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Tandem isomerisation–carbonylation catalysis: highly active palladium(II) catalysts for the selective methoxycarbonylation of internal alkenes to linear esters

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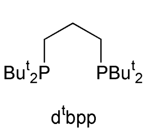
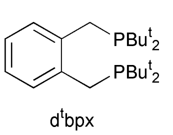
Fast, selective conversion of internal olefins to linear esters is catalysed by Pd(II) complexes of chelating bis(phospha-adamantyl)diphosphines and the catalysis is acutely sensitive to the ligand backbone and even to the diastereomer used; the results are compared with those for the PBu$^t_2$ analogue.

The palladium(II) catalysed methoxycarbonylation of olefins to esters has attracted much attention.[1] Recently, complexes of bulky alkyl diphosphines such as d^{t}bpp[2] and d^{t}bpx[3] have been

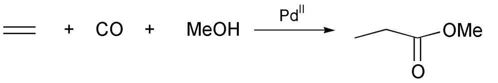


d^{t}bpp

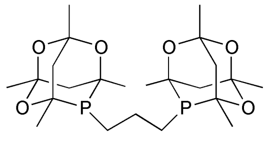


d^{t}bpx

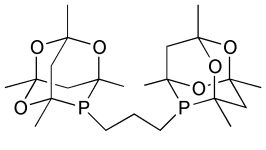
reported to give excellent catalysts for the carbonylation of ethene to methyl propanoate (MeP) [eqn. (1)].

 (1)

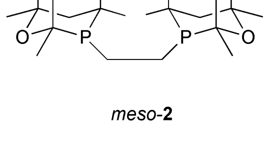
We have previously shown that adamantyl cage diphosphines *meso*/*rac*-**1** and *meso*/*rac*-**2** and their complexes are readily



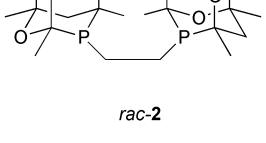
meso-**1**



rac-**1**



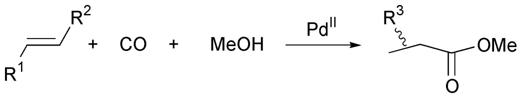
meso-**2**



rac-**2**

prepared.[4] We report here that *in situ* generated palladium(II) complexes of *meso*/*rac*-**1** and **2** catalyse the carbonylation of ethene and terminal olefins with comparable activity and selectivity to their PBu$^t_2$ substituted analogues; more importantly internal alkenes are selectively converted to linear esters, a discovery of potential application in the synthesis of detergents and nylon intermediates.[5]

Diastereomerically enriched *meso*-**1** (80%) and *rac*-**1** (96%) were separated by recrystallisation from MeOH of the *ca.* 1 : 1 diastereomeric mixture. Selected results from the carbonylation catalysis [eqn. (2)] are shown in Table 1.

 (2)

Entry 1 shows that the catalyst from *meso*/*rac*-**1** and Pd(OAc)$_2$ quantitatively forms MEP at a slightly lower rate than its d^{t}bpp analogue.[2,3,5] The effect of the diphosphine backbone is beautifully illustrated by comparison of entries 1 and 2; the C$_2$-bridged *meso*/*rac*-**2** affords a catalyst for alternating CO/C$_2$H$_4$ polymerisation, yielding polyketone of a relatively low molecular weight. Normally the most active catalysts for polyketone formation are based on C$_3$-diphosphines,[7] but the sterically demanding phosphaadamantyl moiety renders the C$_2$-diphosphine more capable of copolymerision of ethene and CO.[8]

The most significant results were obtained with the carbonylation of 1-tetradecene (entry 3) and internal isomers of tetradecene (entry 4). The catalyst derived from *meso*/*rac*-**1** gave similar selectivities to linear esters for *both* substrates; the activity for the isomerisation/carbonylation of the internal olefins is *ca.* 0.4 that of the linear olefins, indicating that isomerisation is rate limiting and the high product linearity is a consequence of the increased rate of carbonylation at the terminal olefinic position. The analogous catalyst with d^{t}bpp (entry 5) showed hardly any activity for this isomerisation/carbonylation reaction. Our results on methoxycarbonylation of internal olefins also compare favourably with traditional cobalt[9] and more recent phosphorus(III)–rhodium systems for related hydroformylation catalysis, which suffer from relatively poor isomerisation activity[10] or low product linearity.[11]

The most unexpected result was the factor of two difference in activity between enriched catalysts from *meso*-**1** and *rac*-**1** for methoxycarbonylation of propene (entries 6 and 7). A similar difference in activity is observed in the conversion of internal C$_{11}$/C$_{12}$ olefins to linear C$_{12}$/C$_{13}$ esters (entries 8 and 9). Our results demonstrate that very subtle changes in the structure of the palladium catalyst can have a large influence on catalytic activity. Activity differences between diastereomeric Pd catalysts for CO/olefin copolymerisation have been reported recently.[12]

The difference in performance between the catalysts derived from the ostensibly similar bulky alkyl diphosphines *meso*/*rac*-**1** and d^{t}bpp, may be associated with the unusual stereoelectronic characteristics of the cage ligand. We have previously shown that the Tolman cone angle[13] for *meso*/*rac*-**1** (θ = 173°) is even larger than that of d^{t}bpp (θ = 155°).[14] The σ/π-bonding ability of *meso*/*rac*-**1** can be assessed from the ν(CO) of the A$_1$ band for the [Ni(CO)$_2$(diphos)] chelates. When diphos = *meso*/*rac*-**1**, ν(CO) is 2002 cm^{-1} which is much higher than its PBu$^t_2$ analogue (1976 cm^{-1}) and even higher than its PPh$_2$ analogue (1997 cm^{-1}). The inference from these IR data is that the P-atom in the phosphatrioxaadamantane cage is electronically more akin to that in a P(aryl)$_2$ than a P(alkyl)$_2$ moiety. The low σ-basicity/high π-acidity of ligands *meso*/*rac*-**1** may be

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Table 1 Palladium catalysed methoxycarbonylation of olefins[6]

Entry	Ligand[a]	Olefin[b]	*P*co/bar	*T*/°C	Rate[c]	Product (yield (%))
1	*meso*/*rac* **1**	Ethene	30	90	10000	MeP (>99)
2	*meso*/*rac* **2**	Ethene	30	90	4000	Polyketone, M_n = 2000
3	*meso*/*rac* **1**	α-C$_{14}$ olefin	30	115	310 (95)	*n*-C$_{15}$ ester (80) *br*-C$_{15}$ esters[e] (20)
4	*meso*/*rac* **1**	Internal[d] C$_{14}$ olefins	30	115	120 (93)	*n*-C$_{15}$ ester (78) *br*-C$_{15}$ esters[e] (22)
5	d^{t}bpp	Internal[d] C$_{14}$ olefins	30	115	5 (10)	*n*-C$_{15}$ ester (75) *iso*-C$_{15}$ esters (25)
6	*rac* (96%) **1**	Propene	20	60	1000	*n*-Butyrate (81) Isobutyrate (19)
7	*meso* (80%) **1**	Propene	20	60	2000	*n*-butyrate (77) Isobutyrate (23)
8	*rac* (96%) **1**	Internal[d] C$_{11}$/C$_{12}$ olefin	15	115	100 (93)	*n*-C$_{12}$/C$_{13}$ esters (82) *br*-C$_{12}$/C$_{13}$ esters[e] (18)
9	*meso* (80%) **1**	Internal[d] C$_{11}$/C$_{12}$ olefin	15	115	160 (97)	*n*-C$_{12}$/C$_{13}$ esters (80) *br*-C$_{12}$/C$_{13}$ esters[e] (20)

[a] *meso*/*rac*-**1** and **2** is *ca.* 1 : 1 mixture of diastereomeric diphosphines. [b] 20 Bar ethene, 20 ml liquid propene or 20 ml olefin feed. [c] mol(mol) Pd h^{-1}; average activity over conversion (% in parentheses) after 5 h (entries 3 and 4), 10 h (entries 5, 8 and 9) or after complete consumption of olefin (ethylene and propylene experiments). [d] Thermodynamically equilibrated internal olefin mixture (<0.2% α-olefins). [e] Of which typically *ca.* 65% α-methyl, 35% higher alkyl branching.

traced to a combination of the effect of the electronegative oxygen atoms α to phosphorus and, perhaps more importantly, the effect of the acute (*ca.* 90°) C–P–C angle imposed by the cage.[15] Palladium–dppp isomerisation–carbonylation catalysts are known,[16] but the rate of hydroformylation of internal octenes was shown to be a factor of eight lower than the initial rate observed with 1-octene[17] and thus we cannot rationalise the observed catalysis on a purely electronic basis.

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6 Typical reaction conditions: 0.1 mmol (22.5 mg) Pd(OAc)$_2$, 0.15 mmol (71 mg) diphosphine and 0.25 mmol (17.2 μL) methanesulfonic acid were dissolved in 50 ml methanol in a 250 ml Hastelloy C autoclave. After flushing the closed autoclave three times with 40 bar N$_2$, it was first pressurised with 20 bar of C$_2$H$_4$ and secondly with 30 bar CO. After 30 min the autoclave was heated to reaction temperature, and kept at this temperature by a Thermo-Electric 100 temperature control unit. The pressure was continuously recorded by using a Transamerica Instruments pressure transducer, series 2000. Activity data during the experiment were calculated from the pressure decrease with time and from the GLC analysis of the reaction product at the end of the reaction period, performed on a Perkin-Elmer 8500 equipped with two capillary columns, DBI 30 m and FFAP 50 m.

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