Synthesis and Crystal Structure of the Organometallic Ruthenium(IV) Derivative [$Ru(C_5Me_5)Cl_2(SC_4H_8)_2$]$ClO_4$†

Blanca R. Manzano,*[,a] **Felix A. Jalon**,[a] **Fernando J. Lahoz**,[b] **Bruno Chaudret***[,c] and **Dominique de Montauzon**[c]

[a] *Universidad de Castilla La Mancha, Departamento de Quimica Inorganica, Organica y Bioquimica, Paseo de la Universidad 4, 13071 Ciudad Real, Spain*

[b] *Departamento de Quimica Inorganica, Instituto de Ciencias de Materiales de Aragon, Universidad de Zaragoza, CSIC, 50009 Zaragoza, Spain*

[c] *Laboratoire de Chimie de Coordination du CNRS, UPR 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique de Toulouse, 205 Route de Narbonne, 31077 Toulouse Cedex, France*

Oxidation of [{$Ru(C_5Me_5)Cl_2$}$_n$] by ferrocenium or in an electrochemical cell was attempted in the presence of various ligands such as phosphines, pyridine and tetrahydrothiophene (SC_4H_8). Only in the latter case was the oxidation possible and a ruthenium(IV) cationic derivative isolated: [$Ru(C_5Me_5)Cl_2(SC_4H_8)_2$]X (X = ClO_4 or PF_6). The crystal structure of the ClO_4^- salt has been determined.

The synthesis of higher-oxidation-state organometallics of late transition elements is presently a very active area of research. Such compounds are expected to display interesting novel reactivity, *e.g.* oxo derivatives of rhenium[1] or electrophilic platinum complexes.[2] Different routes have been developed: the starting material can be a high-oxidation-state oxide or nitride[3] or a low-valent precursor oxidized by oxidative addition,[4–6] oxygen-donor agents[7] or electron transfer.[8] For example, Itoh and co-workers[4] recently reported the oxidative addition of allyl halides to ruthenium(II) compounds which led to stable ruthenium(IV) allyl derivatives. Alkylruthenium(IV) complexes could be obtained by reaction with alkylating agents.[4b] Different high-oxidation-state alkylruthenium derivatives were reported by Wilkinson and co-workers[9] and Shapley and co-workers.[3] Haga *et al.*[10] described the electrochemical oxidation of [$Ru(C_5Me_5)Cl_2L$] (L = tertiary phosphine).

We have studied the chemistry of the electrophilic fragment '$Ru(C_5Me_5)^+$' which shows a high affinity towards aromatic hydrocarbons[11] and is able to aromatize cyclic C_6 derivatives through carbon–hydrogen, oxygen and even carbon bond activation.[12] In search for a similar but higher-oxidation-state fragment, we treated [{$Ru(C_5Me_5)(OMe)$}$_2$] with $KHSO_5$ which is both a weak acid and a single-oxygen donor agent. However this reaction led to a stable and unreactive hydrido oxo cluster.[13]

We describe in this paper our attempts to prepare a more electrophilic fragment through direct oxidation of the ruthenium(III) precursor [{$Ru(C_5Me_5)Cl_2$}$_n$] by electron transfer in the presence of various ligands.

Results and Discussion

We and others have previously described the reactions of this compound with phosphines and pyridine which lead to ruthenium(III) derivatives, namely [$Ru(C_5Me_5)Cl_2L$] [L = pyridine(py) or PR_3 (R = Ph, C_6H_{11} or Pr^i)].[14,15] The reaction with the ferrocenium salt [$Fe(C_5H_5)_2$]PF_6 in the presence of pyridine in acetone does not lead to a ruthenium(IV) species but to [$Ru(C_5Me_5)Cl(py)_2$]PF_6 **1**. This compound was characterized by usual spectroscopic and microanalytical techniques. In particular, it is paramagnetic showing one unpaired electron ($g = 2.21\ \mu_B$). This demonstrates that oxidation did not occur. Electrochemical rationalization of these phenomena will be discussed later. The same reaction using PPh_3 instead of pyridine failed since only [$Ru(C_5Me_5)Cl_2(PPh_3)$] was recovered from the solution. Attempts with a more basic phosphine such as $P(C_6H_{11})_3$ were equally inconclusive.

However use of the sulfur-donor ligand tetrahydrothiophene (SC_4H_8) led to a diamagnetic complex analysing for [$Ru(C_5Me_5)Cl_2(SC_4H_8)_2$]$PF_6$ **2**. Complex **2** is air and water stable. Its ^1H NMR spectrum only shows the C_5Me_5 group at δ 1.73 and the methylene protons of SC_4H_8 at δ 2.28 and 3.19 (correct integration ratio). If the chemical shift of this ligand can be roughly correlated with the electron density on the metal (methyl groups of C_5Me_5 resonate near δ 2 for arene and hydride phospine compounds, near δ 1.7 for 16-electron compounds such as [$Ru(C_5Me_5)Cl(PR_3)$], δ 1.56 for [{$Ru(C_5Me_5)Cl$}$_4$] and δ 1.57 for the ruthenium(IV) adduct [$Ru(C_5Me_5)Br_3(PPh_3)$][15]), it is clear that **2** is not electron deficient probably thanks to the good σ-donor ability of the thioether ligands.

The molecular structure of [$Ru(C_5Me_5)Cl_2(SC_4H_8)_2$]$ClO_4$ **2′** was established by X-ray crystallography. It consists of a ruthenium cation in a half-sandwich, four-legged piano-stool environment or a heavily distorted trigonal bipyramid as suggested by one referee (see Fig. 1). The two chloride groups are in a transoid position (the pseudo-axial sites of the trigonal bipyramid); the same is obviously true for the SC_4H_8 ligands which are clearly co-ordinated through donation of a lone pair of sulfur. The Ru–Cl and Ru–S distances [respectively 2.3894(12) and 2.4252(14) Å, Table 1] are in the normal range for such features.

Electrochemical experiments were carried out in order to rationalize our findings that only the $Ru^{IV}(SC_4H_8)$ complex can be prepared by this method. Thus electrochemical measurements demonstrate that [$Ru(C_5Me_5)Cl_2L$] [L = PPh_3 or $P(C_6H_{11})_3$] complexes cannot be chemically oxidized with [$Fe(C_5H_5)_2$]$^+$. Indeed, in CH_2Cl_2–NBu_4PF_6 0.1 mol dm^{-3} these complexes are reversibly oxidized at a platinum electrode at E_0 = 0.81 V and 0.75 V (*vs.* Ag–AgCl–KCl 0.1 mol dm^{-3}) for L = PPh_3 and $P(C_6H_{11})_3$ respectively. Under the same conditions the oxidation potential of the [$Fe(C_5H_5)_2$]–[$Fe(C_5H_5)_2$]$^+$ couple

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Selected bond distances (Å) and angles (°) for complex $[Ru(C_5Me_5)Cl_2(SC_4H_8)_2]ClO_4$

Ru–Cl(1)	2.369(1)	Ru–Cl(2)	2.391(1)
Ru–S(1)	2.422(1)	Ru–S(2)	2.409(1)
Ru–C(1)	2.191(3)	Ru–C(4)	2.332(3)
Ru–C(2)	2.207(3)	Ru–C(5)	2.270(3)
Ru–C(3)	2.300(3)	Ru–G*	1.907(3)
C(1)–C(2)	1.420(4)	C(1)–C(6)	1.502(5)
C(1)–C(5)	1.444(5)	C(2)–C(7)	1.502(6)
C(2)–C(3)	1.429(5)	C(3)–C(8)	1.491(5)
C(3)–C(4)	1.421(5)	C(4)–C(9)	1.496(6)
C(4)–C(5)	1.417(4)	C(5)–C(10)	1.489(4)
S(1)–C(11)	1.838(4)	S(2)–C(15)	1.827(5)
S(1)–C(14)	1.832(4)	S(2)–C(18)	1.832(4)
C(11)–C(12A)	1.545(8)	C(15)–C(16)	1.481(7)
C(12A)–C(13A)	1.526(11)	C(16)–C(17)	1.469(9)
C(13A)–C(14)	1.566(9)	C(17)–C(18)	1.535(7)
C(11)–C(12B)	1.550(10)	C(13B)–C(14)	1.528(11)
C(12B)–C(13B)	1.528(12)		
Cl(1)–Ru–Cl(2)	137.09(3)	Cl(2)–Ru–S(2)	74.14(3)
Cl(1)–Ru–S(1)	77.54(3)	Cl(2)–Ru–G	111.5(1)
Cl(1)–Ru–S(2)	82.40(3)	S(1)–Ru–S(2)	108.39(3)
Cl(1)–Ru–G	111.5(1)	S(1)–Ru–G	128.6(1)
Cl(2)–Ru–S(1)	76.59(3)	S(2)–Ru–G	122.8(1)
C(2)–C(1)–C(5)	107.5(3)	C(4)–C(3)–C(8)	125.5(3)
C(2)–C(1)–C(6)	127.0(3)	C(3)–C(4)–C(5)	107.9(3)
C(5)–C(1)–C(6)	125.2(3)	C(3)–C(4)–C(9)	125.8(3)
C(1)–C(2)–C(3)	108.0(3)	C(5)–C(4)–C(9)	125.5(3)
C(1)–C(2)–C(7)	125.8(3)	C(1)–C(5)–C(4)	108.1(3)
C(3)–C(2)–C(7)	125.5(3)	C(1)–C(5)–C(10)	126.1(3)
C(2)–C(3)–C(4)	108.5(3)	C(4)–C(5)–C(10)	125.4(3)
C(2)–C(3)–C(8)	125.7(3)		
C(11)–S(1)–C(14)	93.5(2)	C(15)–S(2)–C(18)	94.5(2)
S(1)–C(11)–C(12A)	102.8(3)	S(2)–C(15)–C(16)	104.0(3)
C(11)–C(12A)–C(13A)	105.9(5)	C(15)–C(16)–C(17)	108.7(5)
C(12A)–C(13A)–C(14)	105.8(6)	C(16)–C(17)–C(18)	110.7(4)
C(13A)–C(14)–S(1)	108.0(3)	C(17)–C(18)–S(2)	104.9(3)
S(1)–C(11)–C(12B)	106.5(4)	C(12B)–C(13B)–C(14)	104.6(6)
C(11)–C(12B)–C(13B)	106.3(6)		

* G represents the centroid of the C_5Me_5 ligand.

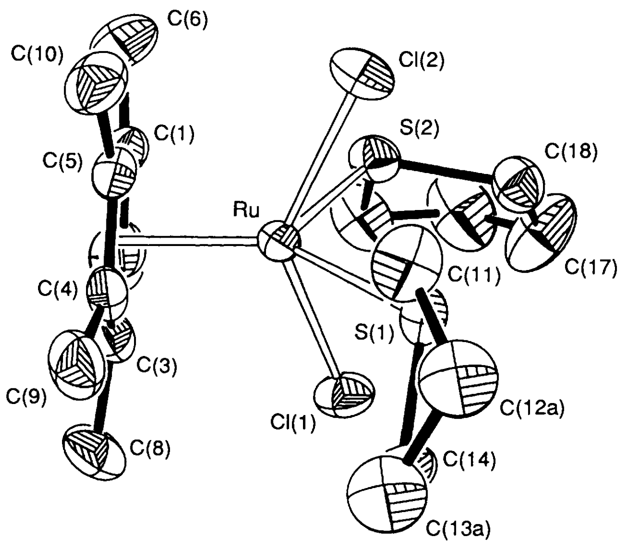

Fig. 1 Structure of $[Ru(C_5Me_5)Cl_2(SC_4H_8)_2]^+$. Hydrogen atoms are omitted for clarity

is $E_0 = 0.45$ V. When L = py an irreversible oxidation peak appeared at $E_{p_{ox}} = 0.90$ V (scan rate = 0.1 V s^{-1}); in the reverse scan a small reduction peak $E_{p_{red}} = -0.02$ V was also observed. Addition of $[Fe(C_5H_5)_2]$ to this solution leads to a shift in the E_0 value of ferrocene (0.41 V) suggesting an interaction with the ruthenium complex. Although these potentials do not favour oxidation of the ruthenium complex by $[Fe(C_5H_5)_2]$, a chemical reaction may be possible, probably the substitution of a Cl^- group by pyridine.

When L = SC_4H_8 an oxidation step occurred at 0.76 V and a reduction step at −0.04 V. On adding $[Fe(C_5H_5)_2]$ to the studied solution, the standard potential of $[Fe(C_5H_5)_2]$–$[Fe(C_5H_5)_2]^+$ became $E_0 = 0.38$ V. In the same way the peak intensity for this couple decreased when compared to a pure solution of ferrocene under the same conditions. Consequently, it is not surprising that the $[Fe(C_5H_5)_2]^+$ solution was found to oxidize slowly $[Ru(C_5Me_5)Cl_2(SC_4H_8)]$. The isolated complex **2** is not electrochemically oxidized to Ru^V or a higher oxidation state but it shows two one-electron reduction waves (Ru^{IV}–Ru^{III} and Ru^{III}–Ru^{II}) at +0.01 and −0.36 V. However these waves are not reversible as demonstrated by cyclic voltamperometry.

Attempts to find other oxidizing agents for the ruthenium(III) derivative $[\{Ru(C_5Me_5)Cl_2\}_n]$ surprisingly revealed that its reaction with $[Au(tht)_2]ClO_4$ leads to $[Ru(C_5Me_5)Cl_2(SC_4H_8)_2]ClO_4$ **2′**. This reaction produced the best crystals which were used for X-ray diffraction.

Finally the reactivity of complex **2** was found to be disappointingly low. Attempts of substitution of Cl^- by SC_4H_8 in the presence of $AgPF_6$ in order to obtain a dicationic complex were unsuccessful, whereas substitution of SC_4H_8 by PPh_3 resulted again in the reduction of **2** to a ruthenium(III) species.

In conclusion, we demonstrated in this study the difficulty in attaining the ruthenium(IV) oxidation state in these cationic compounds containing hard chloride groups. Cationic organometallic ruthenium(IV) compounds are known but with softer ligands.

Experimental

All the reactions were performed under an inert atmosphere of nitrogen or argon. Solvents were dried and distilled before use. Literature methods were used to prepare $[\{Ru(C_5Me_5)Cl_2\}_n]$[16] or $[Au(SC_4H_8)_2]ClO_4$.[17]

Nuclear magnetic resonance spectra were recorded on a Bruker AC 200 spectrometer in CD_3COCD_3 with chemical shifts reported in ppm downfield from $SiMe_4$. Microanalyses were performed by the Centre de Microanalyse du CNRS or in-house. Electrochemical measurements were carried out on an Electro-Kemat 400 (ISMP Technologie) apparatus.

Preparation of $[Ru(C_5Me_5)Cl_2(SC_4H_8)_2]X$.—*With* $[Fe(C_5H_5)_2]PF_6$ *as oxidant.* X = PF_6 **2**. A suspension of $[\{Ru(C_5Me_5)Cl_2\}_n]$ (288 mg, 0.94 mmol) in acetone (15 cm^3) was treated with tetrahydrothiophene (249 mg, 2.82 mmol) and $[Fe(C_5H_5)_2]PF_6$ (310 mg, 0.94 mmol) for 30 min. After filtration, the solution was evaporated to dryness and washed with diethyl ether (3 × 10 cm^3). The brown residue was recrystallized from acetone–diethyl ether. Yield: 76% (Found: C, 34.30; H, 5.20. $C_{18}H_{31}Cl_2F_6PRuS_2$ requires C, 34.40; H, 4.95%).

With $[Au(SC_4H_8)_2]ClO_4$ *as oxidant.* X = ClO_4 **2′**. A suspension of $[\{Ru(C_5Me_5)Cl_2\}_n]$ (100 mg, 0.33 mmol) in acetone (10 cm^3) was treated with $[Au(SC_4H_8)_2]ClO_4$ (160 mg, 0.33 mmol) for 15 min. After filtration and partial evaporation of the solution, the complex was recovered by precipitation with diethyl ether. Yield: 62% (Found: C, 37.40; H, 5.50. $C_{18}H_{31}Cl_3O_4RuS_2$ requires C, 37.10; H, 5.35%).

Preparation of $[Ru(C_5Me_5)Cl(py)_2]PF_6$ **1**.—A suspension of $[\{Ru(C_5Me_5)Cl_2\}_n]$ (150 mg, 0.49 mmol) in acetone (15 cm^3) was treated with pyridine (116 mg, 1.47 mmol) and $[Fe(C_5H_5)_2]PF_6$ (162 mg, 0.49 mmol) for 1 h. After filtration, the solution was evaporated to dryness and washed with diethyl ether (3 × 10 cm^3). The brown-red residue was recrystallized

Table 2 Fractional atomic coordinates (× 10^4; × 10^5 for Ru, S and Cl) for the non-hydrogen atoms of $[Ru(C_5Me_5)Cl_2(SC_4H_8)_2]ClO_4$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	26 191(2)	21 804(2)	5 548(2)
Cl(1)	14 221(7)	18 940(7)	−10 274(6)
Cl(2)	36 987(7)	12 048(6)	18 747(6)
S(1)	13 354(7)	10 242(6)	9 412(6)
S(2)	38 504(7)	12 708(6)	−1 701(6)
C(1)	3 745(3)	3 413(2)	1 034(2)
C(2)	3 067(3)	3 647(2)	82(2)
C(3)	1 992(3)	3 768(2)	188(2)
C(4)	1 998(3)	3 595(2)	1 200(2)
C(5)	3 075(3)	3 384(2)	1 730(2)
C(6)	4 955(3)	3 328(3)	1 309(3)
C(7)	3 439(4)	3 889(3)	−834(3)
C(8)	1 050(3)	4 135(3)	−600(3)
C(9)	1 075(3)	3 776(3)	1 658(3)
C(10)	3 463(3)	3 379(3)	2 831(2)
C(11)	1 308(3)	2 058(3)	2 259(3)
C(12A)*	118(5)	811(7)	2 214(6)
C(13A)*	−562(6)	1 497(7)	1 425(5)
C(12B)*	127(6)	1 291(10)	2 276(7)
C(13B)*	−582(8)	941(8)	1 276(6)
C(14)	−77(3)	1 413(3)	499(3)
C(15)	3 802(4)	1 529(3)	−1 474(3)
C(16)	3 914(5)	541(4)	−1 901(4)
C(17)	3 245(5)	−169(4)	−1 521(4)
C(18)	3 354(3)	−1(3)	−405(3)
Cl(3)	2 294(1)	1 772(1)	4 962(1)
O(1)	1 560(4)	979(3)	4 631(3)
O(2)	3 245(3)	1 561(4)	4 657(4)
O(3)	2 492(5)	1 830(5)	5 991(3)
O(4)	1 854(5)	2 622(3)	4 500(4)

* Atoms involved in partial disorder of a tetrahydrothiophene molecule. A complementary occupancy factor was refined; final values were 0.58(2) for A-labelled atoms and 0.42(2) for B-labelled.

from acetone–diethyl ether. Yield: 30% (Found: C, 40.80; H, 4.30; N, 4.25. $C_{20}H_{25}ClF_6N_2PRu$: C, 41.80; H, 4.40; N, 4.85%).

X-Ray Structure Determination of $[Ru(C_5Me_5)Cl_2(SC_4H_8)_2]ClO_4$.—*Crystal data.* $C_{18}H_{31}Cl_3O_4RuS_2$, $M = 583.0$, monoclinic, space group $P2_1/n$, $a = 12.793(1)$, $b = 13.500(1)$, $c = 13.872(1)$ Å, $\beta = 104.66(1)°$, $U = 2317.8(2)$ Å^3, $Z = 4$, $D_c = 1.671$ Mg m^{-3}, $F(000) = 1192$, λ(Mo-Kα) = 0.710 69 Å, $\mu = 1.207$ mm^{-1}, $T = 20$° C.

Data collection and reduction. A Siemens AED-2 diffractometer with monochromated Mo-Kα radiation was used. A red irregular block 0.380 × 0.342 × 0.458 mm was mounted on a glass fibre. 8910 Intensities were registered to $2\theta_{max}$ 50°. Averaging equivalents gave 4059 unique reflections, of which 3774 with $F \geqslant 5.0\sigma(F)$ were used for all calculations (program system SHELX 76).[18] Cell constants were refined from setting angles of 56 reflections in the range 2θ 20–35°. An absorption correction was applied using the DIFABS program[19] (correction factors 0.932–1.195).

Structure solution and refinement. The structure was solved by Patterson methods and extended by difference syntheses. All atoms were refined anisotropically, except two carbon atoms [C(12) and C(13)] of a tht molecule which were disordered; two complementary occupancy factors were refined for the disordered atoms [final value 0.58(2) for C(12A) and C(13A)]. Hydrogen atoms were localized in several Fourier difference maps and included in the final structure-factor calculations using a riding model. The final *R* value was 0.0307, with $R' = 0.0332$. The weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$, with $g = 0.000\,078$; 253 parameters, maximum $\Delta/\sigma < 0.040$, maximum $\Delta\rho$ 1.02 e Å^{-3}. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 20. Final atomic coordinates are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We thank the Centre National de Recherche Scientifique and the Accion Integrada Hispano-Francesa for financial support and Dr. Ramon Vicente (Universidad de Barcelona) for the magnetic susceptibility measurements.

References

1 W. A. Hermann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1297.
2 A. Sen, *Acc. Chem. Res.*, 1988, **21**, 421.
3 P. A. Shapley, H. S. Kim and S. R. Wilson, *Organometallics*, 1988, **7**, 928; R. W. Marshman, W. S. Bigham, S. R. Wilson and P. A. Shapley, *Organometallics*, 1990, **9**, 1341.
4 (*a*) H. Nagashima, K. Mukai and K. Itoh, *Organometallics*, 1984, **3**, 1314; (*b*) H. Nagashima, K.-I. Ara, K. Yamaguchi and K. Itoh, *J. Organomet. Chem.*, 1987, **319**, C11; (*c*) H. Nagashima, K. Mukai, Y. Shiota, K. Yamaguchi, K.-I. Ara, T. Fukahori, H. Suzuki, M. Akita, Y. Moro-Uka and K. Itoh, *Organometallics*, 1990, **9**, 795.
5 M. O. Albers, D. C. Liles, D. J. Robinson, A. Shaver and E. Singleton, *Organometallics*, 1987, **6**, 2347.
6 I. W. Nowell, K. Tabatabaian and C. White, *J. Chem. Soc., Chem. Commun.*, 1979, 547.
7 J. T. Groves and K. H. Ahn, *Inorg. Chem.*, 1987, **26**, 3831.
8 T. C. Lau, C.-M. Che, W. O. Lee and C. K. Poon, *J. Chem. Soc., Chem. Commun.*, 1988, 1406.
9 P. Stavropoulos, P. D. Savage, R. P. Tooze, G. Wilkinson, B. Hussain, M. Motevalli and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1987, 557; P. D. Savage, G. Wilkinson, M. Motevalli and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1988, 669; J. Arnola, G. Wilkinson, B. Hussain and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1989, 2149.
10 M. Haga, H. Sakamoto and H. Suzuki, *J. Organomet. Chem.*, 1989, **377**, C77.
11 B. Chaudret, F. Jalon, M. Perez-Manrique, F. J. Lahoz, F. J. Plou and R. Sanchez-Delgado, *New. J. Chem.*, 1990, **14**, 331; B. Chaudret, G. Chung and Y. S. Huang, *J. Chem. Soc., Chem. Commun.*, 1990, 749; X. D. He, B. Chaudret, F. Dahan and Y. S. Huang, *Organometallics*, 1991, **10**, 970.
12 B. Chaudret, F. Dahan and X. D. He, *J. Chem. Soc., Chem. Commun.*, 1990, 1111; D. Rondon, B. Chaudret, X. D. He and D. Labroue, *J. Am. Chem. Soc.*, 1991, **113**, 5671.
13 X. D. He, B. Chaudret, F. Lahoz and J. A. Lopez, *J. Chem. Soc., Chem. Commun.*, 1990, 959.
14 T. Arliguie and B. Chaudret, *J. Chem. Soc., Chem. Commun.*, 1986, 985; T. Arliguie, C. Border, B. Chaudret, J. Devillers and R. Poilblanc, *Organometallics*, 1989, **8**, 1308.
15 N. Oshima, H. Suzuki, Y. Moro-Oka, H. Nagashima and K. Itoh, *J. Organomet. Chem.*, 1986, **314**, C46.
16 T. D. Tilley, R. H. Grubbs and J. E. Bercaw, *Organometallics*, 1984, **3**, 274; N. Oshima, H. Suzuki and Y. Moro-Oka, *Chem. Lett.*, 1984, 1161.
17 R. Uson, A. Laguna, M. Laguna, B. R. Manzano, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 839.
18 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
19 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
20 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

Received 15*th August* 1991; *Paper* 1/04287D