Hydrogenation of Acrylic Acids catalysed by Complexes of Rhodium(I) containing Mixed Anhydrides of Acrylic and Diphenylphosphinous Acids†

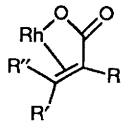
Ahmed Iraqi, Neil R. Fairfax, Sheila A. Preston, Domenico C. Cupertino, Derek J. Irvine and David J. Cole-Hamilton *

Chemistry Department, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK

Complexes of the form $[RhCl(PPh_3)_n(Ph_2PO_2CCR{=}CR'R'')]$ ($n = 1$ or 2) or $[Rh(PPh_3)_2(Ph_2PO_2CCR{=}CR'R'')]PF_6$ (R,R',R'' = H, alkyl or aryl) have been shown to be more effective for the catalytic hydrogenation of acrylic acids in the presence of added base (KOH or NEt_3) than is $[RhCl(PPh_3)_3]$. Mechanistic studies show that the active species is $[Rh(O_2CCR{=}CR'R'')(PPh_3)(Ph_2PO_2CCR{=}CR'R'')]$, in which the mixed anhydride is bound through both the phosphorus atom and the double bond. After hydrogenation of the double bond of the mixed anhydride, new substrate is introduced by a base-catalysed transesterification reaction at the phosphorus atom of the mixed anhydride. This is modelled in the reactions of $[RhCl(PPh_3)_2(Ph_2PO_2CCH_2CH_2Me)]$, which exists in two isomeric forms, one with binding of the mixed anhydride only through P and the other with binding of the mixed anhydride through P and O, or of $[Rh(PPh_3)_2(Ph_2PO_2CCH_2CH_2Me)]PF_6$ with $MeCH{=}CHCO_2^-$, which give $[Rh(O_2CCH{=}CHMe)(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$ in high yield. Hydrogenation of hexa-2,4-dienoic acid gives hex-4-enoic acid and hexanoic acid and evidence is presented that these two products are obtained from hydrogenation of the mixed anhydride (hex-4-enoic acid as product) or of the directly bonded anion (hexanoic acid as product). Attempts to promote high enantioselectivity in the hydrogenation of $PhCH{=}CMeCO_2H$ by using $[Rh(P{-}P^*)(Ph_2PO_2CCMe{=}CHPh)]PF_6$ (P–P* = a chiral diphosphine) were frustrated by the displacement of the mixed anhydride and the formation of $[Rh(P{-}P^*)(Ph_2POPPh_2)]PF_6$. Enantiomeric excesses of only *ca.* 10% were achieved.

We have reported previously on rhodium complexes containing the mixed anhydride ligands $Ph_2PO_2CCR{=}CR'R''$, in which three types of binding, through P, through P and O or through P and the double bond can be observed.[1,2] The exact binding mode obtained depends upon the nature of the substituents on the double bond, the nature of the other ligands in the complex, and the charge on the metal centre.

Many of the more successful stereoselective reactions of double bonds, such as asymmetric hydrogenation of α-amidocinnamic acids[3] or Sharpless epoxidation,[4] are known to involve stabilisation of binding of the double bond by co-ordination of a remote atom (usually oxygen). Even in asymmetric hydrogenations of prochiral acrylic acids, it is often observed[5] that higher conversions and enantiomeric excesses are obtained in the presence of base (NEt_3) and this can probably be attributed to binding of the acid in a chelate fashion (*via* O and the double bond), as in **I**.



I

In view of the observed potential for chelate binding in the mixed anhydride complexes, we have examined them as potential hydrogenation catalysts, with a view to promoting regio- and/or stereo-selective reactions. We now report the results of these studies, for which a preliminary communication has appeared.[6]

† *Non-SI unit employed:* atm = 101 325 Pa.

Results

(*a*) *Catalytic Studies.*—Passing hydrogen through a solution of $[RhCl(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)]$ in benzene causes changes in the ^1H NMR spectrum which clearly show that hydrogen addition occurs to the double bond to give $[RhCl(PPh_3)_2(Ph_2PO_2CCH_2CMe_2H)]$. However, carrying out this reaction in the presence of excess $Ph_2PO_2CCH{=}CMe_2$ does not lead to catalytic hydrogenation of the double bond. This behaviour contrasts with that observed by Jackson *et al.*[7] for the phosphine $Ph_2PCH_2CH{=}CH_2$, where catalytic hydroformylation can be observed using $[RhH(CO)(PPh_3)_3]$. The failure of this reaction in our case presumably arises because of the low lability of the mixed anhydride compared with that of PPh_3 or hydroformylated $Ph_2PCH_2CH{=}CH_2$. For the mixed anhydrides, the reaction is further complicated by the possible formation of $[RhCl(PPh_3)(Ph_2POPPh_2)]$ when more than one molar equivalent of $Ph_2PO_2CCR{=}CR'R''$ is reacted with $[RhCl(PPh_3)_3]$.[8] This reaction has been observed for a range of different alkene substituents, although not for R = H, R' = R'' = Me.[2]

Catalytic chemistry is also not observed if the hydrogenation of $[RhCl(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)]$ is carried out in the presence of the excess $Me_2C{=}CHCO_2H$. This result is not surprising since, although transesterification of trivalent phosphinites is well known,[9] and indeed, unco-ordinated $Ph_2PO_2CCH{=}CMe_2$ reacts with $MeCO_2H$ to give Ph_2PO_2CMe,[1] such acid-catalysed transesterification reactions occur *via* initial protonation of the lone pair. In both phosphorus(V) compounds and metal complexes, the lone pair is not available for protonation and hence acid-catalysed transesterifications do not occur.[10]

In contrast, base-catalysed transesterification of *e.g.* trialkyl phosphates is well known[11] and it has been reported[12] that the phosphinite complex $[Mo(CO)_4(Me_2POC_5H_4N)]$ reacts with lithium salts of allyl alcohols, including $Li[OCH_2CH{=}CMe_2]$,

Table 1 Hydrogenation of substituted propenoic acids and hexene

	% Conversion[a]	
Substrate	$[RhCl(PPh_3)_3]$	$[RhCl(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)]$
$Me_2C{=}CHCO_2H$	26.7	80.0
$PhCH{=}CMeCO_2H$	14	68.2 (13[b])
$MeCH{=}CHCO_2H$	75.8 (31[b])	100 (76[b])
$MeCH{=}CHCH{=}CHCO_2H$	10.6[c]	64.7[d]
Hex-1-ene[e]	22	10

[a] Conditions: [catalyst] = 3×10^{-3} mol dm^{-3}, [substrate] = 6×10^{-2} mol dm^{-3}, KOH = 4×10^{-2} mol dm^{-3}, in acetone (5 cm^3), 17 h, 22 °C, $p(H_2)$ = 3 atm. [b] Conditions as *a*, but t = 2 h. [c] Hexanoic acid. [d] Hex-4-enoic acid (52.3%), hexanoic acid (47.7%). [e] Conditions: [catalyst] = 10^{-3} mol dm^{-3}, [hex-1-ene] = 0.73 mol dm^{-3} in toluene, 10 cm^3, 20 min, 22 °C, $p(H_2)$ = 1 atm.

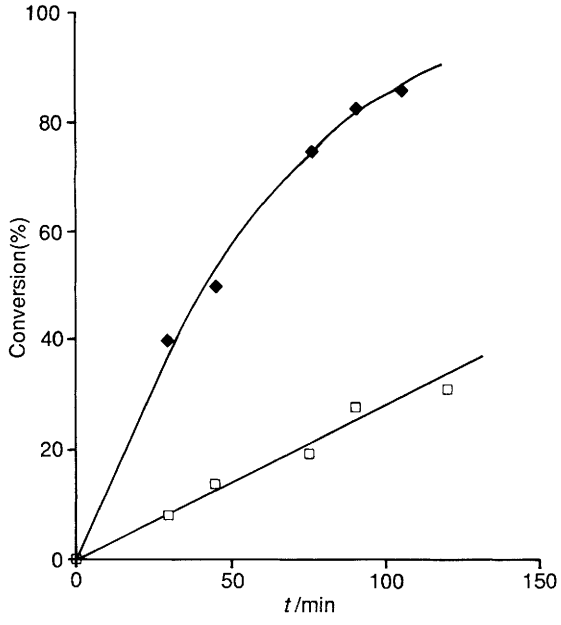


Fig. 1 Time dependence of the hydrogenation of $MeCH{=}CHCO_2H$ (6×10^{-2} mol dm^{-3}) in the presence of $[RhCl(PPh_3)_3]$ (□) (3×10^{-3} mol dm^{-3}) or $[RhCl(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)]$ (◇) (3×10^{-3} mol dm^{-3}) and KOH (4×10^{-2} mol dm^{-3}) in acetone (5 cm^3) at 22 °C; $p(H_2)$ = 3 atm

Table 2 Hydrogenation of 2-methyl-3-phenylpropenoic acid to 2-methyl-3-phenylpropanoic acid and of hexa-2,4-dienoic acid using various catalyst precursors in the presence of triethylamine

Catalyst precursor	t/h	Conversion (%)	
2-methyl-3-phenylpropenoic acid			
$[RhCl(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$	20	100	
$[RhCl(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]$	2	45	
	20	100	
$[Rh(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]PF_6$	2	62	
	20	100	
hexa-2,4-dienoic acid			
		a	*b*
$[RhCl(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$	20	77	23
$[RhCl(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]$	2	24	24
	20	72	19
$[Rh(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]PF_6$	2	23	23
	20	82	18
hex-4-enoic acid			
$[Rh(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]PF_6$	2	20	

[a] Hexanoic acid. [b] Hex-4-enoic acid.

to give transesterification products, *e.g.* $[Mo(CO)_4(Me_2PO\text{-}CH_2CH{=}CMe_2)]$. These observations led us to study the hydrogenation of acrylic acids under basic conditions using *e.g.* $[RhCl(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)]$ as catalyst precursor.

The yields of hydrogenation products from acrylic acids using $[RhCl(PPh_3)_3]$ and $[RhCl(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)]$ under various different conditions are compared in Table 1, together with their relative efficiencies for hydrogenating hex-1-ene, a simple alkene for which chelate binding is not possible. For hex-1-ene, $[RhCl(PPh_3)_3]$ is approximately twice as efficient a hydrogenation catalyst as $[RhCl(PPh_3)_2(Ph_2\text{-}PO_2CCH{=}CMe_2)]$, as would be expected [13] on account of the higher basicity and lower lability of the mixed anhydride than of PPh_3. However, for all of the acrylic acids studied, the mixed anhydride complex is a more efficient catalyst than $[RhCl(PPh_3)_3]$ (see Fig. 1 for the hydrogenation of $MeCH{=}CH\text{-}CO_2H$), suggesting that a different mechanism is operating for hydrogenation of the acrylic acids than for hydrogenation of hex-1-ene. The relative rates for hydrogenation for the different acrylic acids appear to be dominated by steric factors, with the more highly substituted alkenes undergoing hydrogenation more slowly than *e.g.* $MeCH{=}CHCO_2H$. Similar observations have been made [13] in the hydrogenation of simple alkenes in the presence of $[RhCl(PPh_3)_3]$.

A further indication that different mechanisms are operating for $[RhCl(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)]$ from that for $[RhCl(PPh_3)_3]$ comes from the observation that the products obtained from hexa-2,4-dienoic acid with the two catalysts are different. Thus, $[RhCl(PPh_3)_3]$ gives hexanoic acid with traces of hex-2-enoic acid, whilst under similar conditions, at least at short reaction times, the mixed-anhydride containing catalysts give a mixture of hex-4-enoic and hexanoic acids. This reaction is of particular interest since studies on other catalysts for hydrogenation of hexa-2,4-dienoic acid have demonstrated that hex-2-enoic or hex-3-enoic acids are generally the intermediate products.[14,15]

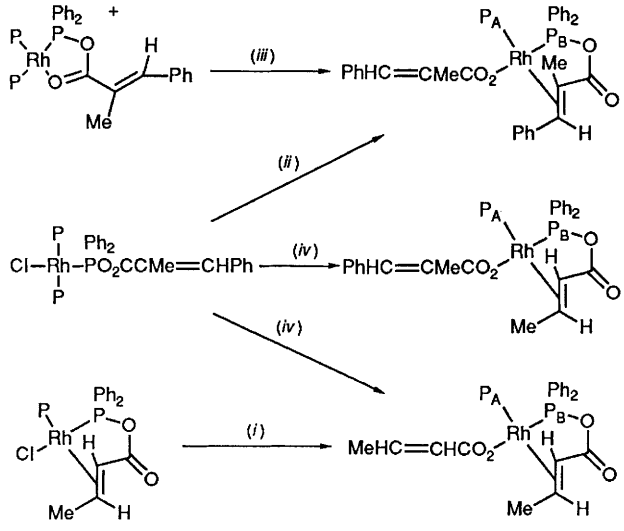
In Table 2, various different complexes have been selected as catalyst precursors to illustrate different modes of binding of the mixed anhydrides but, at least in the early stages of the reactions, the yield and selectivities of the hydrogenation of 2-methyl-3-phenylpropenoic acid or of hexa-2,4-dienoic acid under similar conditions are very similar, possibly indicating that all of these catalyst precursors generate a similar active intermediate.

The effect of the base upon the efficiency of the catalytic process is shown in Table 3 and, although it appears that NEt_3 is more efficient than using the potassium salt of the substrate acrylic acid (prepared either *in situ* from the acid and KOH or added directly) this almost certainly arises from the fact that the potassium salts have very low solubility in the reaction solvent [tetrahydrofuran (thf) or acetone], whilst the triethylammonium salts are totally soluble and these reactions give clear orange solutions.

(*b*) *Mechanistic Studies.*—In order to probe the mechanism

of these unusual reactions catalysed by $[RhCl(PPh_3)_2(Ph_2PO_2CCR{=}CR'R'')]$ and related compounds, we have carried out stoichiometric reactions with a view to isolating key intermediates and identifying individual reaction steps.

Since the catalytic reactions are carried out in the presence of excess $[O_2CCR{=}CR'R'']^-$, we have reacted various precursors with the appropriate acrylic acid anion (as its potassium or triethylammonium salt) in the absence of hydrogen. In all cases, new complexes are observed which have ^{31}P NMR data (Table 4) showing two *cis* phosphorus atoms, one from PPh_3 and the other from a mixed anhydride bound through the phosphorus atom and the double bond. These complexes have been isolated as yellow crystalline solids and characterised as $[Rh(O_2CCR{=}CR'R'')(PPh_3)(Ph_2PO_2CCR{=}CR'R'')]$ (see Scheme 1). ^1H NMR data confirm the presence of two olefinic double bonds—one bound to the metal and the other free (see Table 5).



Scheme 1 Reactions of mixed anhydride complexes of different types with substituted propenoic acids, (*i*) 20× $K[O_2CCH{=}CHMe]$ or 20 × $[NHEt_3][O_2CCH{=}CHMe]$, 30 °C, 2 h, thf, 100%; (*ii*) 15× $K[O_2CCMe{=}CHPh]$, 30 °C, 2 h, thf, 80%; (*iii*) 15× $[NHEt_3][O_2CCMe{=}CHPh]$; 30 °C, 3 h, thf, 90%; (*iv*) 15× $K[O_2CCH{=}CHMe]$, 30 °C, 3 h, thf, 100%; 60% **A**, 40% **B**. P = PPh_3

Table 3 Effect of different bases on the hydrogenation of 2-methyl-3-phenylpropenoic acid catalysed by $[Rh(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]PF_6$ in acetone

Base	*t*/h	Conversion (%)
KOH	17	68
a	18	36[b]
NEt_3	20	100[c]
	2	62[c]

[a] Substrate introduced as potassium salt. [b] 21% in thf. [c] In thf.

Although this type of complex is formed from all of the precursors shown in Scheme 1, complete conversion to it is not always observed. Interestingly, the reaction of $[Rh(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]PF_6$ with $MeHC{=}CHCO_2H$ in the presence of NEt_3 gives a mixture of $[Rh(O_2CCH{=}CHMe)(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$ and $[Rh(O_2CCMe{=}CHPh)(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$ in a ratio 2:3 (Scheme 1).

Reaction of $[Rh(O_2CCH{=}CHMe)(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$ with hydrogen (3 atm, 2 h) in CD_2Cl_2 causes a colour change from yellow to orange and the ^1H NMR spectrum shows signals in the aliphatic region from $-O_2CCH_2CH_2Me$. Although we have been unable to isolate a rhodium containing product from this solution, it is clear that both the double bond of the mixed anhydride *and* that of the co-ordinated anion are hydrogenated.

In an attempt to investigate the step by which the product carboxylic acid is released from the metal complex, we have synthesized $[RhCl(PPh_3)_2(Ph_2PO_2CCH_2CH_2Me)]$ from the reaction of $[RhCl(PPh_3)_3]$ with $Ph_2PO_2CCH_2CH_2Me$. The complex isolated from this reaction has the correct stoichiometry but apparently exists in two forms. One, form **A**, has spectroscopic properties as expected for the complex having the mixed anhydride bound only through the phosphorus atom, whilst form **B** is fluxional. At low temperature the ^{31}P NMR spectrum consists of a doublet of triplets at δ 131.7 and a doublet of doublets at δ 33.6. On warming, these signals broaden and at temperatures above ambient (75 °C for 0.5 h) they disappear irreversibly with the formation of PPh_3, a complex containing two phosphorus atoms, probably $[RhCl(PPh_3)(Ph_2PO_2CCH_2CH_2Me)]$, and a third complex in which all the phosphorus atoms are equivalent (δ 89, J_{Rh-P} = 154 Hz). The non-fluxional form is stable under these conditions.

We assign tentatively the fluxional compound as being an isomer of $[RhCl(PPh_3)_2(Ph_2PO_2CCH_2CH_2Me)]$ which is five-co-ordinate with binding through P and O. The fluxionality probably arises from a Berry pseudorotation but PPh_3 is more easily lost from this complex to form the dimer than from the four-co-ordinate isomer.

Treatment of $[RhCl(PPh_3)_2(Ph_2PO_2CCH_2CH_2Me)]$ with $TlPF_6$ produces almost exclusively $[Rh(PPh_3)_2(Ph_2PO_2CCH_2CH_2Me)]^+$, with binding of the mixed anhydride through P and O, with a small amount (< 3%) of a compound showing a

Table 4 ^{31}P NMR data for rhodium complexes measured in CD_2Cl_2 at 298 K[a]

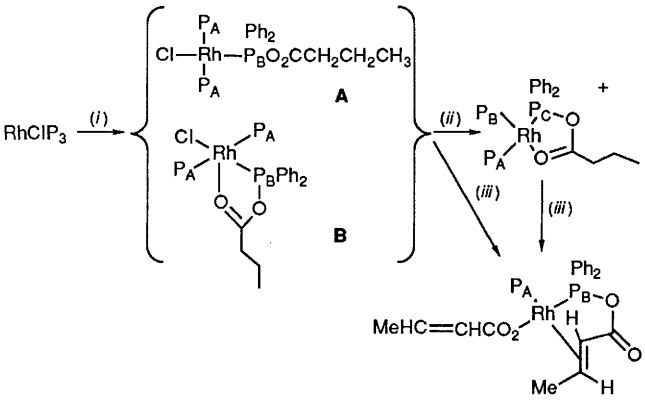
	δ			*J*/Hz					
Complex	P_A	P_B	P_C	Rh–P_A	Rh–P_B	Rh–P_C	P_A–P_B	P_A–P_C	P_B–P_C
$[RhCl(PPh_3)_2(Ph_2PO_2CCH_2CH_2Me)]$	31.8 (dd)	48.5 (dt)	—	142	190	—	38	—	—
	33.0 (br)	131.0 (br)	—	—	—	—	—	—	—
$[RhCl(PPh_3)_2(Ph_2PO_2CCH_2CH_2Me)]$[b]	31.3 (dd)	47.8 (dt)	—	145	192	—	40	—	—
	33.6 (dd)	131.7 (dt)	—	140	220	—	42	—	—
$[Rh(PPh_3)_2(Ph_2PO_2CCH_2CH_2Me)]PF_6$	26.3 (ddd)	48.7 (ddd)	176.5 (ddd)	136	183	162	36	320	36
$[Rh(diop)(Ph_2PO_2CCMe{=}CHPh)]PF_6$	13.4 (ddd)	31.2 (ddd)	170.7 (ddd)	134	177	153	42	326	31
$[Rh(chiraphos)(Ph_2PO_2CCMe{=}CHPh)]PF_6$	58.3 (ddd)	75.2 (ddd)	168.1 (ddd)	137	171	151	46	328	26
$[Rh(PPh_3)(Ph_2PO_2CCH{=}CHMe)$-$(O_2CCH{=}CHMe)]$	25.9 (dd)	127.0 (dd)	—	146	146	—	30	—	—
$[Rh(PPh_3)(Ph_2PO_2CCMe{=}CHPh)$-$(O_2CCMe{=}CHPh)]$	25.3 (dd)	126.0 (dd)	—	139	145	—	31	—	—
$[Rh(PPh_3)(Ph_2PO_2CCH{=}CHMe)$-$(O_2CCMe{=}CHPh)]$	26.31(dd)	127.1 (dd)	—	146	146	—	31	—	—

[a] For assignments, see Schemes. [b] At 213 K.

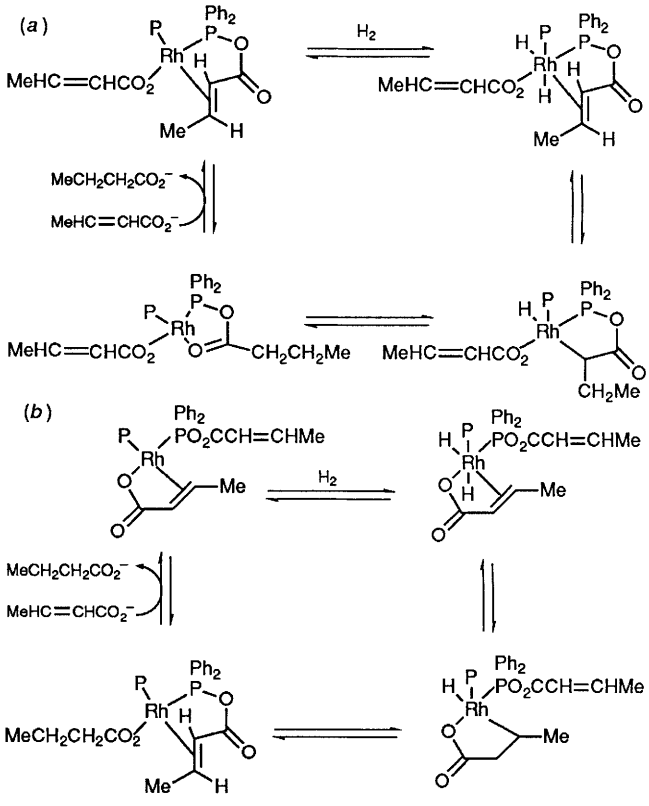
Table 5 ^{1}H NMR spectra (δ) for new rhodium complexes measured in CD_2Cl_2 at 298 K

	Mixed anhydride ligand		$O_2CCR{=}CR'R''$	
Complex	Me	H	Me	H
$[RhCl(PPh_3)_2(Ph_2PO_2CCH_2{}^cCH_2{}^bCH_3{}^a)]$[a]	[a]0.6 (t) 1.26 (m)	[b]0.85 (tq) [c]1.26 (m) 1.60(tq) 2.27 (t)	— —	— —
$[Rh(PPh_3)_2(Ph_2PO_2CCH_2{}^cCH_2{}^bCH_3{}^a)]PF_6$	[a]0.53 (t)	[b]0.98 (tq) [c]2.26 (t)		
$[Rh(PPh_3)(Ph_2PO_2CCH^c{=}CH^bMe^a)(O_2CCH^f{=}CH^cMe^d)]$	[a]1.11 (d)	[b]4.07 (br) [c]3.31 (br)	[d]1.58 (d)	[e]6.27 (m) [f]5.20 (br d)
$[Rh(PPh_3)(Ph_2PO_2CCMe^a{=}CH^bPh)(O_2CCMe^c{=}CH^dPh)]$	[a]1.95 (d)	[b]4.70 (br)	[c]1.75 (s)	*b*
$[Rh(PPh_3)(Ph_2PO_2CCH^c{=}CH^bMe^a)(O_2CCMe^d{=}CH^ePh)]$	[a]1.10 (d)	[b]3.96 (br) [c]3.27 (br)	[d]1.73 (s)	*c*

[a] At 213 K (2 isomers observed). [b] H^d Obscured by phenyl resonance. [c] H^e Obscured by phenyl resonance.



Scheme 2 Preparation and reaction of complexes containing mixed anhydrides of butyric and diphenylphosphinous acids. (*i*) $Ph_2PO_2CCH_2CH_2Me$: (*ii*) $TlPF_6$; (*iii*) 10× $[NHEt_3][O_2CCH{=}CHMe]$. P = PPh_3



Scheme 3 Proposed mechanisms for the hydrogenation of acrylic acids catalysed by $[Rh(O_2CCR{=}CR'R'')(PPh_3)(Ph_2PO_2CCR{=}CR'R'')]$. (*a*) Steps involve reactions of the mixed anhydride; (*b*) steps involve reactions of metal bound anion. P = PPh_3

Discussion

The stoichiometric reactions described above lead us to propose the mechanism shown in Scheme 3 for the hydrogenation of acrylic acids under basic conditions catalysed by rhodium complexes containing ligands which are mixed anhydrides of diphenylphosphinous acids with acrylic acids. The nature of the active species has been identified unequivocally as $[Rh(O_2CCR{=}CR'R'')(PPh_3)(Ph_2PO_2CCR{=}CR'R'')]$ with R, R′ and R″ arising from the substrate acrylic acid not necessarily from the catalyst precursor. These compounds react with H_2 to hydrogenate both double bonds with similar rates, hence the two pathways shown in Scheme 3. The key new catalytic step, which again has been unequivocally demonstrated is the expulsion of the hydrogenated product and reintroduction of the substrate *via* base-catalysed *trans*-esterification at the co-ordinated phosphorus atom. This type of reaction is very rare, although a similar step has been invoked in the mechanism proposed for the deuteriation of the *ortho* positions in phenol catalysed by $[RuH\{C_6H_4OP(OPh)_2\}\{P(OPh)_3\}_3]$;[16] however, in this case the transesterification is of free $P(OPh)_3$ and is acid catalysed.[16]

The selectivity in the hydrogenation of hexa-2,4-dienoic acid is of particular interest since these mixed anhydride catalysts offer the possibility of selectively removing a double bond which is conjugated with two other double bonds. These appear to be the only catalysts available for this kind of reaction. We believe that this selectivity occurs because the mixed anhydride binds preferentially through P and the C^2 double bond. Indeed this binding has been crystallographically demonstrated in the complex $[\{RhCl(Ph_2PO_2CCH{=}CHCH{=}CHMe)\}_2]$.[1] Unfortunately, the observed selectivity is not very high and hexanoic acid is formed at a similar rate to hex-4-enoic acid. These reactions evidently proceed in parallel since hex-4-enoic acid is not readily hydrogenated in this system (Table 2).

Since $[RhCl(PPh_3)_3]$ produces largely hexanoic acid under similar conditions, it seems that this product probably arises from hydrogenation of the hexa-2,4-dienoato ligand bound

* This presumably arises from the small amount of the compound which shows a doublet (δ 89, J_{Rh-P} = 154 Hz) in the ^{31}P NMR spectrum of the starting material.

Table 6 Asymmetric hydrogenation of α-methylcinnamic acid catalysed by rhodium complexes[a]

Catalyst	p/atm	Base	t/h	Conversion (%)	Optical yield (%)[b]
[Rh(chiraphos)($Ph_2PO_2CCMe{=}CHPh$)]PF_6	3	NEt_3	48	44	5
[Rh(diop)($Ph_2PO_2CCMe{=}CHPh$)]PF_6	10	—	18	32	10
	3	NEt_3	62	40	10
	8	NEt_3	18	56	10

[a] [catalyst]:[substrate]:[base] = 1:20:30 in thf at ambient temperature. [b] Measured by ^{1}H NMR spectroscopy of *S*-methyl mandelate ester.

directly to the rhodium [Scheme 3(b)]. In this case, having one less atom in the ring formed on double bound co-ordination will lead to a lesser preference for binding of the C^2 double bond and probably will favour binding of the C^4 double bond, hence giving initially hex-2-enoic acid and subsequently complete hydrogenation. This last mechanism is the same as that occurring using [$RhCl(PPh_3)_3$] and explains why in the latter case hex-2-enoic acid is formed as an intermediate. Our failure to observe hex-2-enoic acid as an intermediate when mixed anhydride complexes are employed as catalyst presumably arises because any hex-2-enoic acid formed will readily be introduced into the mixed anhydride and hydrogenated by the first mechanism of Scheme 3(a).

Assuming this explanation to be correct, it is clear that higher selectivities to *e.g.* hex-4-enoic acid will only be observed if the substrate anion can be prevented from binding directly to the metal. Studies aimed at achieving this goal are in progress.

Asymmetric Catalysis.—In order to try to use the chelate stabilisation of the alkene by co-ordination of $-PPh_2$ to induce high enantioselectivities, we have synthesized complexes of the form [Rh(P–P*)($Ph_2PO_2CCMe{=}CHPh$)]$^+$, either from reactions of [{Rh(P–P*)Cl}$_2$] with the mixed anhydride in the presence of $TlPF_6$ (P–P* = chiraphos)† or from reactions of [{RhCl($Ph_2PO_2CCMe{=}CHPh$)}$_2$] with P–P* (P–P* = diop). Although the reactions are not very clean (some [Rh(P–P*)(Ph_2POPPh_2)]$^+$ is formed as an impurity), ^{31}P NMR studies show that [Rh(P–P*)($Ph_2PO_2CCMe{=}CHPh$)]$^+$ are formed in high yield. These complexes are both active for hydrogenation of 2-methyl-3-phenylpropenoic acid under various basic conditions (Table 6) but rates and, more importantly, enantiomeric excesses, obtained by derivatisation as the *S*-methyl mandelate esters,[17] are not high (≈10%).

In order to try to understand these low enantiomeric excesses, we have investigated the reactions of [Rh(P–P*)($Ph_2PO_2CCMe{=}CHPh$)]$^+$ with [$NHEt_3$][$PhCH{=}CMeCO_2$]. In both cases, complete conversion to [Rh(P–P*)(Ph_2POPPh_2)]$^+$ occurs and this would not be expected to give high optical yields in asymmetric hydrogenation reactions, since chelate binding of the double bond no longer occurs.

This formation of the Ph_2POPPh_2 ligand under these conditions contrasts with the behaviour of *e.g.* [Rh(PPh_3)$_2$($Ph_2PO_2CCR{=}CR'R''$)]$^+$ in which PPh_3 is replaced by an acrylate anion (see above). We believe that for the chiral complexes, which contain bidentate diphosphines, attack of the acrylate anion displaces the mixed anhydride ligand and some of this can then attack co-ordinated mixed anhydride in another molecule of starting complex to give the Ph_2POPPh_2 ligand. The formation of [$RhCl(PPh_3)(Ph_2POPPh_2)$] from [$RhCl(PPh_3)_3$] and $Ph_2PO_2CCH{=}CH_2$ has been shown to involve similar reaction steps.[8,18]

Experimental

Microanalyses were by the University of St. Andrews microanalytical service. NMR spectra were recorded on Brüker Associates WP 80 and AM 300 spectrometers operating in the Fourier transform mode with (for ^{31}P) noise proton decoupling. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer as Nujol mulls between caesium iodide plates.

All manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk line and catheter tubing techniques. All solvents were purified by distillation from calcium hydride (CH_2Cl_2) or sodium diphenylketyl [toluene, light petroleum (b.p. 40–60 °C), diethyl ether and thf].

The complexes [$RhCl(PPh_3)_3$],[19] [$RhCl(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)$],[2] [$RhCl(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)$],[2] [$Rh(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)$]$PF_6$[2] and [$RhCl(PPh_3)(Ph_2PO_2CCH{=}CHMe)$][2] were made by literature procedures.

Syntheses.—Chloro(diphenylphosphino butyrate)bis(triphenylphosphine)rhodium(I). (*a*) *Preparation of* $Ph_2PO_2CCH_2CH_2Me$. To a cooled (−10 °C) solution of $MeCH_2CH_2CO_2H$ (3 g, 34.0 mmol) in thf (50 cm^3) was added a solution of PPh_2Cl (7.5 g, 34.0 mmol) in thf (30 cm^3) over 5 min followed by a solution of NEt_3 (3.44 g, 34.0 mmol) in thf (50 cm^3). The mixture was stirred at (−10 °C) for 1 h, the ammonium salt formed ($NHEt_3Cl$) was then removed by filtration and the solution was evaporated to dryness under reduced pressure to give the product as a viscous colourless liquid. Yield 8.8 g (95%). ^{31}P NMR (C_6D_6); singlet at δ 97.5, ^{1}H NMR: δ 0.8 (t, 3 H), 1.66 (m, 2 H), 2.35 (t, 2 H) and 7.0–8.0 (m, 10 H).

(*b*) To a solution of [$RhCl(PPh_3)_3$] (0.7 g, 0.75 mmol) in thf (40 cm^3) was added a solution of $Ph_2PO_2CCH_2CH_2Me$ (0.21 g, 0.76 mmol) in thf (30 cm^3). On addition the solution gradually became orange. The solution was stirred for 90 min, and the solvent was then reduced in volume *in vacuo* to 3 cm^3. Light petroleum (50 cm^3) was added to precipitate the product as an orange powder that was filtered off and dried *in vacuo*. Yield 0.6 g (85%) (Found: C, 66.85; H, 5.25. $C_{52}H_{47}ClO_2P_3Rh$ requires C, 66.80; H, 5.05%).

Diphenylphosphino butyratebis(triphenylphosphine)rhodium(I) *hexafluorophosphate*. To a solution of [$RhCl(PPh_3)_2(Ph_2PO_2CCH_2CH_2Me)$] (0.164 g, 0.17 mmol) in thf (40 cm^3) was added $TlPF_6$ (0.062 g, 0.17 mmol). On addition a fine white precipitate formed. The mixture was stirred for 1 h, filtered and evaporated to dryness *in vacuo*. The orange solid was analysed by ^{31}P NMR spectroscopy showing *ca.* 95% yield with traces of [$Rh(PPh_3)_2(Ph_2POPPh_2)$]$^+$ as an impurity and a compound showing a doublet at δ 40.2 (J = 181 Hz).

Diphenylphosphino E-2-*methyl*-3-*phenylpropenoate*[(+)-4,5-*bis*(*diphenylphosphinomethyl*)-2,2-*dimethyl*-1,3-*dioxolane*]-*rhodium*(I) *hexafluorophosphate*. To a solution of [{RhCl($Ph_2PO_2CCMe{=}CHPh$)}$_2$] (0.418 g, 0.43 mmol) in thf (30 cm^3) was added a solution of (+)-diop (0.43 g, 0.86 mmol) in thf (30 cm^3). The solution was stirred for 1 h, $TlPF_6$ (0.301 g, 0.86 mmol) was added giving a fine white precipitate (TlCl) which was filtered off after 40 min of reaction. The solution was reduced *in vacuo* to a total volume of 3 cm^3; light petroleum was added giving an orange precipitate which was filtered off and dried under vacuum. Yield 0.9 g, 95%. ^{31}P NMR studies showed contamination with *ca.* 20% [$Rh(diop)(Ph_2POPPh_2)$]PF_6.

(2R,3R)(+)-*Bis*(*diphenylphosphino*)*butane*(*diphenylphosphino* E-2-*methyl*-3-*phenylpropenoate*)*rhodium*(I) *hexafluorophosphate*. To a solution of [{RhCl(C_8H_{14})$_2$}$_2$] (0.171 g, 0.24

† diop is (+)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane; chiraphos is (2*R*,3*R*)-(+)-bis(diphenylphosphino)butane.

mmol) in thf (20 cm^3) was added a solution of (+)-chiraphos (0.204 g, 0.48 mmol) in thf (30 cm^3). The solution was stirred for 45 min, evaporated to dryness *in vacuo*, washed with light petroleum (50 cm^3) and dried *in vacuo*. The residue was dissolved in thf (20 cm^3), $Ph_2PO_2CCMe{=}CHPh$ (0.165 g, 0.46 mmol) in thf (30 cm^3) was added and the solution stirred for 30 min; $TlPF_6$ (0.166 g, 0.48 mmol) was then added giving a fine white precipitate which was filtered off after stirring for 40 min. The solution was reduced *in vacuo* to a total volume of 3 cm^3 before addition of light petroleum (50 cm^3) giving an orange precipitate which was filtered off and dried under vacuum. The orange solid was analysed by ^{31}P NMR showing *ca.* 70% yield with traces of $[\{Rh(chiraphos)Cl\}_2]$ and $[Rh(chiraphos)(Ph_2POPPh_2)]PF_6$ as impurities.

Diphenylphosphino E-2-*methyl*-3-*phenylpropenoate*(2-*methyl*-3-*phenylpropenoato*)(*triphenylphosphine*)*rhodium*(I). This compound was obtained from several experiments:

(*i*) To a suspension of $K[O_2CCMe{=}CHPh]$ (0.5 g, 2.5 mmol) in CH_2Cl_2 (40 cm^3) was added a solution of $[RhCl(PPh_3)_2(Ph_2PO_2CCMeCHPh)]$ (0.15 g, 0.16 mmol) in CH_2Cl_2 (20 cm^3). The mixture was stirred for 2 h and then filtered to eliminate excess $K[O_2CCMe{=}CHPh]$. The solution was evaporated to dryness and the product identified spectroscopically but was contaminated with part of the unreacted starting material $\{[RhCl(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]\}$. 80% Conversion was observed by NMR analyses.

(*ii*) When treating $[Rh(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]PF_6$ with $K[O_2CCMe{=}CHPh]$ in CH_2Cl_2 under similar conditions for 20 h, the isolated product of the reaction contained only 35% $[Rh(PPh_3)(Ph_2PO_2CCMe{=}CHPh)(O_2CCMe{=}CHPh)]$ the rest being the starting material.

(*iii*) Reaction of $[Rh(PPh_3)(Ph_2PO_2CCMe{=}CHPh)]PF_6$ with an excess of $[NHEt_3][PhCH{=}CMeCO_2]$ (prepared *in situ*) in CD_2Cl_2 led after 3 h to the conversion of 90% of the starting material into $[Rh(PPh_3)(Ph_2PO_2CCMe{=}CHPh)(O_2CCMe{=}CHPh)]$.

(*iv*) A similar reaction involving $[RhCl(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]$ and an excess of $[NHEt_3][PhCH{=}CMeCO_2]$ in CD_2Cl_2 led after 20 min to the conversion of 40% of the starting material to $[Rh(PPh_3)(Ph_2PO_2CCMe{=}CHPh)(O_2CCMe{=}CHPh)]$. In all these experiments the products were characterised by NMR spectroscopy.

But-2-*enoato*(*diphenylphosphino but*-2-*enoate*)(*triphenylphosphine*)*rhodium*(I). Different reactions can lead to this compound. It has been isolated in the following experiments:

(*i*) To a solution of $[RhCl(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$ (0.25 g, 0.37 mmol) in thf (70 cm^3) was added $K[O_2CCH{=}CHMe]$ (0.41 g, 3.30 mmol). The mixture was stirred for 2 h and then filtered to eliminate the excess of $K[O_2CCH{=}CHMe]$. The solution was then evaporated under vacuum to 3 cm^3 and light petroleum (50 cm^3) was added to give an orange microcrystalline powder that was filtered off and dried under vacuum. Yield 0.20 g (73%) (Found: C, 64.1; H, 5.3. $C_{38}H_{35}O_4P_2Rh$ requires C, 63.3; H, 4.9%).

(*ii*) A similar reaction, but using $[NHEt_3][MeHC{=}CHCO_2]$ prepared *in situ* from $MeCH{=}CHCO_2H$ and NEt_3, the product was isolated and characterised spectroscopically.

(*iii*) To a suspension of $K[O_2CCH{=}CHMe]$ (0.16 g, 1.29 mmol) in CH_2Cl_2 (20 cm^3) was added a solution of $[RhCl(PPh_3)_2(Ph_2PO_2CCH_2CH_2Me)]$ (0.12 g, 0.13 mmol) in CH_2Cl_2 (30 cm^3). The mixture was stirred for 3 h, filtered to eliminate the excess of $K[O_2CCH{=}CHMe]$ and evaporated *in vacuo* to 2 cm^3. Light petroleum (50 cm^3) was added to give an orange powder that was filtered off and dried *in vacuo*. The product was charactised spectroscopically giving identical ^1H and ^{31}P NMR spectra to those obtained from method (*i*).

(*iv*) A similar reaction in CH_2Cl_2 using $[Rh(PPh_3)_2(Ph_2PO_2CCH_2CH_2Me)]PF_6$ and $K[O_2CCH{=}CHMe]$ led after 10 h to the same product with 100% conversion. The product was identified spectroscopically.

Reaction of $[RhCl(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]$ *with* $K[O_2CCH{=}CHMe]$. To a solution of $[RhCl(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]$ (0.23 g, 0.24 mmol) in thf (50 cm^3) was added $K[O_2CCH{=}CHMe]$ (0.31 g, 2.46 mmol). The mixture was stirred for 3 h and then filtered to remove excess $K[O_2CCH{=}CHMe]$. After evaporation to 3 cm^3, light petroleum (10 cm^3) was added to give an orange powder which was collected and dried *in vacuo*. The product was characterised as a mixture of $[Rh(O_2CCMe{=}CHPh)(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$ and $[Rh(O_2CCH{=}CHMe)(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$ in a 3:2 molar ratio by ^1H and ^{31}P NMR spectroscopy.

Catalytic Experiments.—All hydrogenation reactions were carried out in glass vessels of *ca.* 100 cm^3 capacity with a valve attached for pressuring and depressurising. Ratios of catalyst:substrate:base were 1:20:30 and reactions were carried out under 3 atm of hydrogen (total pressure) at room temperature with magnetic stirring. A typical reaction was as follows: to $[RhCl(PPh_3)_2(Ph_2PO_2CCMe{=}CHPh)]$ (0.028 g, 3×10^{-5} mol) was added $PhCH{=}CMeCO_2H$ (0.097 g, 6×10^{-4} mol) and NEt_3 (0.091 g, 9×10^{-4} mol) in thf (5 cm^3). The flask was evacuated before pressuring to 3 atm total pressure with H_2.

At the end of the catalytic reactions involving KOH as co-catalyst, the suspension was evaporated to dryness and the resulting solid was dissolved in D_2O for NMR analysis. When NEt_3 was used as co-catalyst, the catalytic solution was evaporated to dryness and the residue dissolved in CH_2Cl_2 (15 cm^3). This solution was acidified with 1 mol dm^{-3} hydrochloric acid (50 cm^3). The organic layer was then extracted, dried over $MgSO_4$ and evaporated to dryness *in vacuo* to lead to the organic acids which were characterised by ^1H NMR spectroscopy in $CDCl_3$.

Measurement of Optical Activity.[17]—The enantiomeric composition of the hydrogenated α-methylcinnamic acid was determined by conversion of the two enantiomers obtained into diastereoisomers by reaction with (*S*)-(+)-methyl mandelate. The resulting ratio of the esters was determined by direct ^1H NMR integration.

In a typical experiment, to $PhCH_2CMeHCO_2H$ (0.3 g, 1.8 mmol) (obtained from the hydrogenation of α-methylcinnamic acid) and 4-dimethylaminopyridine (0.045 g, 0.35 mmol) in CH_2Cl_2 (15 cm^3) at −10 °C, was added (*S*)-(+)-methyl mandelate (0.3 g, 1.8 mmol) and dicyclohexylcarbodiimide (0.377 g, 1.8 mmol) and the mixture was stirred for 3 h. After filtration the solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 (20 cm^3). The solution was washed with 0.5 mol dm^{-3} HCl solution (20 cm^3) and then with a saturated solution of $NaHCO_3$ and dried over $MgSO_4$ before evaporation to dryness and ^1H NMR analysis.

In some experiments the enantiomeric composition of the hydrogenated α-methylcinnamic acid product was determined by polarimetry, this method proved less reliable than the one described above.

Acknowledgements

We thank the SERC for a fellowship (to A. I.) and for a CASE. studentship (to D. J. I.) jointly with BP Research International, the RSC (to N. R. F.) and the University of St Andrews (to S. A. P.) for studentships, and Johnson Matthey plc for generous loans of rhodium salts.

References

1 D. C. Cupertino and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 1987, 443.
2 A. F. Borowski, A. Iraqi, D. C. Cupertino, D. J. Irvine, D. J. Cole-Hamilton, M. H. Harmon and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1990, 29.
3 J. Halpern, *Pure Appl. Chem.*, 1983, **55**, 99 and refs. therein.

4 C. J. Burns, C. A. Martin and K. B. Sharpless, *J. Org. Chem.*, 1989, **54**, 2826.
5 See for example C. Botteghi, S. Gladiali, M. Bianchi, U. Matteoli, P. Frediani, P. Vergamini and E. Benedetti, *J. Organomet. Chem.*, 1979, **140**, 221 and refs. therein; D. Sinau, D. Lafont, P. Descotes and T. Dayrit, *Nouveau J. Chim.*, 1983, **7**, 291 and refs. therein.
6 S. A. Preston, D. C. Cupertino, P. Palma-Ramirez and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1986, 977.
7 W. R. Jackson, P. Perlmutter and G. H. Suh, *J. Chem. Soc., Chem. Commun.*, 1987, 724; W. R. Jackson, P. Perlmutter and E. E. Tasdelen, *J. Chem. Soc., Chem. Commun.*, 1990, 763.
8 D. J. Irvine, D. J. Cole-Hamilton, J. C. Barnes and P. K. G. Hodgson, *Polyhedron*, 1989, **8**, 1575.
9 See G. M. Kosolapoff and L. Maier, *Organic Phosphorus Compounds*, Wiley, New York, 1972, vol. 4, p. 497 and refs. therein.
10 D. H. Gerlach, W. G. Peet and E. L. Muetterties, *J. Am. Chem. Soc.*, 1972, **94**, 4545.
11 See G. M. Kosolapoff and L. Maier, *Organic Phosphorus Compounds*, Wiley Interscience, New York, 1973, vol. 6, p. 237, and refs. therein.
12 R. T. De Pue, D. B. Collum, J. W. Ziller and M. R. Churchill, *J. Am. Chem. Soc.*, 1985, **107**, 2131.
13 F. H. Jardine, *Prog. Inorg. Chem.*, 1981, **28**, 63, and refs. therein.
14 L. Simandi, F. Nagy and E. Budo, *Acta Chem.* (*Budapest*), 1968, **58**, 39; *Chem. Abstr.*, 1969, **70**, 56916r.
15 M. Kuwahara, T. Kato and M. Takasumi, *Nippon Kagaku Kaishi*, 1979, 675; *Chem. Abstr.*, 1979, **91**, 56301v.
16 L. N. Lewis, *Inorg. Chem.*, 1985, **24**, 4433.
17 D. Parker, *J. Chem. Soc., Perkin Trans. 2*, 1983, 83.
18 D. J. Irvine, C. Glidewell, D. J. Cole-Hamilton and J. C. Barnes, *J. Chem. Soc., Dalton Trans.*, 1991, 1765.
19 J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1967, **10**, 68.

Received 21*st February* 1991; *Paper* 1/00845E