coordinating. For a series of diphenylphosphinoalkanes of general formula $Ph_2P(CH_2)_mPPh_2$ the most efficient catalyst system for the production of high-molecular-weight polyketones is that with $m = 3$. High rates with conversions of more than one million molecules of carbon monoxide and ethylene per palladium center are obtained. In methanol, the majority of the copolymer chains produced are polyketo-esters of general formula $H(CH_2CH_2CO)_nOMe$; analyses of methanol-soluble oligomer fractions shows that diesters $MeOCO(CH_2CH_2CO)_nOMe$ and diketones $H(CH_2CH_2CO)_nCH_2CH_3$ are also formed. Two interlinked catalytic cycles are invoked to account for the formation of polyketones with keto-ester, diester and diketone end groups.

Introduction

The discovery by Reppe [1] in the late 1940s of a nickel-catalyzed copolymerization of carbon monoxide with ethylene to give alternating copolymers generated considerable interest in both industrial and academic circles. Attention was focused on these high-melting (so-called) polyketones because of both the low cost of carbon monoxide feedstock, which accounts for half of the weight of the copolymer, and their potential use as starting materials for the preparation of other types of functionalized polymers.

Up to now, however, the potential of these alternating polyketones has not been explored. A major reason for this is simply that there is no commercial process for

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* Dedicated to the memory of Professor Piero Pino.

their production. Considerable efforts have been directed towards development of such a process [2], including free-radical initiated [3] and gamma-ray induced [4] copolymerization, both of which gave mainly random copolymers which were low-melting; only under extreme pressures was material approaching 50% weight carbon monoxide produced.

Developments in transition-metal chemistry have led to discoveries of new catalyst systems which are capable of producing high-molecular-weight perfectly alternating polyketones. However, until now, none of these has satisfied the economic requirements for use in an industrial process. Such catalysts, all derived from Group VIII transition-metal complexes, have been reported by both industrial and academic research groups. Catalysts based on cobalt [5] and rhodium [6] showed some activity for the formation of low-molecular-weight cooligomers. Only nickel [7] and palladium [8] catalysts gave the required high-molecular-weight copolymer. The activities and yields of these catalyst systems were, however, far too low for economic commercial production.

We now report on a class of very efficient palladium catalyst systems for the production of perfectly alternating copolymers of carbon monoxide and olefins [9], which provides for the first time ready access to these polymers.

Results

Our interest in the copolymerization of carbon monoxide with olefins originated from a general investigation into carbonylation reactions catalyzed by homogeneous transition-metal compounds. One reaction studied was the hydrocarboalkoxylation of ethylene to give methyl propionate (eq. 1).

$$H_2C{=}CH_2 + CO + MeOH \rightarrow CH_3CH_2COOMe \qquad (1)$$

The catalysts initially tested were palladium systems formed by the combination of palladium acetate with an excess of triphenylphosphine (TPP) and a Brønsted acid. In methanol solution, with hydrogen chloride as the acid component, the reaction proceeded under mild conditions at a moderate rate to give methyl propionate with high selectivity (> 98%). Replacement of hydrogen chloride by *p*-toluenesulfonic acid resulted in a considerable rate enhancement without loss of selectivity (Table 1). With stoichiometric quantities of TPP and/or acid the activity was negligible.

A surprising and remarkable change in selectivity was observed upon replacement of the excess of triphenylphosphine by an equimolar quantity of the bidentate ligand 1,3-bis(diphenylphosphino)propane (DPPPr). Under the same reaction conditions use of the catalysts containing the latter ligand led to production of a perfectly alternating copolymer of ethylene with carbon monoxide with essentially 100% selectivity (eq. 2).

$$n\ H_2C{=}CH_2 + n\ CO + MeOH \rightarrow \underset{(I)}{H(CH_2CH_2CO)_nOMe} \qquad (2)$$

With hydrogen chloride as the acid component the activity for copolymer formation was only moderate. However, as with the methyl propionate reaction, the rate was greatly enhanced when *p*-toluenesulfonic acid was used; under the mild reaction conditions specified in Table 1, the rate was increased by more than two

Table 1

Palladium-catalyzed reactions of carbon monoxide with ethylene and methanol [a]

Ligand added [b]		Acid or salt added		Conditions		Selectivity [c] $H(CH_2CH_2CO)_nOCH_3$		Reaction rate [d] (g/g Pd.h)
Type	(mmol)	Type	(mmol)	Temp. (°C)	Press. (MPa)	($\bar{n}$)	(%)	
TPP	3.0	none	–	115	4.5	–	–	–
TPP	3.0	HCl	2.0	115	4.5	1	98.0	80
TPP	3.0	HO_3STol	2.0	115	4.5	1	98.0	5000
TPP	0.2	HO_3STol	0.2	115	4.5	–	–	–
DPPPr	0.15	HCl	2.0	115	4.5	50	99.9	30
DPPPr	0.15	HO_3STol	2.0	115	4.5	50	99.9	5000
DPPPr	0.10	HO_3SCF_3	0.20	90	4.0	150	99.9	6900
DPPPr	0.10	HO_3STol	0.20	90	4.0	150	99.9	6200
DPPPr	0.10	HBF_4	0.20	90	4.0	115	99.9	5000
DPPPr	0.10	$HOOCCH_3$	10.0	90	4.0	–	–	–
DPPPr	0.10	$HOOCCl_3$	0.20	90	4.0	>100	99.9	300
DPPPr	0.10	$HOOCCF_3$	0.20	90	4.0	200	99.9	6000
DPPPr [e]	0.012	HO_3STol	0.02	65	4.5	400 [f]	99.9	3200
DPPPr [e]	0.012	$Cu(O_3STol)_2$	0.02	65	4.5	700 [f]	99.9	4500

[a] Reaction carried out in 50 ml MeOH with $Pd(OAc)_2$ (0.1 mmol, except [e]); $C_2H_4/CO = 1$; at 115 °C the pressure was allowed to decrease in batch mode; at 90 and 65 °C the pressure was maintained by feeding a 1:1 mixture of carbon monoxide and ethylene (see Experimental). [b] TPP is triphenylphosphine; DPPPr is 1,3-bis(diphenylphosphino)propane. [c] The averaged degree of polymerization ($\bar{n}$) determined by end-group analysis from ^{13}C NMR spectra, except [f], where end groups were not visible; for $\bar{n} = 1$ the product is methyl propionate. [d] Reaction time was between 1 and 5 h; the rate is the average measured during the reaction period. [e] Reaction carried out in 200 ml MeOH with $Pd(OAc)_2$ (0.01 mmol). [f] Estimated from measurement of the limiting viscosity number (LVN).

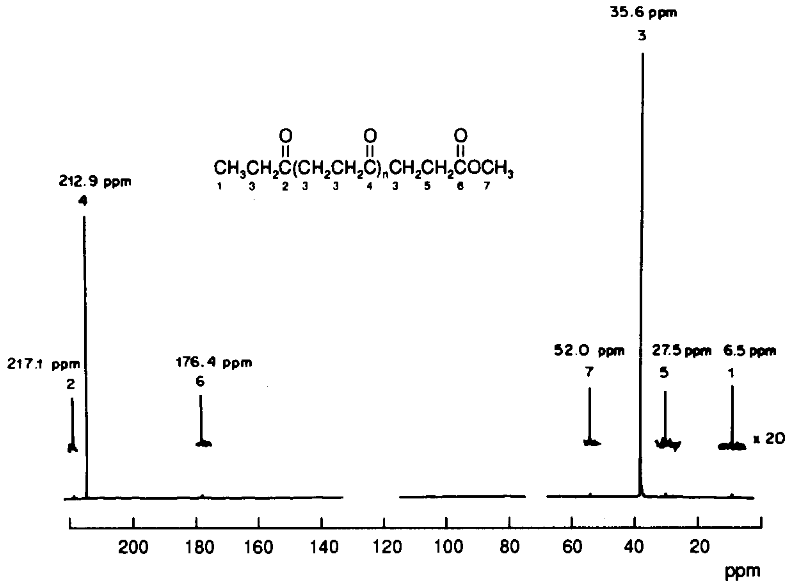


Fig. 1. Typical ^{13}C NMR spectrum of a perfectly alternating copolymer of carbon monoxide and ethylene dissolved in a mixture of hexafluoroisopropanol (90%) and deuterobenzene (10%); end-group regions are magnified by a factor of 20. Signals are relative to tetramethylsilane. Resonances due to solvent are not shown.

orders of magnitude. Significantly, only a stoichiometric quantity of the acid was required; an excess did not cause a further significant increase in rate. Other acids which gave comparably high reaction rates were tetrafluoroboric acid, trifluoromethylsulfonic acid, and trifluoroacetic acid. With trichloroacetic acid, however, the rate enhancement was less pronounced, and with acetic acid negligible activity was observed. Also noteworthy is the observation that replacement of *p*-toluenesulfonic acid by its copper salt resulted in a further increase in both the reaction rate and the molecular weight of the copolymer produced (Table 1).

The copolymer, which is insoluble in methanol, separated during the reaction as a snow-white high-melting powder (257 ° C). It was characterized by the normal analytical techniques. The ^{13}C NMR spectrum of a solution of this copolymer in hexafluoroisopropyl alcohol is shown in Fig. 1. The resonances at 212.9 and 35.6 ppm are assigned to the backbone carbonyl and methylene carbons respectively. The end-group carbon resonances are also visible; those at 217.1 and 176.4 ppm are assigned to the carbonyl group carbon of the ketonic and ester end-groups, respectively, and those at 6.5 and 52.0 ppm to the corresponding methyl-group carbons. The methylene carbon which is alpha to the ester end group resonates at 27.5 ppm; the resonance of the methylene carbon of the ethyl end group is not visible, and is assumed to coincide with that of the backbone methylenes at 35.6 ppm.

These catalyst systems were also found to be efficient for the terpolymerization of carbon monoxide with ethylene in combination with other olefins. For example, in methanol with propene as the additional olefin an alternating carbon monoxide/olefin terpolymer is produced in which C_3 units randomly replace ethylene units along the chain according to the general formula: R[(CO)Z]$_n$COOMe where Z represents the structures: {$-CH_2CH_2-$}; {$-CH_2CH(CH_3)-$}; {$-CH(CH_3)CH_2-$}; {$-CH_2CH_2CH_2-$}. The alkyl end group R can be either an ethyl, n-propyl, or isopropyl group. The terpolymer is also a high-melting white powder; however, the melting point is lower than that of the ethylene/carbon monoxide copolymer (257 ° C). The lowering of the melting point is directly proportional to the number of C_3 groups built into the polymer chain. For example, at 6 and 17 wt % propene incorporation the melting points of the terpolymers are around 220 and 170 ° C, respectively.

The propene is predominantly incorporated in the chain in the 1,2- or 2,1-mode. A small fraction is incorporated in the 1,3 mode; this was deduced from the solution ^{13}C NMR spectrum of a terpolymer containing around 20% C_3 units in which {$-C_3COC_3CO-$} diads were observed. In addition to the signals found for the pure copolymer, there are resonances at 45.1, 41.5 and 15.5 ppm, which are assigned to the methylene, methyne and methyl carbon atoms of the incorporated C_3 group, respectively. Also visible, at 34.4 ppm, is the resonance for the methylene carbon atom of the C_2 group adjacent to the carbonyl carbon bonded to the methyne. The latter carbonyl carbon resonance is not visible and is assumed to coincide with that of the end-group ethyl ketonic carbonyl carbon at 217.1 ppm. In addition to being incorporated into the polymer chain, propene also forms propyl ketonic end groups; the resonances at 13.0 and 17.3 ppm, are assigned to the methyl and adjacent methylene carbon atoms of the n-propyl group, respectively. The resonance of the methylene carbon adjacent to the end-group carbonyl atom coincides with that of the corresponding methylene carbon atom of the ethyl ketonic end group.

A series of catalyst systems examined for this terpolymerization reaction is given in Table 2. With the acid-promoted catalyst systems it was generally observed that

Table 2

Palladium-catalyzed reactions of carbon monoxide with ethylene, propylene and methanol: the effect of added copper tosylate and benzoquinone [a]

Acid or salt added		Benzoquinone added (mmol)	Propylene [b] concentration (wt%)	Melting [c] point (° C)	LVN [d] (dl/g)	Reaction rate [e] (g/g Pd.h)
Type	(mmol)					
HO_3STol	0.02	0.0	0.0	257	1.4	3200
$Cu(O_3STol)_2$	0.02	0.0	0.0	257	2.2	4500
$HOOCCF_3$	0.20	0.0	12.5	220	0.7	1000
$Cu(O_3STol)_2$	0.02	0.0	12.5	220	2.6	1500
$HOOCCF_3$	0.20	0.0	15.0	220	0.7	1000
$HOOCCF_3$	0.20	1.0	15.0	220	0.7	2000
$Cu(O_3STol)_2$	0.02	0.0	15.0	220	1.3	2000
$Cu(O_3Stol)_2$	0.02	0.3	15.0	225	1.4	4000

[a] Reaction carried out in 125 ml MeOH with $Pd(OAc)_2$ (0.010 mmol), 1,3-bis(diphenylphosphino)propane (DPPPr, 0.012 mmol) at a temperature of 65 ° C, and at a pressure of 4.5 MPa maintained in continuous mode; $C_2H_4/CO = 1$ (see Experimental). [b] Initial concentration; propylene consumed during the reaction was not replenished. [c] The melting point of pure copolymer is 257 ° C; a melting point of 220 ° C is that of a terpolymer with around 6 wt% of propene built into the polymer chains; this correlation was determined by analysis of ^{13}C NMR spectra. [d] LVN is the limiting viscosity number and its value increases with increasing average molecular weight of the copolymer. [e] Reaction time was between 1 and 5 h; the rate was the average measured during the reaction period.

under similar conditions both the production rate and the molecular weight of the terpolymers produced were lower than those observed for copolymers. This difference was, however, significantly less pronounced when copper *p*-toluenesulfonate was used instead of the corresponding acid. Furthermore, the rate of terpolymerization was approximately doubled by the addition of an excess (based on palladium) of benzoquinone. These effects were additive, with the result that terpolymers with molecular weights comparable to those of copolymers were produced under similar conditions.

With the above reported catalyst systems high activities were observed only when the added acid or copper promoter contained an anion which showed weak coordinating ability towards the palladium metal center. It was therefore suggested, that an important function of the promoter was to replace the strongly coordinated acetate groups on palladium with weaker coordinating anions. This suggestion was supported by two observations: first, that treatment of diacetatopalladium(II) with, for example, *p*-toluenesulfonic acid or trifluorosulfonic acid in acetonitrile resulted in quantitative displacement of the acetate groups to give respectively neutral or cationic complexes $[Pd(MeCN)_2(O_3STol)_2]$ or $[Pd(MeCN)_4](O_3SCF_3)_2$, and second that these complexes when isolated and combined with the ligand DPPPr, without addition of acid, gave catalyst systems of similar activity for copolymer formation to those formed *in situ* by the combination of diacetatopalladium(II), ligand DPPPr and the appropriate acid.

The dramatic difference in product selectivity between catalyst systems formed with the monodentate ligand TPP, which gave predominantly methyl propionate, and those formed with the bidentate ligand DPPPr, which gave exclusively high-molecular-weight polyketone, prompted a study of the effect of a subtle variation in the nature of the bidentate ligand. The variation studied was in the number of carbon atoms separating the diphenylphosphino groups in bidentate ligands of general formula $Ph_2P(CH_2)_mPPh_2$, for $m = 1$–6. The six catalyst systems studied were prepared in the same manner by mixing equimolar quantities of ligand with

Table 3

Palladium-catalyzed reactions of carbon monoxide with ethylene and methanol: the effect of variation of the chain length between bidentate phosphine groups [a]

Ligand added $Ph_2P(CH_2)_mPPh_2$ Formula	Abbreviation	Product [b] $H(CH_2CH_2CO)_nOCH_3$ ($\bar{n}$)	Reaction rate [c] (g/g Pd.h)
$Ph_2P(CH_2)PPh_2$	(DPPMe)	2	1
$Ph_2P(CH_2)_2PPh_2$	(DPPEt)	100	1000
$Ph_2P(CH_2)_3PPh_2$	(DPPPr)	180	6000
$Ph_2P(CH_2)_4PPh_2$	(DPPBu)	45	2300
$Ph_2P(CH_2)_5PPh_2$	(DPPPe)	6	1800
$Ph_2P(CH_2)_6PPh_2$	(DPPHe)	2	5

[a] Reaction carried out in 150 ml MeOH with $Pd(MeCN)_2(O_3STol)_2$ (0.1 mmol), and $Ph_2P(CH_2)_mPPh_2$ (0.1 mmol); $C_2H_4/CO = 1$; the temperature was maintained at 84° C; the pressure was maintained at 4.5 MPa in continuous mode (see Experimental). [b] The averaged degree of polymerization ($\bar{n}$) determined by end-group analysis from ^{13}C NMR spectra, except for the low molecular weight products, where a combination of GC and NMR was used. [c] Reaction time was between 1 and 5 h; the rate was the highest measured during the reaction period.

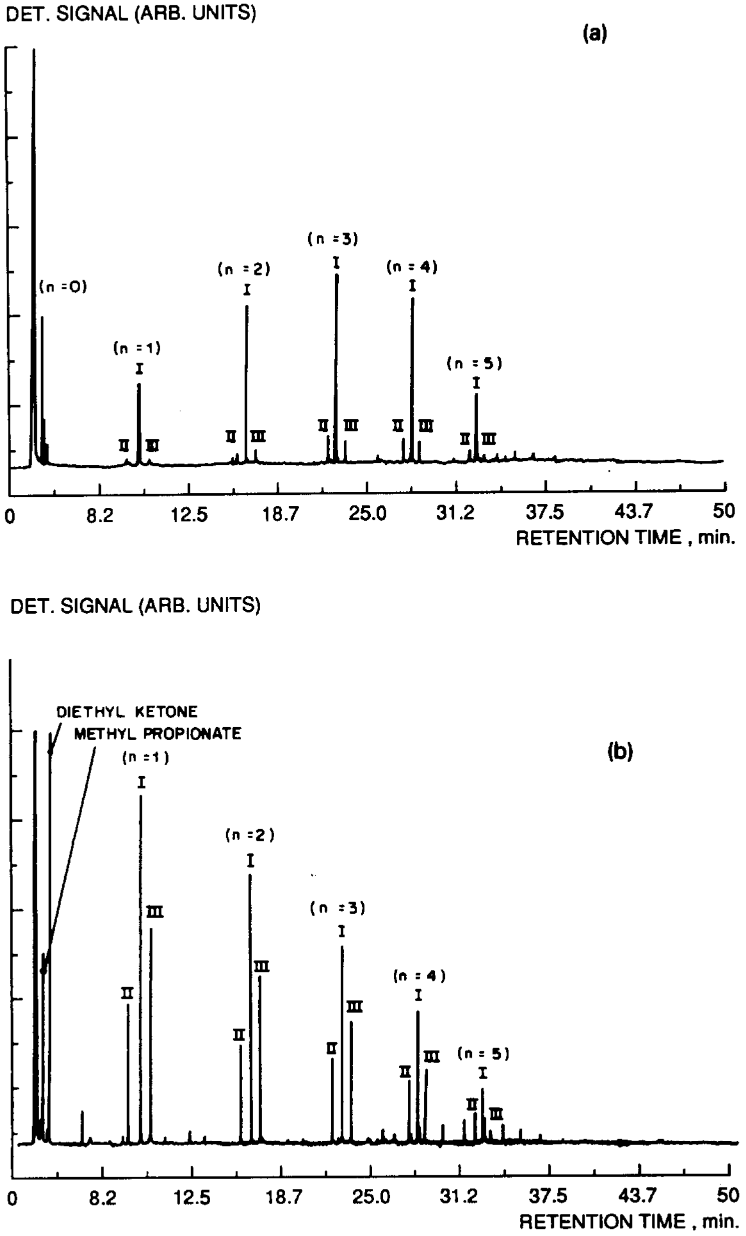


Fig. 2. Gas chromatograms of low-molecular-weight co-oligomers of carbon monoxide and ethylene catalyzed by an equimolar mixture of $[Pd(MeCN)_2(O_3STol)_2]$ and DPPBu in methanol solution: (a) at 85 °C and 4.5 MPa; (b) at 120 °C and 4.5 MPa. From mass spectroscopy: (I) $CH_3CH_2(COCH_2CH_2)_n COOMe$; (II) $MeO(COCH_2CH_2)_n COOMe$; (III) $CH_3CH_2(COCH_2CH_2)_n COCH_2CH_3$. Small signals between triplets are due to oligomers containing furan defect structures.

$[Pd(MeCN)_2(O_3STol)_2]$ in methanol solution. These catalysts were tested for the reaction between carbon monoxide, ethylene and methanol. The results are shown in Table 3.

It can be seen that a variation in ligand resulted in significant changes in both reaction rate and the molecular weight of the copolymer produced. Thus, the rate was negligible for DPPMe ($m = 1$), and increased rapidly for DPPEt ($m = 2$) to reach a maximum for DPPPr ($m = 3$). A further increase in chain length led to a progressive decrease in the rate from DPPBu ($m = 4$), to DPPPe ($m = 5$) down to DPPHe ($m = 6$), for which negligible activity was again observed. The molecular weight of the copolymer produced showed a similar variation: it decreased significantly in the order DPPPr > DPPEt > DPPBu > DPPPe. Indeed, for DPPPe approximately 90% of the product was methanol-soluble co-oligomer.

Gas-chromatographic and mass-spectroscopic analysis of oligomer fractions formed in the above reactions showed, intriguingly, that not only were keto-ester molecules of the general formula I formed, as indicated by the above-described ^{13}C NMR analysis of copolymers, but also diester and diketones of general formulae II and III.

$$CH_3CH_2(COCH_2CH_2)_nCOOMe \quad (I,\ n \geqslant 0)$$

$$MeO(COCH_2CH_2)_nCOOMe \quad (II,\ n \geqslant 1)$$

$$CH_3CH_2(COCH_2CH_2)_nCOCH_2CH_3 \quad (III,\ n \geqslant 0)$$

Gas chromatograms of oligomer fractions for $n = 0$–5 are shown in Fig. 2. The oligomers were produced with the catalyst formed from an equimolar mixture of $[Pd(MeCN)_2(O_3STol)_2]$ and the ligand DPPBu. Comparison between product distributions obtained at 85 °C (Fig. 2a) and 125 °C (Fig. 2b) shows that at the lower temperature the major products were the keto-esters (I), which were formed with > 95% selectivity. Higher temperatures tended to favor the production not only of low-molecular-weight material but also of symmetrical diesters and diketones; at 125 °C the selectivity for the latter molecules was approximately 50%.

From these results it seems plausible that the high-molecular-weight copolymer described above also contains chains with diester and diketo end groups; the ^{13}C NMR end-group analysis cannot, of course, distinguish between chains I, II and III when n is large. However, as the copolymerizations were generally carried out at moderate temperatures it is assumed that the major component of the copolymer is the keto-ester (I), as shown in eq. 2.

Copolymers with predominantly diketone or diester end-groups can, however, be produced. Diketone selectivity was increased by, for example, carrying out the copolymerization under a hydrogen partial pressure; in aprotic solvents the diketone III was formed exclusively. Diester yields of up to 85% were obtained by conducting the reaction in the presence of a large excess (based on palladium) of benzoquinone dissolved in the methanol solution. This is a stoichiometric reaction (based on end groups) and hydroquinone was subsequently formed.

A general and attractive feature of the above-described catalyst systems is that they can show high activities. Moreover, under suitable conditions, catalyst decay can be minimized to such an extent that conversions well in excess of one million catalytic cycles can be obtained.

Discussion

The above results indicate that the more efficient palladium(II) catalyst systems for the copolymerization of carbon monoxide with olefins have two prominent characteristics in common. These are, (i) that the neutral ligand is capable of suitable bidentate coordination, and (ii) that the anionic ligands are so-called weakly coordinating, and can be easily displaced from the coordination sphere by an incoming nucleophile to give an electrophilic cationic palladium center.

Effect of anionic ligands

The formation of a more electrophilic palladium center with the weakly coordinating anions was indicated by ^{31}P NMR spectroscopic monitoring of the stages in the preparation of the acid-promoted catalyst systems. For example, addition of two mole equivalents of *p*-toluenesulfonic acid to an equimolar mixture of diacetatopalladium(II) and DPPPr in acetone solution resulted in a down-field shift of the phosphorus signal from 11.1 to 17.5 ppm (relative to H_3PO_4). This deshielding of the phosphorus atoms can be attributed to the donation of electron density from the DPPPr phosphorus atoms to a more electrophilic palladium center which is produced upon replacement of acetate anions by *p*-toluenesulfonate anions (eq. 3):

$$[(\mathrm{DPPPr})\mathrm{Pd}(\mathrm{OAc})_2] + 2\ \mathrm{HO_3STol} \rightarrow [(\mathrm{DPPPr})\mathrm{Pd}(\mathrm{O_3STol})_2] + 2\ \mathrm{HOAc} \qquad (3)$$

Vacant coordination sites at which the catalytic transformations occur are then considered to be formed under the reaction conditions by nucleophilic substitution of the anions for monomer or solvent molecules, i.e. for complete nucleophilic substitution (eq. 4):

$$[(\mathrm{DPPPr})\mathrm{Pd}(\mathrm{O_3STol})_2] + 2(\mathrm{Nuc}) \rightarrow [(\mathrm{DPPPr})\mathrm{Pd}(\mathrm{Nuc})_2]^{2+} + 2(\mathrm{O_3STol})^- \qquad (4)$$

The higher reactivity of catalyst systems formed with such anions is thought to stem, at least in part, from the easier access of the substrate molecules methanol, olefin, and carbon monoxide to coordination sites on the metal center. Another contributing factor may be that with a lower electron density on the palladium center, the binding energies of the palladium with the comonomers may be lower because of less back-donation from metal to ligand. The intermediate palladium species which are involved in the catalytic cycles would therefore be less stable, with the result that transformations between them would require relatively lower activation energies and so proceed at a higher rate.

Effect of neutral ligands

As described above, ligand variation in the palladium-catalyzed reactions between carbon monoxide, ethylene, and methanol can lead to large changes in the products formed. The majority of these products are, however, although physically different, structurally closely related. For example, low-boiling methyl propionate is related to high-melting copolymer through the general formula $H(CH_2CH_2CO)_n$ OMe, where for methyl propionate $n = 1$. Methyl propionate can be viewed, therefore, as the first member of a series of linear alternating polyketo-ester molecules.

Although we have not carried out detailed mechanistic studies on the relationship between ligand characteristics and product distributions, we consider it worthwhile to comment on the large difference between the characteristics imparted to the catalysts by the monodentate and the bidentate phosphine.

The two catalyst systems compared are *p*-toluenesulfonic acid-promoted systems formed either with an excess of monodentate TPP or with an equimolar quantity of bidentate DPPPr. The former catalyst system gives mainly methyl propionate; whereas the latter produces high-molecular-weight polyketone (experiments at 115 °C in Table 1).

We suggest that the initiation steps in both catalyst systems are the same, namely reaction of the palladium complex with methanol to give a palladium methoxy species, followed by nucleophilic attack by carbon monoxide and subsequent displacement of the anionic ligand (eqs. 5 and 6):

$$[L_2PdX_2] + MeOH \rightarrow [L_2PdOMeX] + HX \qquad (5)$$

$$[L_2PdOMeX] + CO \rightarrow [L_2Pd(CO)OMe]X \qquad (6)$$

The next step involves migratory insertion of the coordinated carbon monoxide molecule into the palladium-methoxy bond to give a palladium carbomethoxy species, a reaction known from related platinum(II) chemistry [10]. Nucleophilic attack by an ethylene molecule would then give a palladium(II) ethylenecarbomethoxy species (eqs. 7 and 8):

$$[L_2Pd(CO)OMe]X \rightarrow [L_2PdCOOMeX] \qquad (7)$$

$$[L_2PdCOOMeX] + C_2H_4 \rightarrow [L_2Pd(C_2H_4)COOMe]X \qquad (8)$$

The next steps involve insertion of the coordinated ethylene molecule into the carbomethoxy group to give the palladium dimethylenecarbomethoxy species, followed by reaction with methanol to give methyl propionate and regenerate active catalyst species (eqs. 9 and 10):

$$[L_2Pd(C_2H_4)COOMe]X \rightarrow [L_2PdC_2H_4COOMeX] \qquad (9)$$

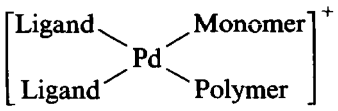
$$[L_2PdC_2H_4COOMeX] + H\mathit{OMe} \rightarrow [L_2Pd\mathit{OMe}X] + CH_3CH_2COOMe \qquad (10)$$

Alternatively, instead of this chain termination, chain propagation may occur by sequential coordination of a second molecule of carbon monoxide and its insertion into the palladium dimethylenecarbomethoxy group. Subsequent alternating insertions of ethylene into metal–acyl bonds [11] and carbon monoxide into metal–alkyl bonds [12] would then generate the polyketone copolymer chain. This chain-propagation process is in competition with chain termination, which results from attack by methanol (eqs. 11 and 12):

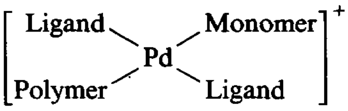
$$[L_2PdC_2H_4COOMeX] + nCO + nC_2H_4 \rightarrow [L_2Pd(C_2H_4CO)_{n+1}OMeX] \qquad (11)$$

$$[L_2Pd(C_2H_4CO)_{n+1}OMeX] + H\mathit{OMe} \rightarrow$$
$$[L_2Pd\mathit{OMe}X] + H(CH_2CH_2CO)_{n+1}OMe \qquad (12)$$

The relative rates of these two processes determine the average molecular weight of the copolymer produced. The product distributions are therefore governed by competition between attack at the proposed intermediate species $[L_2Pd(C_2H_4CO)_n OMeX]$ either by comonomer, with subsequent insertion into the growing chain (eq. 11), or by methanol, with subsequent displacement of the polymer (eq. 12). Such a d^8, 16-electron species would be expected to be square planar, and could exist in both *cis* and *trans* forms; these are represented generally as species of type IV, in which the anion X^- has been replaced by ethylene or carbon monoxide monomer:



(*cis*-IV)



(*trans*-IV)

Clearly, if the insertion of monomer into the palladium–polymer carbon bond involves only the adjacent in-plane sites it is only in the *cis*-form that chain growth can occur. It is suggested, therefore, that this factor plays an important role in the observed difference in product selectivity between catalysts formed from monodentate ligands, for example TPP, for which the major product is methyl propionate, and those formed from bidentate ligands, for example DPPPr, for which high-molecular-weight copolymer is formed.

Thus, with bidentate DPPPr the two phosphine groups are likely to bind exclusively in a *cis* configuration to a single palladium center [13]: this maximizes the concentration of species for which propagation is possible. Two monodentate phosphines, however, can coordinate with both *cis* and *trans* stereochemistry [14]. Irrespective of the relative thermodynamic stabilities of these isomers, if they are in equilibrium any isomerization of *cis*-IV to *trans*-IV will lead to an interruption of chain propagation and so will tend to decrease the ratio of the rate of propagation to the rate of termination. This would lead to a general lowering of the average molecular weight of the product formed, and in the extreme case, as found with TPP, the almost exclusive product is methyl propionate.

Given that the proposed mechanism of the formation of methyl propionate involves insertion of ethylene into the palladium–carbomethoxy bond (eq. 8), which also requires a *cis* orientation, it is perhaps curious that the TPP catalyst system should be so selective in giving methylpropionate, and that only a trace of higher oligomer is formed. This could be a consequence of the fact that at the high reaction temperatures required for optimal production rate (115 ° C) a large excess of TPP and acid is required to ensure catalyst stability, and it is well documented that TPP can act as an efficient catalyst for *cis–trans* isomerizations. The more rapid is this isomerization the greater will be the tendency to give low-molecular-weight products. Indeed, other workers in the field have shown that at lower temperatures (70 ° C; 3.5 MPa) the dicationic catalyst precursor $[(PPh_3)_2Pd(MeCN)_2]^{2+}$ in methanol solution converted carbon monoxide into methyl propionate and a significant amount of keto-ester oligomers [15]. Our corresponding bidentate catalyst precursor $[(DPPPr)Pd(MeCN)_2]^{2+}$, which is assumed to be formed *in situ* in the catalysts systems given in Table 3, gave under approximately comparable reaction conditions (84 ° C; 4.5 MPa) exclusively high-molecular-weight copolymer. The fact that the rate of reaction catalyzed by the latter bidentate system is higher by three orders of magnitude is considered to result from the much higher concentration of the active *cis* form required for the insertion steps.

Another factor to be considered is that, in the *trans*-IV isomer, the polymer chain is *trans* to either coordinated carbon monoxide or ethylene, whereas, in the *cis*-IV isomer, the chain is *trans* to a phosphine group. Because both carbon monoxide and ethylene ligands have appreciably higher *trans* effects than a phosphine ligand [16], the activation energy for the termination reaction would be expected to be lower for *trans*-IV than *cis*-IV. Hence, not only is the propagation prevented in the *trans*-IV isomer, but the rate of termination is expected to be higher than that in the *cis* isomer. Both effects would tend to favor production of lower molecular weight material from a system in which *cis–trans* isomerization occurs when compared with a system in which only the *cis* isomer is involved.

Brief attention is now given to the effect of variation of the number of carbon atoms separating the diphenylphosphino groups for a series of bidentate ligands of general formula $Ph_2P(CH_2)_mPPh_2$. The proposed reaction mechanism involves a series of nucleophilic attacks and substitutions at square-planar palladium(II) species, and such transformations are commonly believed to proceed via a trigonal-bipyramidal transition state [16]. It is thought, therefore, that an important requirement for the bidentate ligand is that it should stabilize both the square-planar ground state and the trigonal-bipyramidal transition state, and, for efficient catalysis, that there is a low energy barrier between the two states. Clearly, the chain length (m) would be expected to influence this transformation, and it would seem that for high reaction rates chain lengths of 3 and 4 carbon units satisfy this requirement better than shorter or longer chains. However, in the absence of a detailed mechanistic study it would be premature to speculate further on the observed variation in activity and selectivity with chain length.

Whereas the mechanistic scheme outlined in eqs. 5–12 explains how methyl propionate and keto-ester polyketones I can be formed, it does not account for the production of polyketones with diester II and diketone end groups III. These were found in approximately equimolar amounts in the oligomer fractions (see Fig. 2).

To account for the formation of II and III, the proposed intermediate species $[L_2Pd(C_2H_4CO)_nOMeX]$ are again considered to play a crucial part. These species are formed after propagation involving an equal number of sequential insertions of carbon monoxide followed by ethylene. Methanol attack occurs directly after insertion of ethylene and results in methanolysis of the palladium–methylene bond to give an ethyl ketonic end group (eq. 12). However, if methanol attack occurred directly after insertion of carbon monoxide, subsequent methanolysis of the resulting palladium–acyl bond would give an ester end group, thus producing the diester II (eqs. 13 and 14):

$$[L_2Pd(C_2H_4CO)_{n+1}OMeX] + CO \rightarrow [L_2PdCO(C_2H_4CO)_{n+1}OMeX] \quad (13)$$

$$[L_2PdCO(C_2H_4CO)_{n+1}OMeX] + H\mathit{OMe} \rightarrow [L_2PdHX] + \mathit{MeO}CO(CH_2CH_2CO)_{n+1}OMe \quad (14)$$

A consequence of this mode of termination is that the palladium methoxy catalyst species would not be regenerated; instead, we suggest that a palladium hydride is formed that is also active for copolymerization. This copolymerization is thought to proceed in an analogous manner to that which is initiated by the palladium methoxy species except that the first step involves ethylene insertion into the palladium–hydride bond instead of carbon monoxide insertion into the palladium–methoxy bond (eqs. 15 and 16).

$$[L_2PdHX] + C_2H_4 \rightarrow [L_2PdCH_2CH_3X] \quad (15)$$

$$[L_2PdCH_2CH_3X] + CO \rightarrow [L_2PdCOCH_2CH_3X] \quad (16)$$

Chain propagation then proceeds by sequential insertion of ethylene followed by carbon monoxide. If termination by attack of methanol occurred after insertion of a carbon monoxide molecule, the keto-ester would be formed with regeneration of the palladium hydride (eqs. 17 and 18):

$$[L_2PdCOCH_2CH_3X] + nC_2H_4 + nCO \rightarrow [L_2Pd(COCH_2CH_2)_{n+1}HX] \quad (17)$$

$$[L_2Pd(COCH_2CH_2)_{n+1}HX] + MeOH \rightarrow [L_2PdHX] + MeO(COCH_2CH_2)_{n+1}H \quad (18)$$

If, however, attack of methanol occurs after the insertion of an ethylene molecule, subsequent methanolysis will give a ketone end group, thus producing the diketone III (eqs. 19 and 20):

$$[L_2Pd(COCH_2CH_2)_{n+1}HX] + C_2H_4 \rightarrow [L_2PdCH_2CH_2(COCH_2CH_2)_{n+1}HX] \quad (19)$$

$$[L_2PdCH_2CH_2(COCH_2CH_2)_{n+1}HX] + MeOH \rightarrow [L_2PdOMeX] + CH_3CH_2(COCH_2CH_2)_{n+1}H \quad (20)$$

This final termination step regenerates the palladium methoxy species, which is suggested to be formed in the initiation step as shown in eq. 5. The mechanistic sequence postulated in eqs. 3–20, which rationalizes the formation of the three polymer chains of general formulae I, II and III, comprises two interdependent catalytic cycles (**A** and **B**) connected by the transformations shown in eqs. 14 and 20. This can be seen more clearly in the scheme presented in Fig. 3.

As regards the effect of quinone on both activity and selectivity, the higher selectivity to the diester could be attributed to oxidation by the quinone of the proposed palladium hydride species, thus providing a route for its conversion in cycle **B** into the palladium methoxy species in cycle **A**; for example:

$$[L_nPd\text{-}H] + OC_6H_4O + MeOH \rightarrow [L_nPd\text{-}OMe] + HOC_6H_4OH$$

The increase in rate in the presence of quinone may therefore indicate that cycle **B** is slower than cycle **A**. In agreement with this (possible solvent effects being neglected) reactions in aprotic solvents in which the copolymerizations are initiated by dihydrogen, presumably by the formation of a palladium hydride species, are consistently slower than reactions under the same conditions in methanol.

The increase in both the reaction rate and the molecular weight of terpolymer when reactions are carried out in the presence of copper cations indicates that the role of the copper is preferentially to increase the rate of propagation with respect to that of termination. Without further study it would be premature to discuss possible mechanisms by which this might occur. However, since preliminary kinetic measurements have indicated olefin insertion to be the rate-determining step, we believe that interaction of the copper cations with the proposed palladium acyl intermediate species may play a role in increasing the rate of insertion of olefin into the palladium acyl bond (see eq. 19).

Although the above mechanistic arguments provide a plausible rationalization as to why chelating ligands are important for the palladium-catalyzed copolymerization reactions, the mechanism by which the strictly alternating copolymer chain is formed remains obscure. Particularly surprising is the observation that even though

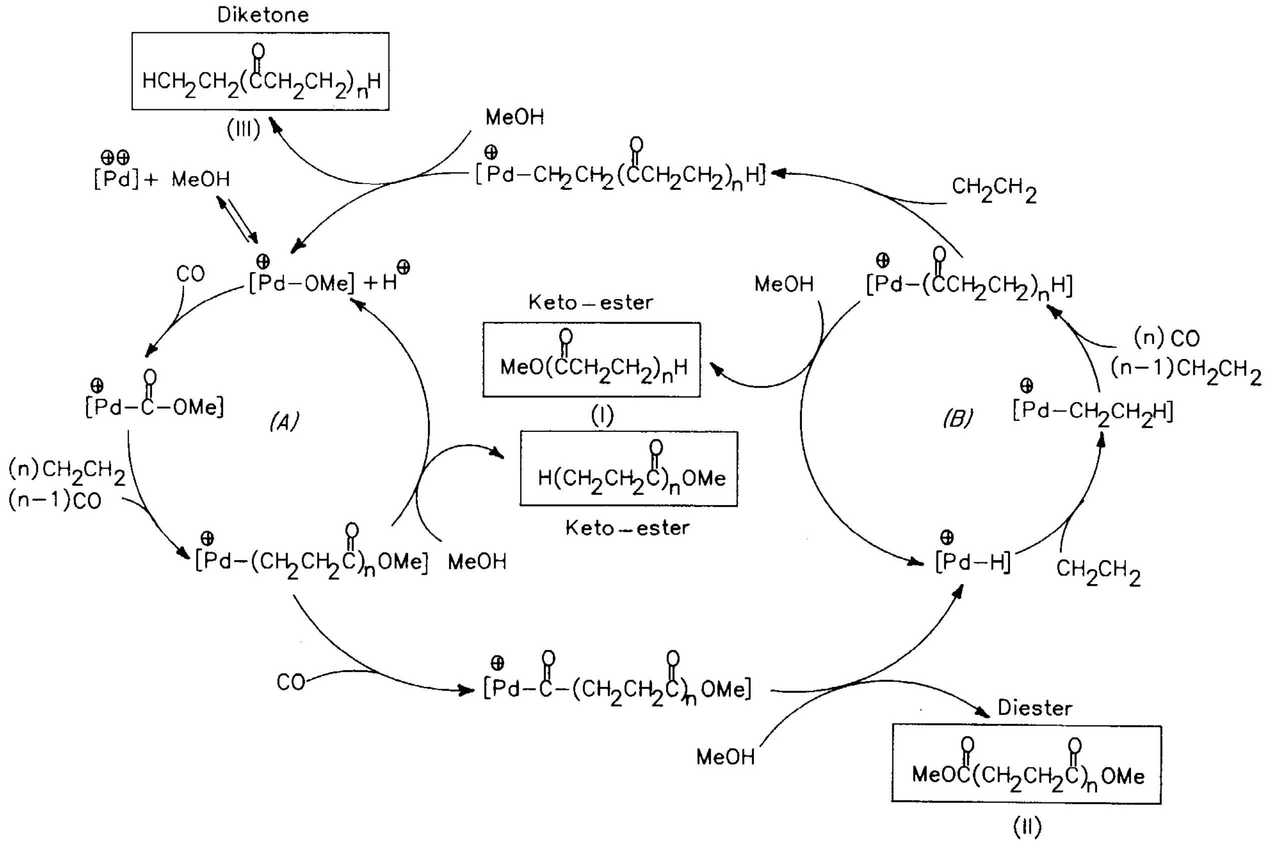


Fig. 3. Proposed catalytic cycles for the formation of keto-ester (I), diester (II) and diketone (III) polyketones in the palladium-catalyzed copolymerization of carbon monoxide and ethylene.

the same palladium compounds are efficient catalysts for the dimerization of ethylene in the absence of carbon monoxide [17], the integrity of the strictly alternating structure of the copolymer is maintained even at extremely low concentrations of carbon monoxide. This phenomenon was strikingly illustrated in a batch reaction which was carried out under these conditions: initially alternating copolymer was produced until all carbon monoxide had been consumed, after which n-butenes were produced. Even this copolymer contained no defects, thus showing that consecutive insertion of two ethylene molecules into the copolymer chain did not occur. It is also remarkable that β-H elimination as a termination process does not take place in the presence of CO, as is evidenced by the absence of terminal olefinic conjugated ketone-end groups in the polymer produced under these conditions.

Further detailed studies of the elementary steps are required to gain insight into the factors that control these very highly selective copolymerizations.

Experimental

Equipment

^{13}C and ^{31}P NMR spectra were recorded on a Bruker WM 250 spectrometer. Gas chromatographic analysis was performed on a Finnigan-9610 gas chromatograph fitted with a Chrompack 25 m CP-sil-5 capillary column coupled to a Finnigan-4000 triple stage quadrupole mass spectrometer; electron impact ionization was used.

Materials

All reagents were used as supplied by the manufacturers: acetonitrile, methanol (p.a.), Brønsted acids, their silver and copper salts, and diacetatopalladium(II) were obtained from Merck; phosphines from Strem; carbon monoxide from Matheson (purity > 99%). Ethylene and propene were of polymer grade and obtained from in-house sources. All operations involving preparation of catalyst systems and syntheses of palladium complexes were carried out under dry nitrogen by standard Schlenk techniques.

Preparation of $[Pd(MeCN)_2(O_3STol)_2]$

To a clear dark orange solution of diacetatopalladium(II) (0.663 g; 2.95 mmol) in acetonitrile (45 g) a solution of *p*-toluenesulfonic acid (3.0 g; 15.8 mmol) in acetonitrile (30 g) was added dropwise with stirring; the color gradually changed to pale yellow. Subsequently diethyl ether (70 ml) was added, and this resulted in precipitation of fine pale yellow microcrystals. The suspension was set aside for 1 h, the supernatent liquid was decanted, and the crystals were washed with diethyl ether, dried under a slight vacuum, and shown to be $[Pd(MeCN)_2(O_3STol)_2]$ (1.47 g; 93.8% yield). Elemental analysis. Found: C, 40.4; H, 3.8; N, 5.4; S, 11.3. $C_{18}H_{20}N_2O_6S_2Pd$ calc.: C, 40.7; H, 3.8; N, 5.3; S, 12.1%.

Preparation of $[Pd(MeCN)_4](O_3SCF_3)_2$

To a clear dark orange solution of diacetatopalladium(II) (0.679 g; 3.03 mmol) in acetonitrile (45 g) neat trifluoromethanesulfonic acid (1.33 g; 8.84 mmol) was added dropwise with stirring; the color changed to pale yellow. Subsequently diethyl ether (80 ml) was added, and this resulted in precipitation of a fine pale yellow powder.

The suspension was set aside for 2 h, the supernatent liquid was decanted, and the residual powder washed with diethyl ether, dried under a stream of nitrogen, and shown to be $[Pd(MeCN)_4](O_3SCF_3)_2$ (1.37 g; 79.6% yield). Elemental analysis. Found: C, 21.0; H, 1.8; N, 10.1; S, 11.4. $C_{10}H_{12}N_4F_6O_6S_2Pd$ calc.: C, 21.1; H, 2.1; N, 9.9; S, 11.3%.

Copolymerization of carbon monoxide with ethylene

Polymerizations were carried out in a 250-ml magnetically driven Hasteloy^{TM} autoclave. The reactor was purged with reactant gases and degassed solvent was added; subsequently, the catalyst components were introduced separately in the order ligand, palladium compound, and additional component. The autoclave was then pressurized with carbon monoxide and ethylene at room temperature and heated to the chosen reaction temperature during 15 minutes. In these experiments the pressure was allowed to fall during the reaction period (batch mode). In experiments conducted at constant pressure (continuous mode) the purged reactor, containing methanol, was first heated to the chosen temperature and then pressurized with the reactant gases in the desired ratio and a concentrated solution of the catalyst was then injected. During the reaction the pressure was maintained by a continuous supply of a mixture equimolar amounts of carbon monoxide and ethylene. The uptake of feed gas was measured by a calibrated mass-flow meter in the feed line. At the end of the chosen period the reaction was stopped, the autoclave was rapidly cooled, and the unreacted gases were vented. The product slurry was filtered off, washed with fresh methanol, and dried in a vacuum oven at 70 ° C to give a snow-white powder.

The averaged catalyst activity was calculated from both the weight of polymer produced and the total gas fed in during the reaction period; the figures were generally in good agreement. The maximum rate was measured by the highest reading of the mass-flow meter in the feed line.

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References

1 W. Reppe and A. Magin, U.S. Patent 2,577,208 (1951).
2 For a review article see A. Sen, Adv. Polym. Sci., 73/74 (1986).
3 M.M. Brubaker, U.S. Patent 2,495,286 (1950).
4 P. Colombo, L.E. Kukacka, J. Fontana, R.N. Chapman and M. Steinberg, J. Polym. Sci., A-1 4 (1966) 29; M. Steinberg, Polym. Eng. Sci., 17 (1977) 335.
5 W.F. Gresham and R.E. Brooks, U.S. Patent 2,542,767 (1951).
6 Y. Iwashita and M. Sakuraba, Tetrahedron Lett., 26 (1971) 2409; A. Sen and J.S. Brumbaugh, J. Organomet. Chem., 279 (1985) C5.

7 T.M. Shryne and H.V. Holler, U.S. Patent 3,984,388 (1976); U. Klabunde, T.H. Tulip, D.C. Roe and S.D. Ittel, J. Organomet. Chem., 334 (1987) 141; U. Klabunde and S.D. Ittel, J. Mol. Catal., 41 (1987) 123.
8 A. Gough, British Patent 1,081,304 (1967); D.M. Fenton, U.S. Patents 3,530,109 (1970) and 4,076,911 (1978); K. Nozaki, U.S. Patents 3,689, 460 (1972), 3,694,412 (1972) and 3,835,123 (1974); A. Sen and T.-W. Lai, J. Am. Chem. Soc., 104 (1982) 3520.
9 E. Drent, European Patent Applications, 121,965 (1984) and 181,014 (1986); J.A.M. van Broekhoven, E. Drent and E. Klei, European Patent Application, 213,671 (1987); J.A.M. van Broekhoven van E. Drent, European Patent Application 235,865 (1987).
10 H.E. Bryndza, Organometallics, 4 (1985) 1686.
11 J.S. Brumbaugh and A. Sen, J. Am. Chem. Soc., 110 (1988) 803; W.M. Vetter and A. Sen, J. Organomet. Chem., 378 (1989) 485; J.S. Brumbaugh, R.R. Whittle, M. Parvez and A. Sen, Organometallics, 9 (1990) 1735.
12 A. Yamamoto, in Organotransition Metal Chemistry, Wiley Interscience, 1986, p. 246.
13 D.M.A. Minahan, W.E. Hill and C.A. McAuliffe, Coord. Chem. Rev., 55 (1984) 31; C.T. Hunt and A.L. Balch, Inorg. Chem., 21 (1982) 1242; W.L. Steffen and G.J. Palenik, Inorg. Chem., 15 (1976) 2432; G.J. Palenik, M. Mathew, W.L. Steffen and G. Beran, J. Am. Chem. Soc., 97 (1975) 1059.
14 D.G. Cooper and J. Powell, Can. J. Chem., 51 (1973) 1634; D.A. Redfield and J.H. Nelson, Inorg. Chem., 12 (1973) 15.
15 T.-W. Lai and A. Sen, Organometallics, 3 (1984) 866.
16 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, in Principles and Applications of Organotransition Metal Chemistry, University Science Books, 1987; F.A. Cotton and G. Wilkinson, in Advanced Inorganic Chemistry, 5th ed., Wiley Interscience, 1988.
17 E. Drent, Pure Appl. Chem., 62 (1990) 661.