The dicarbonylation and hydrodimerization of unsaturated hydrocarbons via heterogeneous palladium catalysis

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Received 13 June 1995; accepted 21 November 1995

Graphite and polymer-supported palladium catalysts, coupled with copper/lithium cocatalysts, have been found very effective for the oxidative carbonylation of unsaturated hydrocarbons. Hex-3-ene-1,6-dioate has been generated in 85% selectivity from 1,3-butadiene, α-olefins yield dimethyl succinate derivatives. Butadiene hydrodimerization via analogous platinum catalysis selectively provides 1,6-octadiene, or 2,7-octadienyl formate. Mechanisms for the product selectivity are described.

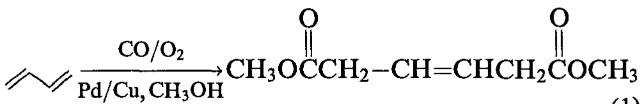
Keywords: dicarbonylation of hydrocarbons; hydrodimerization of hydrocarbons; palladium-catalyzed dicarbonylation; palladium-catalyzed hydrodimerization

1. Introduction

Since the initial development of the Wacker process in 1958, there have been numerous new applications discovered for palladium catalysts in organic syntheses [1,2]. Some industrially important examples include telomerization [3], dimeric carbonylation of butadiene [4], oxalate synthesis [5], olefin/ketone processes [6], hydrodimerization of butadiene [7] and oxidative carbonylation [8]. Recently, significant advances in palladium chemistry have been achieved by the Kurarey process [9]. This production of 1-octene from butadiene dimerization involves a liquid phase reaction with a palladium catalyzed butadiene telomerization, hydrogenation of the octa-2,7-dien-1-ol to *n*-octanol, and dehydrating to 1-octene [10,11]. Related chemistry, but in acetic acid, yields 1-octene via acetate elimination [10,12].

Hydrocarbonylation of 1,3-butadiene with palladium(II)–phosphine complexes to give 3-pentenoates was reported [8] by Tsuji in 1972. In 1979, the synthesis of dimethyl hex-3-ene-1,6-dioate from 1,3-butadiene was revealed in a study of palladium-catalyzed carboxylation by Stille et al. [13]. More recently, researchers at Atlantic Richfield Company [14] and others [15] have claimed improvements in this process, in terms of both product selectivity and catalyst stability. The overall process scheme provides a new potential route to adipic acid – a critical component in Nylon 66 manufacture.

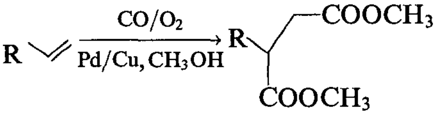
We have had an ongoing interest in palladium-catalyzed butadiene derivatization reactions [16,17] and here we present our results on the use of specific heterogeneous palladium catalysts [#1], in combination with certain cocatalyst species, for 1,3-butadiene oxidative carbonylation to generate dimethyl hex-3-ene-1,6-dioate – a precursor of adipic acid – in up to 85% selectivity:



$$\xrightarrow[\text{Pd/Cu, CH}_3\text{OH}]{\text{CO/O}_2} CH_3O\overset{O}{\overset{\|}{C}}CH_2-CH=CHCH_2\overset{O}{\overset{\|}{C}}OCH_3 \qquad (1)$$

The supported Pd catalysts are typically in combination with copper(II) chloride and lithium chloride, as well as the polymer-supported Cu(II) analogs.

In an extension of that work, α-olefin substrates, particularly propylene and 1-octene, have also been converted to the corresponding dimethyl succinate derivatives, in 89% selectivity, using a similar class of catalyst:



(2)

Contrasting the work on oxidative carbonylation of 1,3-butadiene, we have also applied polymer-supported platinum catalysis to the hydrodimerization of 1,3-butadiene with formic acid as the hydrogen source. It has been discovered that selectivity to 1,6- vs. 1,7-octadiene and 2,7-octadienyl formate is controlled primarily by

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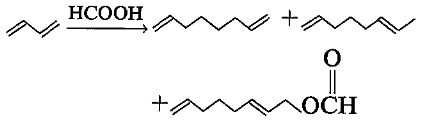
[#1] A palladium graphite heterogeneous catalyst for the synthesis of polycinnamide was recently reported in 209th ACS meeting, see ref. [18].

the presence of polymeric amine, as well as the reaction conditions:



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2. Experimental

2.1. Oxidative dicarbonylation of 1,3-butadiene by Pd/graphite

A typical experimental example is as follows: To a 300 ml stainless steel, magnedrive reactor was charged palladium (1.0 wt%)-on-graphite (1.0 g), copper(II) chloride, hydrate (1.2 g), lithium chloride (0.084 g), methanol (0.96 g) and 2,2-dimethoxypropane (20 g). The autoclave was sealed, 20.0 g of 1,3-butadiene was then added, followed by pressuring with CO (500 psi) and O_2 (100 psi). The system was heated to 100°C and total pressure was raised to 1500 psi with CO. These conditions were held for 2 h. During the reaction process, the pressure dropped to 1250 psi. The reactor was cooled to room temperature and an off-gas sample was taken. The excess gas was vented and a brown liquid product with solid catalysts at the bottom was recovered (33.3 g).

The glc analysis of liquid products and off-gas samples indicated the following product selectivities:

dimethyl hex-3-ene-1,6-dioate (I)	28%
methyl 5-methoxy-3-pentenoate (II)	5%
4-vinyl-1-cyclohexene (III)	22%
dimethyl carbonate (IV)	31%
dimethyl oxalate (V)	13%

Estimated selectivity to dimethyl hex-3-ene-1,6-dioate (basis butadiene carbonylated) is 85%. The off-gas analysis showed:

carbon monoxide	92.6%
carbon dioxide	1.1%
total heavies material	5.2%

2.2. Oxidative dicarbonylation of propylene by Pd/graphite

To a 300 ml stainless-steel, magnedrive reactor was charged palladium (1.0 wt%)-on-graphite (0.50 g), cuprous chloride, hydrate (0.60 g), lithium chloride (0.042 g), methanol (0.96 g) and 2,2-dimethyoxypropane (20 g). The autoclave was sealed and then 10.0 g of propylene was charged and followed by pressuring CO (500 psi) and O_2 (100 psi). The system was heated to 100°C and pressure was raised to 2000 psi with CO. These conditions were held for 2 h. During the reaction process, the pressure dropped to 1700 psi. The reactor was cooled to room temperature and an off-gas sample was taken. The excess gas was vented and a brown liquid product with solid catalyst at the bottom was recovered (23.0 g). The glc analysis of liquid products and off-gas samples indicated the following product selectivities:

dimethyl α-methyl-succinate	64%
dimethyl carbonate	32%
unknown	4%

The off-gas analysis showed:

carbon monoxide	77.3%
carbon dioxide	0.2%
total heavies material	17.5%

2.3. Oxidative dicarbonylation of 1-octene by Pd/graphite

The above procedures were repeated using 1-octene as the olefin substrate, product analyses showed:

dimethyl *n*-hexyl-succinate	66%
dimethyl carbonate	29%
unknown	5%

2.4. Oxidative carbonylation of ethylene by polymer-supported Pd

Preparation of polyvinylpyrrolidone-supported palladium-catalyst: A mixture of palladium chloride (1.75 g), cupric chloride (13.5 g) and polyvinylpyrrolidone (22.2 g) in ca. 500 ml methanol was stirred at room temperature overnight. The solid material was obtained by filtration and washed thoroughly with additional methanol. The solid material was dried at 50°C under vacuum for 2 h. The resulting solid (27.2 g), brown in color, was analyzed. Metal content showed 3.83% palladium and 2.28% copper.

Ethylene oxidative carbonylation: A 183 ml glass-lined reactor was charged with palladium/copper catalyst (3.0 g), lithium chloride (0.084 g), methanol (0.5 g), 2,2-dimethoxypropane (15.0 g) and ca. 9.0 g ethylene. The reactor was pressured with carbon monoxide (500 psi) and oxygen (200 psi) and then was heated to 100°C. At this temperature, the pressure of 1200 psi was recorded. The system was pressured with carbon monoxide to 2000 psi and held for 2 h reaction time. During the reaction process, 350 psi of pressure uptake was observed. The reactor was allowed to cool to room temperature and excess gas was vented. The resulting liquid product and solid catalyst (ca. 22.5 g) was obtained. The glc analysis of liquid materials showed 17% dimethyl succinate and 13% methyl 3-methoxypropionate in solution. The product selectivity was estimated to be 53% for dimethyl succinate, 41% for methyl 3-methoxypropionate, 0% for dimethyl carbonate and ca. 6% for dimethyl oxalate.

2.5. Hydrodimerization of 1,3-butadiene to octadienes by platinum

To a 300 ml stainless magnedrive reactor were charged platinum(II) acetylacetonate (0.039 g, 0.1 mm), formic acid (12.0 g, 0.26 M), solid AMBERLYST A21 (10.0 g) and tetrahydrofuran (6.0 g). The reactor was sealed and purged of air with carbon dioxide. Then, butadiene (about 32 g, 0.6 M) was introduced into the reactor along with pure CO_2 to a total pressure of 120 psi. The system was heated to 100–120°C and maintained at this temperature range for 4 h. The maximum pressure of 500 psi was observed during the reaction process. At the end of this time, the reactor was allowed to cool to ambient temperature. A light-yellow, clear product solution was obtained (31.0 g) by decantation, or by filtering off the solid AMBERLYST A21. The top layer of this liquid product (29.0 g) was analyzed by gas–liquid chromatography and showed to have the following composition (in %):

butadiene	23
THF	21
1,7-octadiene	1.8
1,6-octadiene	29
4-vinylcyclohexene	25

The product selectivities were estimated to be: 52% 1,6-octadiene, 3% 1,7-octadiene and 45% 4-vinylcyclohexene.

2.6. *Hydrodimerization of 1,3-butadiene to octadienyl formate by platinum*

To a 300 ml stainless steel magnedrive reactor were charged platinum(II) acetylacetonate (0.039 g, 0.1 mm), formic acid (12.0 g, 0.26 mmol) and THF (6.0 g). The reactor was flushed with carbon dioxide, then charged with 1,3-butadiene (45 g) and carbon dioxide to 100 psi total pressure. The system was heated to 118°C within a 20 min period. Then the reaction temperature was maintained within the range of 118–124°C for the period of 1.5 h. The maximum pressure was 420 psi during the reaction period. The system was cooled and then the excess gas was vented. A very light yellow solution (25.8 g) was recovered, which gave the following gas chromatography analysis (in %):

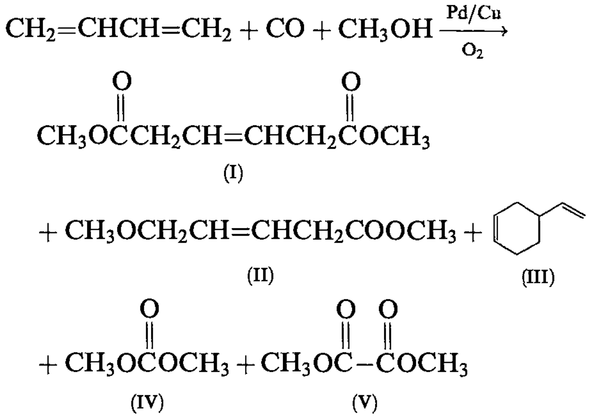
1,3-butadiene	23.8
THF	17.8
1,7-octadiene	3.0
1,6-octadiene	21.0
4-vinylcyclohexene	17.6
2,7-octadienyl formate	12.9

The production of 2,7-octadienyl formate was calculated to be 22 000 g/(g-atm-Pt h) based on Pt catalyst charged.

3. Results and discussion

3.1. *Oxidative dicarbonylation of 1,3-butadiene*

Our result using heterogeneous palladium catalysts for the butadiene oxidative carbonylation is described by the following [19]:



$$CH_2{=}CHCH{=}CH_2 + CO + CH_3OH \xrightarrow[O_2]{Pd/Cu} \underset{(I)}{CH_3O\overset{O}{\overset{\|}{C}}CH_2CH{=}CHCH_2\overset{O}{\overset{\|}{C}}OCH_3} + \underset{(II)}{CH_3OCH_2CH{=}CHCH_2COOCH_3} + (III) + \underset{(IV)}{CH_3O\overset{O}{\overset{\|}{C}}OCH_3} + \underset{(V)}{CH_3O\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}OCH_3} \quad (4)$$

The use of various palladium catalysts and their effects on the product distributions are summarized in table 1. Compounds (I) and (II) are derived from 1,3-butadiene oxidative dicarbonylation and monocarbonylation, respectively. 4-vinyl-1-cyclohexane is the Diels–Alder adduct of 1,3-butadiene under thermal reaction conditions. Dimethyl carbonate and dimethyl oxalate are produced by methanol carbonylation catalyzed by Pd/Cu. Product formation and distribution are sensitive primarily to reaction conditions and the nature of the palladium catalyst. In particular, it is worth noting that:

(a) Palladium-on-graphite, in comparison with Pd-on-alumina or Pd-on-kaolin, catalyzes oxidative carbonylation to give products (I) and (II) in improved selectivities.

(b) Production of desired dimethyl hex-3-ene-1,6-dioate (I) is lower, and selectivity to less desirable dimethyl carbonate is higher, when no lithium cocatalyst is used.

(c) The ratio of dimethyl hex-3-ene-1,6-dioate (I) to less desirable methyl 3-methoxy-3-pentenoate (II) is lower in the absence of the dehydrating agent, 2,2-dimethoxypropane. It appears that the presence of water disfavors the dicarbonylation.

(d) Productivity to adipic acid precursor I is lower when less oxygen is used. In this case, the pathway for the oxidative carbonylation is surpressed. Similarly, at lower total carbon monoxide plus oxygen partial pressures, the product distribution favors carbonate (IV) and 4-vinyl-1-cyclohexene (III), formation.

(e) The operating temperature can have a significant impact upon the formation of product (I). A temperature of ca. 100°C is preferable to 80°C.

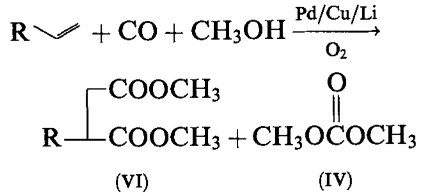
3.2. *Oxidative dicarbonylation of α-olefins*

The palladium/graphite catalyst in combination with copper(II) chloride and lithium chloride has also been applied by us to the oxidative carbonylation of propylene and 1-octene [20]. The system was found to be as effective as palladium(II) chloride for the synthesis of alkyl succinate esters:

Table 1
Synthesis of dimethyl hex-3-ene-1,6-dioate from butadiene, carbon monoxide and methanol

Example	Reaction charge				Reaction conditions	Temp. Time	Wt gain	Product selectivities (%)				
	Pd-catalyst[c]	LiCl co-catalyst (g)	MeOH (g)	2,2-di-methoxy-propane (g)				I	II	III	IV	V
1	0.5% Pd on Kaolin (2.0 g)	0.084	0.96	20[a]	1500 psi; $CO/O_2 = 7$	100°C 2 h	–	3	1	14	72	7
2	0.5% Pd on Kaolin (2.0 g)	0.084	0.96	20[a]	1500 psi; $CO/O_2 = 7$	100°C 2 h	0	–	–	13	84	–
3	0.5% Pd on Al_2O_3 (2.0 g)	0.085	0.96	20[a]	1500 psi; $CO/O_2 = 15$	100°C 5 h	3.6	–	–	–	81	–
4	1% Pd on graphite (1.0 g)	0	0.96	20[a]	1500 psi; $CO/O_2 = 15$	100°C 2 h	4.1	15	5	16	76	3
5	1% Pd on graphite (1.0 g)	0.084	10	0[a]	1500 psi; $CO/O_2 = 15$	100°C 2 h	3.0	26	19	33	8	1
6	1% Pd on graphite (1.0 g)	0.084	0.96	20[a]	2000 psi; $CO/O_2 = 20$	100°C 2 h	2.6	21	3	15	42	10
7	1% Pd on graphite (1.0 g)	0.084	0.96	10[b]	875 psi; $CO/O_2 = 8$	100°C 2 h	5.8	8	~0	30	61	~0
8	1% Pd on graphite (1.0 g)	0.084	0.96	20[b]	825 psi; $CO/O_2 = 8$	80°C	2.2	9	2	15	75	0
9	1% Pd on graphite (1.0 g)	0.084	0.96	20[b]	2000 psi; $CO/O_2 = 20$	80°C 2 h	0.5	2	0	14	75	1

[a] Butadiene used (20 g).
[b] Butadiene used (40 g).
[c] $CuCl_2$–$2H_2O$, 1.2 g also added.



$$\mathrm{R{\diagdown\!\!\diagup} + CO + CH_3OH \xrightarrow[O_2]{Pd/Cu/Li} R\!-\!\left[\begin{matrix}COOCH_3\\COOCH_3\end{matrix}\right. + CH_3O\overset{\overset{O}{\|}}{C}OCH_3} \quad (5)$$

(VI) (IV)

Derivatives (VI) and (IV) were the major products. The ratio of (VI) and (IV) is significantly influenced by the choice of palladium precursor – Pd/graphite or $PdCl_2$. The dimethyl carbonate by-product formation reached ca. 30% selectivity with Pd/graphite – in comparison with 10% for the $PdCl_2$ system.

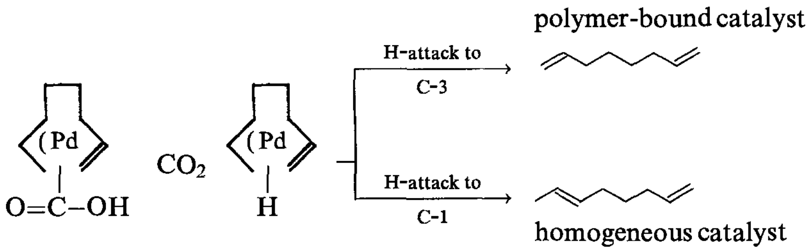
Similarly, the polyvinylpyrrolidone-supported palladium and cupric chloride can also be the active catalyst for producing dimethyl succinate from ethylene (see Experimental section, and ref. [21]).

3.3. *Hydrodimerization of 1,3-butadiene*

The phosphinated polystyrene-bound palladium(0) catalyst has been reported as an effective catalyst for butadiene hydrodimerization to form octadienes [15]. In contrast to this, 1,6-octadiene was obtained in the homogeneous palladium acetate system (eq. (6) below). The ligands coordinated to the palladium catalyst appear to be the important parameter in regard to product selectivity. In one report [7], 93% selectivity for 1,7-octadiene was obtained through the use of $Pd(OAc)_2$ plus Et_3P, in contrast to 99% selectivity for 1,6-octadiene in the absence of phosphine ligand (eq. (7)).

In our studies [22,23] (table 2) using platinum(II) acetylacetonate catalyst in the presence of a polymeric amine promoter, 91–95% selectivity to 1,6-octadiene and 9–5% to 1,7-octadiene was achieved with catalyst turnover numbers of 22 000 g octadiene/(g-atm-Pt h). This Pt catalyst system differs from the Pd analogous catalyst in the selectivity of 1,7-octadiene formations. In the absence of polymeric amine, a novel formation of 2,7-octadienyl formate can be achieved (eq. (8)). During 2,7-octadienyl formate product formation, 1,6-octadiene was the major octadiene. A polar and aprotic solvent, THF, is preferred to facilitate these reactions. The catalyst turnover, as high as 22 000 g/(g-atm h), was observed for the formate production (table 3). Mechanism for the production of 1,6-octadiene, vs. 2,7-octadienyl formate, is described in fig. 1. A π-allyl platinum formate intermediate is proposed. Presence of basic polymeric amine facilitates the release of CO_2 and a proton source which leads to the formation of octadienes rather than 2,7-octenyl formate.

The use of the polymeric amine for this reaction affords two significant features. First, there is a high selectivity toward 1,6-octadiene formation; in some cases a mole ratio of greater than 90 : 10 molar ratio of 1,6- to 1,7-octadiene is achieved. Secondly, there is great ease in separating the desired product from the solid amine. The decantation or filtration procedures can be used for separation. Octadienes are useful in various polymer syntheses and in the syntheses of diacids, diesters, diols and diamines.



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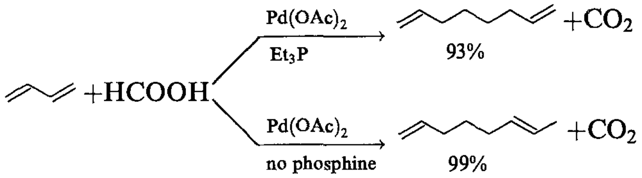

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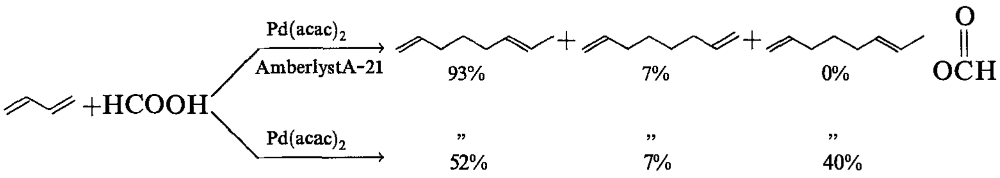

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Table 2
1,6-octadiene synthesis via butadiene dimerization

Ex.	Catalyst	Formic acid	Amine used	Solvent used	Butadiene charged (g)	Initial & max. CO_2 pressure (psi)	Reaction temp. (°C)	Reaction time (h)	Product selectivity (%)			
									1,6-octadiene	1,7-octadiene	4-vinyl-cyclohexene	others
1	$Pt(acac)_2$ (0.1 mm)[a] (0.039 g)	12.0 g (0.26 M)	AMBERLYST® A-21 (10.0 g)	THF (6.0 g)	32	120–500	100–120	4	52 (75 mm)	3 (4.7 mm)	45	0
2	$Pt(acac)_2$ (0.1 mm) (0.039 g)	12.0 g (0.26 M)	none	THF (6.0 g)	45	100–420	100–120	1.5	36 (49 mm)	5 (7.2 mm)	31	28
3	$Pt(acac)_2$ (0.1 mm) (0.039 g)	none	none	THF (6.0 g)	32	100–415	100–130	4	trace	trace	~ 100 (50 mm)	0
4	$Pt(acac)_2$ (0.1 mm) (0.039 g)	12.0 g (0.26 M)	AMBERLYST® A-21 (5.0 g)	THF (6.0 g)	21	150–465	120	2	58 (30 mm)	6 (3 mm)	36	
5	$Pt(acac)_2$ (0.1 mm) (0.039 g)	120 g (0.26 M)	AMBERLYST® A-21 (5.0 g)	THF (12.0 g)	21	110–340	110	5.5	59 (34 mm)	4 (2 mm)	32	5
6	$Pt(acac)_2$ (0.1 mm) (0.039 g)	12.0 g (0.26 M)	recycled from ext. 5	THF (12.0 g)	23	100–335	110–118	5.5	56 (48 mm)	7 (6 mm)	36	0

[a] mm = milimoles.

Table 3
2,7-octadienyl formate synthesis from butadiene and formic acid

Ex.	Catalyst	Formic acid (g)	Solvent used	Butadiene charged (g)	Initial & max. CO_2 pressure (psi)	Reaction temp. Time	2,7-octadienyl formate		1,6-octadiene (g)	1,7-octadiene (g)	4-vinylcyclohexene (g)
							weight (g)	turnover (g/(g-atm-Pt h))			
1	$Pt(acac)_2$ (0.039 g, 0.1 mm)	12.0	THF (6.0 g)	45	100–420	100–120°C 1.5 h	3.4	22 000	5.4	0.8	4.6
2	$Pt(acac)_2$ (0.039 g, 0.1 mm)	18.0	THF (6.0 g)	60	100–520	103–133°C 4.5 h	1.7	11 000	21.5	–	3.6
3	$Pt(acac)_2$ (0.039 g, 0.1 mm)	12.0	THF (6.0 g)	45	100–680	115°C 5.5 h	0.86	1 600	2.6	0.26	4.8
4	$Pt(acac)_2$ (0.039 g, 0.1 mm)	6.0	acetone (6.0 g)	65	150–510	119–125°C 3.0 h	1.6	5 300	3.3	0.35	6.5
5	$Pt(acac)_2$ (0.039 g, 0.1 mm)	18.0	none	32	110–430	100–125°C ~ 5.0 h	0.32	640	0.36	0	1.32
6	$Pd(Ph_3P)_4$ (0.115 g, 0.1 mm)	6.0	acetone (6.0 g)	65	170–650	110–120°C 3.0 h	0	0	2.1	2.8	5.2

A mechanism, similar to the analogous palladium catalysis, is proposed in fig. 1.

4. Conclusions

Analogous to homogeneous palladium carbonylation catalysts, graphite- or polymer-supported palladium catalyst can also achieve a reasonable catalyst activity and product selectivity. Palladium-on-graphite coupled with copper/lithium cocatalysts, in particular, performs well in terms of both product selectivity and productivity in the oxidative dicarbonylation of 1,3-butadiene to dimethyl hex-3-ene-1,6-dioate. The same is true for analogous heterogeneous palladium-on-carbon catalysts used for converting α-olefins to alkyl succinate esters.

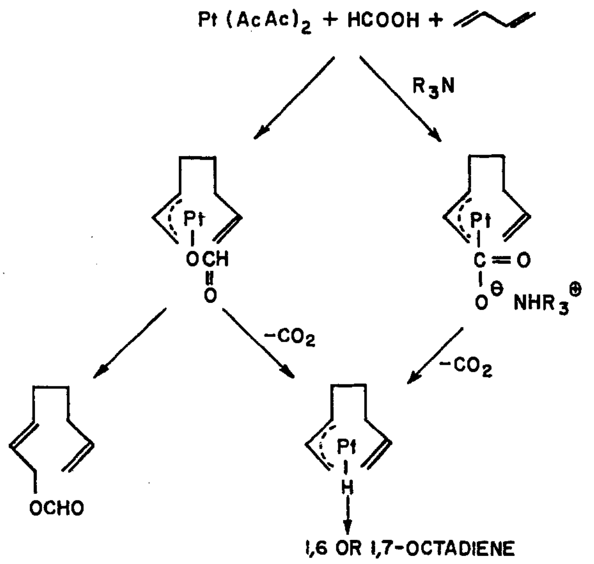

Fig. 1. Platinum catalyst for hydrodimerization.

In the case of hydrodimerization of 1,3-butadiene, the $Pt(acac)_2$ catalyst precursor gives 1,6-octadiene as the predominant product in the presence of polymeric amine. In the absence of polymeric amine, however, a novel synthesis of 2,7-octadienyl formate has been discovered.

Acknowledgement

We wish to thank Huntsman Corp. for permission to publish this work and Messrs. M. Swenson and R. Gonzales for experimental assistance.

References

[1] J. Tsuji, *Organic Synthesis With Palladium Compounds* (Springer, Berlin, 1980).
[2] R.F. Heck, *Palladium Reagents in Organic Synthesis* (Academic Press, New York, 1985).

[3] J. Tsuji, Adv. Organomet. Chem. 17 (1979) 141.
[4] J. Kiji, T. Okano, K. Odagiri, N. Uesheshima and H. Konishi, J. Mol. Catal. 18 (1983) 109.
[5] D.M. Fenton, J. Org. Chem. 39 (1974) 701.
[6] J. Tsuji, Synthesis (1984) 369.
[7] C.U. Pittman Jr., J. Mol. Catal. 15 (1982) 377.
[8] J. Tsuji, Y. Mori and H. Hara, Tetrahedron 28 (1972) 3721.
[9] Europ. Chem. News (18 Jan., 1993) 24.
[10] Chem. Systems Report 91S3, *n-Octanol and Octene-1 from Butadiene* (Sept. 1992).
[11] N. Yoshimura and M. Tamura, US Patent 4,356,333 (1982) to Kuraray Company, Limited.
[12] L.H. Slaugh, US Patent 5,030,792 (1991) to Shell Oil Company.
[13] J.K. Stille and R. Divakaruni, J. Org. Chem. 44 (1979) 3474.
[14] H.S. Kesling, US Patent 4,281,173 (1981) to Atlantic Richfield Company.
[15] K. Kaneda, H. Kurosaki, M. Terasawa, T. Imanaka and S. Teranishi, J. Org. Chem. 46 (1981) 2356.
[16] J.F. Knifton, J. Catal. 60 (1979) 27.
[17] J.F. Knifton, Annals NY Acad. Sci. 333 (1980) 264.
[18] M. Jikei, M. Miyauchi, Y. Ishida, M. Kakimoto and Y. Imai, Abstract, polymer No. 220, 209th ACS meeting, Anaheim, CA, 2–6 April 1995.
[19] J.J. Lin and J.F. Knifton, US Patent 4,552,976 (1985) to Texaco Inc.
[20] J.J. Lin, US Patent 4,554,374 (1985) to Texaco Inc.
[21] J.J. Lin, US Patent 4,667,053 (1987) to Texaco, Inc.
[22] J.J. Lin and D.C. Alexander, US Patent 4,536,604 (1985) to Texaco Inc.
[23] J.J. Lin and D.C. Alexander, US Patent 4,554, 375 (1985) to Texaco Inc.