DALTON
FULL PAPER

Use of silver oxide in the synthesis of areneruthenium metallacyclic complexes

David L. Davies, John Fawcett, Roland Krafczyk, David R. Russell and Kuldip Singh

Department of Chemistry, University of Leicester, Leicester, UK LE1 7RH

Silver oxide has been used as a base and halide abstracting agent in the synthesis of areneruthenium metallacyclic complexes of dianionic chelating ligands. The structures of [Ru{N(COMe)C(CHR)C(O)O}(PPh_3)(arene)] (R = Ph, arene = *p*-cymene; R = H, arene = $C_6H_3Me_3$-1,3,5) have been determined by X-ray diffraction. The scope of this methodology has been investigated and is not as great as for related platinum complexes.

The use of silver oxide in the formation of platinum–carbon bonds was reported by Cairns *et al.*[1] in 1977. Since then Kemmitt, Henderson and co-workers[2–13] have extended this methodology to cover the syntheses of a wide range of metallacyclic complexes containing metal–carbon and –hetero-atom bonds. They have also extended the range of metals to which this method can be applied.[14] The reaction makes use of the basic nature of silver oxide to abstract acidic protons of element–hydrogen bonds and has the additional driving force of the formation of the insoluble silver chloride. To our knowledge this procedure has not yet been applied to ruthenium.

We and others have previously synthesized a number of areneruthenium complexes containing biologically relevant chelating monoanionic ligands, *e.g.* amino acidates.[15–21] A dianionic, tridentate peptide complex has also been prepared and the applications of these complexes in peptide synthesis have been described.[22] Areneruthenium complexes with chiral ligands and/or chiral metal centres particularly with hard donor atom ligands have found applications in asymmetric catalysis, for example transfer hydrogenation of ketones[23] and Diels–Alder reactions.[24] We describe here the synthesis of some new metallacyclic ruthenium complexes containing dianionic hard donor atom ligands, the structures of two such compounds, and some observations on the scope of the silver oxide methodology for the synthesis of areneruthenium metallacycles. All new complexes were characterised by ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy, mass spectrometry and microanalysis (Table 1).

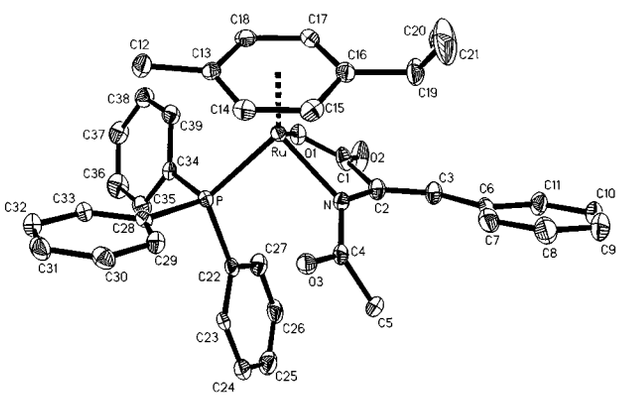
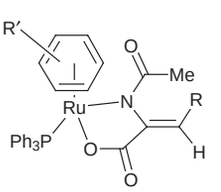


Fig. 1 Molecular structure of compound **2b** showing 30% probability ellipsoids for all non-hydrogen atoms



2a arene = mesitylene, R = Ph
2b arene = *p*-cymene, R = Ph
3a arene = mesitylene, R = H
3b arene = *p*-cymene, R = H

Results and Discussion

Refluxing [$RuCl_2(PPh_3)$(arene)] (arene = $C_6H_3Me_3$-1,3,5 **1a** or *p*-cymene **1b**) with a stoichiometric amount of 2-acetamidocinnamic acid and an excess of Ag_2O in dichloromethane leads to the formation of complex **2a** or **2b** respectively. The ^{31}P-{^{1}H} NMR spectra of the products show peaks at δ 39.6 (**2a**) and 35.2 (**2b**) respectively, as expected for a PPh_3 bound to ruthenium. The ^{1}H NMR spectra show the presence of the co-ordinated arene, PPh_3 ligand and the twice deprotonated ligand. In both complexes the acetyl methyl is observed at rather high field, δ 0.81 and 0.87 for **2a** and **2b** respectively, due to it being within the anisotropic region of two phenyl groups, one of the PPh_3 and that of the cinnamate. This can be observed in the crystal structure of **2b** (Fig. 1). In both complexes the ruthenium is a chiral centre; as a result the aromatic protons of the *p*-cymene are formally inequivalent. For **2b** three signals are observed at δ 5.00, 5.36 and 5.53 in a ratio 1 : 1 : 2, however the diastereotopic methyls of the isopropyl are not resolved and give a 6 H doublet at δ 1.22.

Using a similar procedure, reaction of compound **1a** or **1b** with 2-acetamidoacrylic acid and an excess of Ag_2O gives **3a** or **3b** respectively. The ^{31}P-{^{1}H} NMR spectra show peaks at δ 40.9 (**3a**) and 40.0 (**3b**) as expected for PPh_3 bound to ruthenium. The ^{1}H NMR spectra are similar to those of **2a** and **2b** above. The geminal protons are observed as singlets at δ 4.44 and 5.49 for **3a** and 4.42 and 5.57 for **3b**. The acetyl methyl group is observed at δ 1.47 and 1.41 for **3a** and **3b** respectively; in these cases the smaller high field shifts, compared to those in **2a** and **2b**, arise from the methyl being within the anisotropic region of only one phenyl group, of the PPh_3. The chirality at ruthenium is now fully reflected in the signals of the *p*-cymene of **3b**, a doublet being observed for each of the four aromatic protons and the diastereotopic methyls being easily resolved as two doublets at δ 1.12 and 1.21. The FAB mass spectra and microanalyses are in accord with the formulations.

We have determined the structures of compounds **2b** and **3a** (Figs. 1 and 2) to confirm the N,O bonding mode of the ligand. The structures show pseudo-octahedral geometry around the ruthenium atoms with the arene occupying three *fac* co-ordination sites. The metal co-ordination sphere is completed by a triphenylphosphine and a dianionic N,O bidentate ligand obtained through deprotonation of the amide and acid protons

Table 1 Selected spectroscopic and microanalytical data for new complexes

	NMR (δ, *J*/Hz)		Analysis[a]			
Complex	^{31}P-{^{1}H}	^{1}H	C	H	N	*mz*
2a	39.64	0.81 [s, 3 H, C(O)Me], 2.06 (s, 9 H, C_6Me_3), 5.00 (s, 3 H, C_6H_3), 6.83 (s, 1 H, C*H*Ph), 7.4 (m, 20 H, Ph)	62.2 (62.38)	5.29 (5.22)	1.92 (1.92)[b]	687 (M^+)
2b	35.20	0.87 [s, 3 H, C(O)Me], 1.22 (d, 6 H, J = 7, CH*Me*$_2$), 1.84 (s, 3 H, Me-4), 2.80 (spt, 1 H, J = 7, C*H*Me$_2$), 5.00 (d, 1 H, J = 6, C_6H_4), 5.36 (d, 1 H, J = 7, C_6H_4), 5.53 (m, 2 H, C_6H_4), 6.83 (s, 1 H, C*H*Ph), 7.5 (m, 5 H, Ph)	49.25 (49.61)	3.88 (4.03)	1.38 (1.39)[c]	701 (M^+)
3a	40.92	1.47 [s, 3 H, C(O)Me], 1.84 (s, 9 H, C_6Me_3), 4.44 (s, 1 H, =CH_2), 4.90 (s, 3 H, C_6H_3), 5.49 (s, 1 H, =CH_2), 7.4 (m, 15 H, Ph)	62.04 (62.94)	5.21 (5.28)	2.36 (2.29)	612 ([M + H]$^+$)
3b	39.98	1.12 [d, 3 H, J = 7, CH*Me*), 1.21 (d, 3 H, J = 7, CH*Me*), 1.41 [s, 3 H, C(O)Me], 1.76 (s, 3 H, Me-4), 2.73 (spt, 1 H, J = 7, C*H*Me$_2$), 4.42 (s, 1 H, =CH_2), 4.48 (d, 1 H, J = 6, C_6H_4), 5.42 (d, 1 H, J = 6, C_6H_4), 5.54 (d, 1 H, J = 6, C_6H_4), 5.57 (s, 1 H, =CH_2), 5.77 (d, 1 H, J = 6, C_6H_4), 7.5 (m, 15 H, Ph)	54.90 (54.68)	5.30 (4.69)	1.89 (1.88)[d]	626 ([M + H]$^+$)
4	48.86	1.88 [s, 3 H, C(O)Me], 1.91 (s, 9 H, C_6Me_3), 4.68 (s, 3 H, C_6H_3), 7.20 (s, 1 H, NH), 7.4 (m, 15 H, Ph), 9.26 (d, 1 H, J = 7, CH)	62.50 (62.94)	5.07 (5.28)	2.26 (2.29)	612 ([M + H]$^+$)
5	34.28	1.89 (m, 2 H, CH_2), 1.95 (s, 9 H, C_6Me_3), 2.34 (t, 2 H, J = 8, CH_2), 2.49 (t, 2 H, J = 8, CH_2), 4.67 (s, 3 H, C_6H_3), 7.5 (m, 15 H, Ph)	56.71 (57.46)	4.68 (4.97)[e]		627 ([M + H]$^+$)

[a] Calculated values in parentheses. [b] Includes 2.5 mol of H_2O. [c] Includes 2.5 mol of $CHCl_3$. [d] Includes 1 mol of $CHCl_3$. [e] Includes 1 mol of CH_2Cl_2.

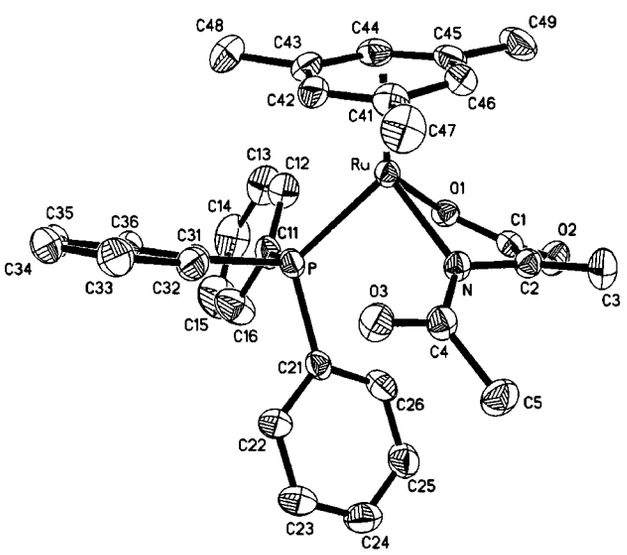


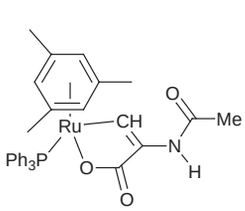
Fig. 2 Molecular structure of compound **3a** showing 30% probability ellipsoids for all non-hydrogen atoms

of the respective acetamido acids. The bond lengths and angles for the two complexes are very similar (Table 2). The Ru–P distances 2.356(2) and 2.3545(13) Å for **2b** and **3a** respectively are the same as that [2.3538(8) Å] found in [$RuCl_2(PPh_3)$-($C_6H_3Me_3$-1,3,5)].[25] The O(1)–Ru–N chelate bite angles 77.4(2) and 77.15(13)° for **2b** and **3a** respectively are statistically the same as that, 78.1(4)°, found in the alaninate complex [RuCl-(L-ala)($C_6H_3Me_3$-1,3,5)].[21] The co-ordination around the amide nitrogen is very nearly planar, the sum of the angles being 359.3° for **2b** and 360° for **3a**. In both cases the amide COMe group is virtually in the same plane allowing some delocalisation along N, C(4) and O(3). This is reflected in the N–C(2) bond lengths [1.406(8) (**2b**) and 1.412(5) Å (**3a**)] being considerably longer than the N–C(4) lengths [1.345(8) (**2b**) and 1.331(6) Å (**3a**)]. The C(2)–C(3) bond length 1.346(9) Å in **2b** is longer than that 1.310(6) Å in **3a**, which combined with the orientation of the phenyl ring C(6)–C(11) suggests some delocalisation of this phenyl ring with the C(2)–C(3) double bond in **2b**.

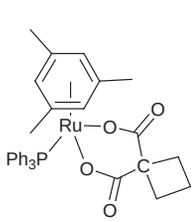
On one occasion during the synthesis of compound **3a** we observed formation of a second species [δ(^{31}P) 48.86] after longer reaction times. Kemmitt *et al.*[11] have previously observed that this ligand can rearrange from an N,O chelate to a C,O bonded form on platinum. Refluxing **3a** in dichloromethane gave no change in the ^{31}P NMR spectrum. However, addition of more ligand and Ag_2O followed by refluxing gave clean conversion into the C,O bonded isomer **4a**. The ruthenium bound CH is observed at δ 9.26 as a doublet due to coupling to phosphorus, whilst a singlet at δ 7.20 is assigned to the amide NH. The acetyl methyl is now at the more usual chemical shift of δ 1.88 since it is not affected by any phenyl groups. This isomerisation reaction was also attempted with **3b**, however in this case more products were observed which we have been unable to separate.

Table 2 Selected bond lengths (Å) and angles (°) for compounds **2b** and **3a**

2b		**3a**	
Ru–O(1)	2.073(4)	Ru–O(1)	2.090(3)
Ru–N	2.084(5)	Ru–N	2.088(4)
Ru–P	2.356(2)	Ru–P	2.3545(13)
Ru–C(13)	2.274(7)	Ru–C(41)	2.209(5)
Ru–C(14)	2.207(7)	Ru–C(42)	2.210(5)
Ru–C(15)	2.164(6)	Ru–C(43)	2.257(5)
Ru–C(16)	2.241(7)	Ru–C(44)	2.235(5)
Ru–C(17)	2.226(7)	Ru–C(45)	2.239(5)
Ru–C(18)	2.231(7)	Ru–C(46)	2.233(5)
N–C(2)	1.406(8)	N–C(2)	1.412(5)
N–C(4)	1.345(8)	N–C(4)	1.331(6)
C(4)–O(3)	1.248(8)	C(4)–O(3)	1.248(5)
C(2)–C(1)	1.512(9)	C(2)–C(1)	1.507(6)
C(1)–O(1)	1.292(8)	C(1)–O(1)	1.287(5)
C(1)–O(2)	1.226(8)	C(1)–O(2)	1.230(5)
C(2)–C(3)	1.346(9)	C(2)–C(3)	1.310(6)
O(1)–Ru–N	77.4(2)	O(1)–Ru–N	77.15(13)
O(1)–Ru–P	81.78(13)	O(1)–Ru–P	85.20(9)
P–Ru–N	89.5(2)	P–Ru–N	89.93(10)
O(1)–C(1)–O(2)	122.1(6)	O(1)–C(1)–O(2)	124.1(4)
C(2)–C(1)–O(2)	123.0(7)	C(2)–C(1)–O(2)	121.5(4)
C(1)–C(2)–N	111.1(6)	C(1)–C(2)–N	112.0(4)
C(2)–N–Ru	110.2(4)	C(2)–N–Ru	106.1(3)
C(4)–N–Ru	124.7(4)	C(4)–N–Ru	129.9(3)
C(2)–N–C(4)	124.4(6)	C(2)–N–C(4)	124.0(4)



4



5

In an attempt to investigate the mechanism of formation of complexes **2** and **3** we studied the reaction of **1a** with the methyl ester of 2-acetamidoacrylic acid in the presence of Ag_2O. No reaction was observed, which suggests that in the formation of **2** and **3** deprotonation and co-ordination of the carboxylic acid occurs first followed by chelation/deprotonation of the amide. Consistent with this, reaction of **1a** with cyclobutane-1,1-dicarboxylic acid and Ag_2O gives the desired metallacycle **5**. Complex **5** shows a singlet in the ^{31}P-{^1H} NMR spectrum whilst the ^1H NMR spectrum displays two triplets at δ 2.34 and 2.49 and a multiplet at δ 1.89 which is partially obscured by the arene methyls but easily visible in the COSY NMR, for the cyclobutane protons, in addition to signals for the mesitylene.

Reaction of compound **1a** with dibenzyl sulfone and Ag_2O, which forms a four-membered ring on platinum, was attempted but no products were observed. It may be that the steric congestion at the octahedral ruthenium makes this reaction less favourable than for the square-planar platinum. It should be noted that in many reactions some $Ag(PPh_3)$-containing species were formed as by-products as evidenced by peaks in the mass spectra, *m/z* 369 and 371 $[Ag(PPh_3)]^+$, and 631 and 633, $[Ag(PPh_3)_2]^+$ showing the expected 1:1 ratio for ^{107}Ag:^{109}Ag. Occasionally, broad features in the ^{31}P-{^1H} NMR spectra of the crude reaction mixtures were observed, possibly due to $[Ag(PPh_3)]$ species undergoing exchange. In conclusion, the silver oxide methodology can be applied to the synthesis of areneruthenium metallacyclic species. However, certainly with PPh_3 as the ancillary ligand, the range of metallacycles accessible is limited, possibly due to steric crowding around the ruthenium.

Experimental

Light petroleum (b.p. 40–60 °C) and diethyl ether were dried by refluxing over purple sodium–benzophenone under nitrogen, dichloromethane by refluxing over calcium hydride and methanol from magnesium turnings and iodine. The complexes $[RuCl_2(PPh_2)(arene)]$ (arene = $C_6H_3Me_3$-1,3,5 **1a** or *p*-cymene **1b**) were made by the literature procedure.[26] The reactions described were carried out under nitrogen; however, once isolated as pure solids the compounds are air-stable and precautions for their storage are unnecessary. The ^1H NMR spectra were recorded on a Bruker AM300 spectrometer. Microanalyses were performed by Butterworth Laboratories Ltd., Middlesex. The FAB mass spectra were recorded on a Kratos Concept mass spectrometer using a 3-nitrobenzyl alcohol matrix.

Preparation of [Ru{N(COMe)C(CHR)C(O)O}(PPh_3)(arene)]

A mixture of 2-acetamidocinnamic acid (55 mg, 0.27 mmol), compound **1a** (150 mg, 0.27 mmol) and Ag_2O (125 mg, 0.54 mmol) was refluxed in dichloromethane (15 cm^3) for 1.5 h. The mixture was filtered through Celite and the solvent evaporated to give an orange solid. Recrystallisation from dichloromethane–hexane gave **2a** (102 mg, 55%). A similar procedure was used starting with 2-acetamidocinnamic acid (55 mg, 0.27 mmol), **1b** (125 mg, 0.27 mmol) and Ag_2O (125 mg, 0.54 mmol) to give **2b** (105 mg, 56%).

A mixture of 2-acetamidoacrylic acid (35 mg, 0.27 mmol), compound **1a** (150 mg, 0.27 mmol) and Ag_2O (125 mg, 0.54 mmol) was refluxed in dichloromethane (15 cm^3) for 1.5 h. The mixture was filtered through Celite and the solvent evaporated to give a yellow solid. Recrystallisation from dichloromethane–hexane gave **3a** (100 mg, 61%). A similar procedure was used starting with 2-acetamidoacrylic acid (35 mg, 0.27 mmol), **1b** (150 mg, 0.27 mmol) and Ag_2O (125 mg, 0.54 mmol) to give **3b** (80 mg, 47%).

Isomerisation of compound 3a to 4

A mixture of compound **3a** (113 mg, 0.18 mmol), 2-acetamidoacrylic acid (12 mg, 0.09 mmol) and Ag_2O (42 mg, 0.18 mmol) was refluxed in dichloromethane (15 cm^3) for 2.5 h. After filtration through Celite the solvent was reduced in volume and addition of heptane gave a yellow solid which was identified as **4** (58 mg, 51%).

Reactions of compound 1a

With methyl 2-acetamidoacrylate. A mixture of methyl 2-acetamidoacrylate (39 mg, 0.27 mmol), compound **1a** (150 mg, 0.27 mmol) and Ag_2O (125 mg, 0.54 mmol) was refluxed in dichloromethane for 3 h and then in chloroform for 5 h during which time there was no change in the ^{31}P-{^1H} NMR spectrum and so the reaction was abandoned.

With cyclobutane-1,1-dicarboxylic acid. A mixture of compound **1a** (125 mg, 0.27 mmol), cyclobutane-1,1-dicarboxylic acid (36 mg, 0.25 mmol) and Ag_2O (109 mg, 0.47 mmol) was refluxed in dichloromethane (15 cm^3) for 3 h. The mixture was filtered through Celite and the solvent evaporated to give an orange solid. Recrystallisation from dichloromethane–light petroleum gave **5** (80 mg, 57%).

Crystallography

Crystal data. $C_{39}H_{38}NO_3PRu\cdot3CHCl_3$ **2b**, $M = 1058.85$, monoclinic, space group $P2_1/c$, $a = 22.593(4)$, $b = 11.252(2)$, $c = 18.784(4)$ Å, $\beta = 106.11(1)°$, $U = 4588(2)$ Å^3, (by least squares refinement of optimised setting angles for 39 reflections in the range $5.2 < \theta < 12.4°$), 190 K, $Z = 4$, $D_c = 1.533$ g cm^{-3}, $F(000) = 2144$. Orange needle, crystal size $0.48 \times 0.44 \times 0.11$ mm, μ(Mo-Kα) = 0.940 mm^{-1}, absorption correction transmission factors 0.74–0.97. Data collection range $2.5 < \theta < 25.0°$, $\pm h$, $-k$, $+l$, 8662 data measured, 7022 independent reflections ($R_{int} = 0.0401$). $R1 = 0.0609$ [for data $I > 2\sigma(I)$] and $wR2 = 0.1381$ (for all data), for 568 parameters and 15 restraints (to solvent geometry) (*R* factors defined in ref. 25), weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 12.18P]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$, goodness of fit = 1.022, maximum $\Delta/\sigma = 0.113$, maximum $\Delta\rho = 0.57$ e Å^{-3}.

$C_{32}H_{32}NO_3PRu\cdot2CHCl_3$ **3a**, $M = 849.36$, monoclinic, space group $P2_1/n$, $a = 10.667(3)$, $b = 11.154(2)$, $c = 30.814(4)$ Å, $\beta = 91.36(2)°$, $U = 3665.2(13)$ Å^3 (by least squares refinement of optimised setting angles for 52 centred reflections with $5.6 < \theta < 11.4°$), 293 K, $Z = 4$, $D_c = 1.539$ g cm^{-3}, $F(000) = 1720$. Orange block, crystal size $0.60 \times 0.33 \times 0.18$ mm, μ(Mo-Kα) = 0.944 mm^{-1}, absorption correction transmission factors 0.65–0.81. Data collection range $2.6 < \theta < 30.0°$, $\pm h$, $+k$, $+l$, 10 304 data measured, 7577 independent reflections ($R_{int} = 0.0202$). $R1 = 0.0519$ [for data $I > 2\sigma(I)$] and $wR2 = 0.1218$ (for all data), for 415 parameters, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0430P)^2 + 2.33P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$, goodness of fit = 1.031, maximum $\Delta/\sigma = 0.002$, maximum $\Delta\rho = 0.709$ e Å^{-3}.

For both compounds **2b** and **3a** crystals were grown from chloroform–heptane and data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo-Kα radiation, $\lambda = 0.7107$ Å. The data were corrected for Lorentz and polarisation effects and semiempirical absorption corrections based on ψ scans were applied. The structures were solved by Patterson methods and refined by full-matrix least squares on F^2 using the program SHELXTL PC.[27] All hydrogen atoms were included in calculated positions (C–H 0.96 Å) using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. For **2b** two of the three chloroform solvent molecules are disordered over two sites [Cl atoms attached to C(2s) are disordered 66:34 whilst those attached to C(3s) are disordered 75:25]. All the C–Cl bond distances of

the solvent molecules were restrained to a target distance of 1.770(5) Å.

CCDC reference number 186/1019.

See http://www.rsc.org/suppdata/dt/1998/2349/ for crystallographic files in .cif format.

Acknowledgements

We thank Johnson Matthey for a loan of $RuCl_3$, and Dr. R. D. W. Kemmitt for helpful discussions.

References

1 M. A. Cairns, K. R. Dixon and M. A. R. Smith, *J. Organomet. Chem.*, 1977, **135**, C33.
2 J. Fawcett, W. Henderson, R. D. W. Kemmitt and D. R. Russell, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 2595.
3 W. Henderson, R. D. W. Kemmitt, J. Fawcett, L. J. S. Prouse and D. R. Russell, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 1791.
4 W. Henderson, R. D. W. Kemmitt, L. J. S. Prouse and D. R. Russell, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 259.
5 W. Henderson, R. D. W. Kemmitt, L. J. S. Prouse and D. R. Russell, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 1853.
6 W. Henderson, R. D. W. Kemmitt, L. J. S. Prouse and D. R. Russell, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 781.
7 W. Henderson, R. D. W. Kemmitt, S. Mason, M. R. Moore, J. Fawcett and D. R. Russell, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 59.
8 W. Henderson, R. D. W. Kemmitt and A. L. Davis, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 2247.
9 W. Henderson, J. Fawcett, R. D. W. Kemmit, C. Proctor and D. R. Russell, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3085.
10 R. D. W. Kemmitt, S. Mason, M. R. Moore, J. Fawcett and D. R. Russell, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 1535.
11 R. D. W. Kemmitt, S. Mason and D. R. Russell, *J. Organomet. Chem.*, 1991, **415**, C9.
12 R. D. W. Kemmitt, S. Mason, J. Fawcett and D. R. Russell, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 851.
13 R. D. W. Kemmitt, S. Mason, M. R. Moore and D. R. Russell, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 409.
14 W. Henderson, J. Fawcett, R. D. W. Kemmitt and D. R. Russell, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3007.
15 R. Kramer, K. Polborn, H. Wanjek, I. Zahn and W. Beck, *Chem. Ber.*, 1990, **123**, 767.
16 W. S. Sheldrick and S. Heeb, *J. Organomet. Chem.*, 1989, **377**, 357.
17 W. S. Sheldrick and S. Heeb, *Inorg. Chim. Acta*, 1990, **168**, 93.
18 G. Capper, D. L. Davies, J. Fawcett and D. R. Russell, *Acta Crystallogr.*, *Sect. C*, 1995, **51**, 578.
19 D. Carmona, A. Medoza, F. J. Lahoz, L. A. Oro, M. P. Lamata and E. San Jose, *J. Organomet. Chem.*, 1990, **396**, C17.
20 D. Carmona, F. J. Lahoz, R. Atencio, L. A. Oro, M. P. Lamata and E. San Jose, *Tetrahedron-Asymmetry*, 1993, **4**, 1425.
21 L. C. Carter, D. L. Davies, K. T. Duffy, J. Fawcett and D. R. Russell, *Acta Crystallogr.*, *Sect. C*, 1994, **50**, 1559.
22 W. Beck and R. Kramer, *Angew. Chem.*, *Int. Ed. Engl.*, 1991, **30**, 1467.
23 R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, 1997, **30**, 97.
24 D. L. Davies, J. Fawcett, S. A. Garratt and D. R. Russell, *Chem. Commun.*, 1997, 1351.
25 D. L. Davies, J. Fawcett, R. Krafczyk and D. R. Russell, unpublished work.
26 M. A. Bennett and A. K. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1974, 233.
27 G. M. Sheldrick, SHELXTL PC, release 4.2, Siemens Analytical X-ray Instruments, Madison, WI, 1991.

Received 7*th April* 1998; *Paper* 8/02646C