Letter

A cationic allenylideneruthenium(II) complex with two bulky hemilabile phosphine ligands

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Received (in Strasbourg, France) 31st May 2001, Accepted 6th July 2001
First published as an Advance Article on the web 17th August 2001

The allenylidene complex [RuCl(=C=C=CPh$_2$)(κ^2-*P*,*O*-Cy$_2$PCH$_2$CH$_2$OCH$_3$)$_2$]PF$_6$ (2) has been prepared from [RuCl$_2$(κ^2-*P*,*O*-Cy$_2$PCH$_2$CH$_2$OCH$_3$)$_2$] (1) and HC≡C-C(OH)Ph$_2$ in the presence of AgPF$_6$. Protonation of 2 with HBF$_4$ in diethyl ether leads to the formation of the dicationic ruthenium carbyne [RuCl(≡CCH=CPh$_2$)(κ^2-*P*,*O*-Cy$_2$PCH$_2$CH$_2$OCH$_3$)(κ-*P*-Cy$_2$PCH$_2$CH$_2$OCH$_3$)]$^{2+}$, which is catalytically less active in olefin metathesis than related species with RuHCl(≡CCH$_3$) as a molecular unit. The molecular structure of 2 has been determined by X-ray crystallography.

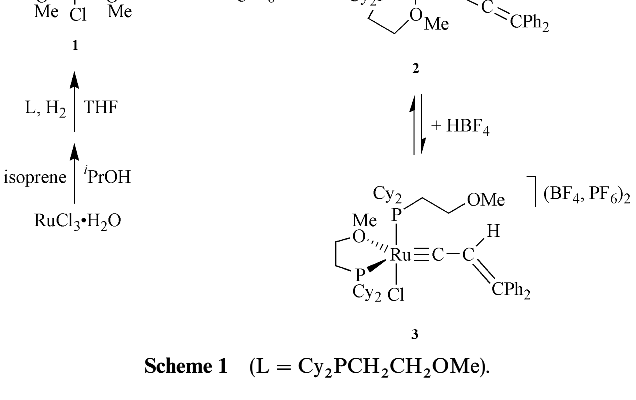
Among the ruthenium(II) compounds which are catalytically active in olefin metathesis, the cationic allenylidene complex [(*p*-cymene)RuCl(=C=C=CPh$_2$)(PCy$_3$)]$^+$, recently described by Dixneuf, Fürstner and co-workers,[1] is noteworthy insofar as the metal center possesses an 18-electron configuration, in contrast to the Grubbs catalyst [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] and various derivatives thereof.[2] Assuming that the actual catalyst, derived from [(*p*-cymene)RuCl(=C=C=CPh$_2$)(PCy$_3$)]$^+$ as the precursor, is generated after dissociation of the weakly bound arene ligand, the question arose whether other ruthenium(II) compounds having an 18-electron count and one or two labile or hemilabile ligands could also be used as catalysts in olefin metathesis. We considered as a promising candidate the chelate complex [RuCl$_2$(κ^2-*P*,*O*-Cy$_2$PCH$_2$CH$_2$-OCH$_3$)$_2$] (**1**), which contains two phosphine ligands related in size to PCy$_3$ and which smoothly reacts with substrates such as CO, CH$_3$CN, SO$_2$ and PhC≡CH by breaking at least one of the Ru–O bonds.[3,4]

Following our experience with the synthesis of bis(phosphine)ruthenium(II) complexes,[5] the preparative procedure for **1** given by Lindner *et al.*[3] was somewhat modified. Treatment of RuCl$_3\cdot$3H$_2$O with isoprene in 2-propanol at 80 °C afforded the dimer [RuCl$_2$(η^3:η^3-C$_{10}$H$_{16}$)]$_2$,[6] which was not isolated and reacted *in situ* with Cy$_2$PCH$_2$CH$_2$OMe under a H$_2$ atmosphere to give compound **1** in 82% yield. For the conversion of **1** to the cationic complex **2**, we used the methodology developed by Dixneuf *et al.* for the synthesis of ruthenium allenylidenes with R$_2$PCH$_2$PR$_2$ as a chelating ligand.[7] The reaction of **1** with the propargylic alcohol HC≡CC(OH)Ph$_2$ in acetone in the presence of one equiv. of AgPF$_6$ afforded, after chromatographic workup and recrystallization from CH$_2$Cl$_2$–pentane, compound **2** in 78% yield (Scheme 1). The red solid is only moderately air-sensitive, soluble in polar solvents such as CH$_2$Cl$_2$ and acetone, and shows in CH$_3$NO$_2$ the conductivity of a 1 : 1 electrolyte. The ^{31}P NMR spectrum of **2** displays two distinct signals for the phosphorus nuclei of the phosphine ligands, indicating that the two PCy$_2$ units are *cis* disposed. Further characteristic features of **2** are the strong C=C=C stretching mode at 1919 cm^{-1} in the IR spectrum and the three low-field resonances at δ 301.2, 220.2 and 152.4 in the ^{13}C NMR spectrum, the latter being assigned to the α-, β- and γ-carbon atoms of the allenylidene moiety, respectively, in agreement with reference data.[8,9]

The molecular structure of the cation of complex **2** is shown in Fig. 1.†[10] The coordination geometry corresponds to a slightly distorted octahedron with the two phosphorus and the two oxygen atoms in *cis* positions. The angles of the *trans*-arranged units O1–Ru–C1, P1–Ru–O2 and P2–Ru–Cl are 177.21(12), 172.36(7) and 163.18(3)°, respectively. The distance Ru–C1 [1.840(3) Å] is practically identical to that in the neutral allenylideneruthenium(II) compound [RuCl$_2$-(=C=C=CPh$_2$)(κ - *P* - ^{i}Pr$_2$PCH$_2$CO$_2$Me)(κ^2 - *P*,*O* - ^{i}Pr$_2$PCH$_2$ - CO$_2$Me)] [1.84(1) Å].[11] The two carbon–carbon bond lengths in the Ru=C=C=C chain are 1.273(4) and 1.357(4) Å and thus quite similar to those found in [(η^5-C$_9$H$_7$)-Ru(=C=C=CPh$_2$)(PPh$_3$)]$^+$,[12] as well as in other ruthenium allenylidenes.[8,9]

The cationic allenylidene complex **2** is much less active than the Dixneuf–Fürstner compound [(*p*-cymene)RuCl(=C=C=CPh$_2$)(PCy$_3$)]$^+$, both in ROMP of cyclooctene and RCM of *N*,*N*-diallyltosyl amide. We assume that, despite the hemilabile coordination mode of the Cy$_2$PCH$_2$CH$_2$OMe ligands in **2**, the olefin can not compete with the OMe donor groups which are part of a five-membered chelate ring.

However, addition of HBF$_4$ in diethyl ether to a solution of **2** in CH$_2$Cl$_2$ leads to the formation of the cationic vinylcarbyne complex **3** in which one of the potentially bidentate phosphine ligands is coordinated only *via* the phosphorus atom to ruthenium. In agreement with the proposed structure (see Scheme 1), the ^{31}P NMR spectrum of **3** shows two doublets at δ 65.1 and 55.7 with a ^{31}P–^{31}P coupling constant of 17.4 Hz, indicating that the two phosphorus



Scheme 1 (L = Cy$_2$PCH$_2$CH$_2$OMe).

DOI: 10.1039/b104787f

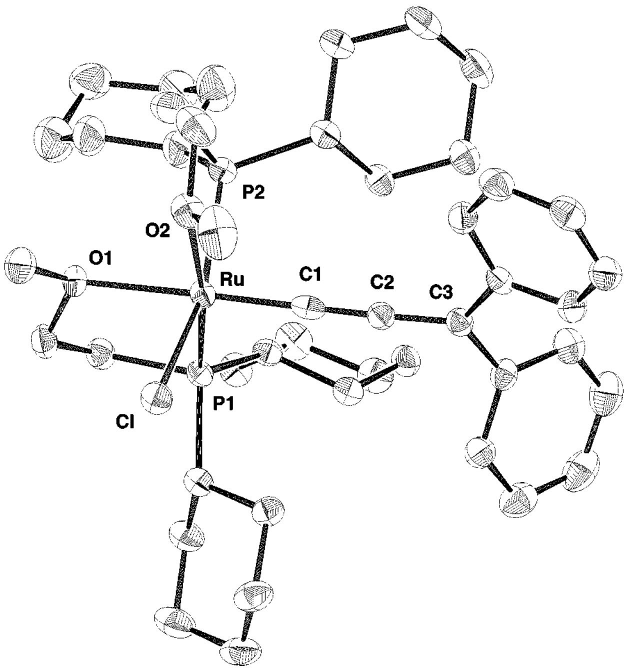


Fig. 1 Molecular structure of the cation of **2** with anisotropic uncertainty parameters depicting 50% probability (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and bond angles (°): Ru–C1 1.840(3), Ru–O1 2.241(2), Ru–O2 2.277(3), Ru–P1 2.2612(11), Ru–P2 2.3613(14), Ru–Cl 2.4159(11), C1–C2 1.273(4), C2–C3 1.357(4); C1–Ru–O1 177.21(12), C1–Ru–O2 93.67(12), C1–Ru–P1 93.95(10), C1–Ru–P2 91.75(11), C1–Ru–Cl 98.33(11), O1–Ru–O2 89.03(9), O1–Ru–P1 83.35(7), O1–Ru–P2 88.00(7), O1–Ru–Cl 82.56(7), O2–Ru–P1 172.36(7), O2–Ru–P2 79.76(9), O2–Ru–Cl 86.17(8), P1–Ru–P2 99.54(5), P1–Ru–Cl 93.19(5), P2–Ru–Cl 163.18(3), Ru–C1–C2 178.7(3), C1–C2–C3 176.7(4).

atoms are *cis* disposed. The resonance for the carbyne carbon atom of **3** appears at δ 315.0 in the ^{13}C NMR spectrum, at about the same position (δ 316.1) as that found for the methylcarbyneruthenium(II) cation $[RuHCl(\equiv CCH_3)(OEt_2)(PCy_3)_2]^+$.[13] Based on a COSY experiment, the signal for the β-carbon atom of the vinylcarbyne unit appears at δ 129.7 and is split into a doublet due to a ^{13}C–^{1}H coupling of 163.8 Hz. The ^{1}H NMR spectrum of **3** displays a triplet for the vinylic proton at δ 6.37 and two singlets for the OCH_3 protons at δ 4.06 and 3.39.

Not unexpectedly, the protonation of **2** to give **3** can be easily reversed and thus our attempts to isolate a stable salt of the vinylcarbyneruthenium(II) cation with BF_4^- or PF_6^- as the couterion failed. Addition of diethyl ether to a solution of **3** in CH_2Cl_2 (in the presence of excess BF_4^- or PF_6^-) only led to the regeneration of the precursor **2**. Due to these observations, we did not study in detail the catalytic capability of **3**. We note, however, that we recently succeeded in preparing salts of the vinylcarbyneiridium(I) cations *trans*-$[IrCl\{\equiv CCH{=}C(Ph)R\}(P^iPr_3)_2]^+$ (R = ^{t}Bu, Ph) which, in the absence of a base, are stable both in the solid state and in solution.[14]

Experimental

All experiments were carried out under an atmosphere of argon using Schlenk techniques. The phosphine $Cy_2PCH_2CH_2OMe$ was prepared as described in the literature.[15] NMR spectra were recorded at room temperature on a Bruker AMX 400 instrument, IR spectra on a Perkin-Elmer 1420 spectrometer and mass spectra (FAB-MS) on a Finnigan 90 MAT spectrometer. Melting points were determined by DTA. Conductivity measurements (Λ) were carried out in CH_3NO_2. Abbreviations used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broadened signal; coupling constants *J* in Hz.

Syntheses

Modified procedure for *trans*-$[RuCl_2(\kappa^2\text{-}P,O\text{-}Cy_2PCH_2CH_2OCH_3)_2]$, 1. A suspension of $RuCl_3 \cdot 3H_2O$ (180 mg, 0.69 mmol) in 2-propanol (10 cm^3) was treated with isoprene (3 cm^3, 30.0 mmol) and stirred for 6 h at 80 °C. After cooling the reaction mixture to room temperature, the solvent was evaporated *in vacuo* and the pale brown residue washed repeatedly with pentane. The residue was dissolved in THF (20 cm^3) and $Cy_2PCH_2CH_2OMe$ (528 mg, 2.34 mmol) was added to the solution. The reaction mixture was stirred under a hydrogen atmosphere for 5 min at room temperature, which led to the precipitation of a pink microcrystalline solid. The solid was filtered off, washed three times with 5 cm^3 portions of pentane and dried *in vacuo*: yield 387 mg (82%). Compound **1** was characterized by comparison of the NMR spectroscopic data with those reported in the literature.[3]

$[RuCl({=}C{=}C{=}CPh_2)(\kappa^2\text{-}P,O\text{-}Cy_2PCH_2CH_2OCH_3)_2]PF_6$, 2. A suspension of **1** (56 mg, 0.08 mmol) and $HC{\equiv}CC(OH)Ph_2$ (22 mg, 0.11 mmol) in acetone (7 cm^3) was treated with a solution of $AgPF_6$ (21 mg, 0.08 mmol) in acetone (3 cm^3) and stirred for 24 h at room temperature. The solvent was evaporated *in vacuo*, the dark red residue was dissolved in CH_2Cl_2 (4 cm^3) and the solution chromatographed on Al_2O_3 (neutral, activity grade I, length of column 5 cm). With CH_2Cl_2–acetone (4 : 1) a dark red fraction was eluted and concentrated to *ca.* 1 cm^3 *in vacuo*. Addition of pentane (10 cm^3) led to the precipitation of a red solid, which was separated from the mother liquor, washed twice with 10 cm^3 portions of pentane and dried *in vacuo*: yield: 62 mg (78%); mp 112 °C (decomp.) Anal. found: C, 54.93; H, 6.85%. $C_{45}H_{68}ClF_6O_2P_3Ru$ requires: C, 54.90; H, 6.96%. Λ (CH_3NO_2) 39.5 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C=C=C) 1919, ν(PF_6^-) 840 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 7.92–7.27 (10 H, m, C_6H_5), 4.25 (4 H, m, CH_2OCH_3), 3.99, 3.90 (3 H each, both s, OCH_3), 2.65 (2 H, m, PCH_2), 2.43–0.93 (46 H, br m, PCH_2 and C_6H_{11}); δ_C (100.6 MHz) 301.2 [dd, *J*(P,C) 17.8, *J*(P′,C) 19.1, Ru=C], 220.0 (s, Ru=C=*C*), 152.4 (s, Ru=C=C=*C*), 145.3 (s, *ipso*-C of C_6H_5), 130.9, 129.3, 129.2 (all s, C_6H_5), 72.2, 71.6 (both s, CH_2OCH_3), 62.0, 61.8 (both s, OCH_3), 46.6 [d, *J*(P,C) 25.4, *ipso*-C of C_6H_{11}], 40.9 [d, *J*(P,C) 22.9, *ipso*-C of C_6H_{11}], 37.8 [d, *J*(P,C) 26.7, *ipso*-C of C_6H_{11}], 36.8 [d, *J*(P,C) 17.8, *ipso*-C of C_6H_{11}], 31.0, 30.7 (both s, C_6H_{11}), 29.6 [d, *J*(P,C) 3.8, C_6H_{11}], 29.3, 29.2 (both s, C_6H_{11}), 28.9 [d, *J*(P,C) 8.9, C_6H_{11}], 28.6 (s, C_6H_{11}), 28.5 [d, *J*(P,C) 5.1, C_6H_{11}], 27.73 [d, *J*(P,C) 7.6, C_6H_{11}], 27.69, 27.59, 27.55, 27.50, 27.4 (all s, C_6H_{11}), 26.8 [d, *J*(P,C) 14.0, C_6H_{11}], 26.5 (s, C_6H_{11}), 26.3 [d, *J*(P,C) 12.7, C_6H_{11}], 25.8, 25.7, 25.3 (all s, C_6H_{11}), 23.5 [d, *J*(P,C) 24.2, PCH_2], 22.0 [d, *J*(P,C) 22.9, PCH_2]; δ_P (162.0 MHz) 61.9, 49.3 [both d, AB system, *J*(P,P) 26.2], −144.4 [sept, *J*(F,P) 710.7, PF_6^-]; δ_F (376.5 MHz) −73.2 [d, *J*(P,F) 710.7, PF_6^-]. FAB MS (70 eV): *m*/*z* (%) 839 (1.8, $[M - PF_6]^+$).

Generation of $[RuCl(\equiv CCH{=}CPh_2)(\kappa^2\text{-}P,O\text{-}Cy_2PCH_2CH_2OCH_3)(\kappa\text{-}P\text{-}Cy_2PCH_2CH_2OCH_3)](PF_6, BF_4)_2$, 3. A solution of **2** (50 mg, 0.05 mmol) in CH_2Cl_2 (8 cm^3) was treated with an excess of a 1.6 M solution of HBF_4 in diethyl ether (0.1 cm^3, 0.16 mmol) at room temperature. A rapid change of colour from red to green occurred. The solvent was evaporated *in vacuo* and the remaining oily green residue characterized spectroscopically. Attempts to recrystallize **3** from CH_2Cl_2–diethyl ether led to the regeneration of the starting material **2**. NMR data for **3** (CD_2Cl_2): δ_H (400 MHz) 7.87–7.32 (10 H, m, C_6H_5), 6.37 [1 H, t, *J*(P,H) 2.6, Ru≡CCH], 4.37–4.09 (3 H, m, C*H*$_2$OCH$_3$), 4.06 (3 H, s, κ-*O*-OCH$_3$), 3.86 (1 H, m, C*H*$_2$OCH$_3$), 3.39 (3 H, s, OCH$_3$), 2.65 (2 H, m, PCH$_2$), 2.43–1.09 (46 H, m, PCH$_2$ and C$_6$H$_{11}$); δ_C (100.6 MHz) 315.0 [dd, *J*(P,C) = *J*(P′,C) 14.6, Ru≡C], 184.6 (s, CH=*C*), 137.1, 136.7 (both s, *ipso*-C of C$_6$H$_5$), 136.8, 135.7, 132.9, 131.8, 130.0 (all s, C$_6$H$_5$), 129.7 (s, *C*H=C), 75.8, 70.5 (both s, *C*H$_2$OCH$_3$), 63.8, 61.6 (both s, OCH$_3$), 47.9 [d, *J*(P,C) 26.7, *ipso*-C of C$_6$H$_{11}$], 39.8 [d, *J*(P,C) 21.6, *ipso*-C of C$_6$H$_{11}$], 38.6 [d, *J*(P,C) 25.4, *ipso*-C of C$_6$H$_{11}$], 37.2 [d, *J*(P,C) 16.5, *ipso*-C of C$_6$H$_{11}$], 30.2, 30.1, 29.72, 29.66 (all s, C$_6$H$_{11}$), 29.6, 29.5 (both m, C$_6$H$_{11}$), 27.6 (s, C$_6$H$_{11}$), 27.4 [d, *J*(P,C) 11.4, C$_6$H$_{11}$], 27.2 (s, C$_6$H$_{11}$), 26.8 [d, *J*(P,C) 12.7, C$_6$H$_{11}$], 26.7 [d, *J*(P,C) 10.2, C$_6$H$_{11}$], 26.5 [d, *J*(P,C) 11.4, C$_6$H$_{11}$], 25.7, 25.4, 25.3, 25.2 (all s, C$_6$H$_{11}$), 22.5 [d, *J*(P,C) 25.4, PCH$_2$], 22.4 (s, C$_6$H$_{11}$), 21.3 [d, *J*(P,C) 25.4, PCH$_2$]; δ_P (162.0 MHz) 65.1, 55.7 [both d, AB system, *J*(P,P) 17.4].

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (SFB 347), the Fonds der Chemischen Industrie and BASF AG. We also thank Mrs R. Schedl and Mr C. P. Kneis (DTA and elemental analysis), Dr G. Lange and Mr F. Dadrich (mass spectra) and Mr S. Stellwag for experimental assistance.

Notes and references

† Crystal data for **2**: C$_{45}$H$_{68}$ClF$_6$O$_2$P$_3$Ru, $M = 984.48$; crystal size $0.25 \times 0.25 \times 0.10$ mm^3; triclinic, space group $P\bar{1}$, $a = 13.272(3)$, $b = 15.701(3)$, $c = 16.934(3)$ Å, $\alpha = 107.00(3)$, $\beta = 110.32(3)$, $\gamma = 98.76(3)°$, $Z = 2$, $V = 3034.9(11)$ Å^3, $\rho_{\text{ber.}} = 1.369$ g cm^{-3}; $T = 173(2)$ K; $2\Theta = 56.10°$; 40584 data, 13532 unique data ($R_{\text{int}} = 0.0579$), 8150 observed data [$I > 2\sigma(I)$]; IPDS (Stoe), Mo-Kα radiation ($\lambda = 0.71073$ Å), graphite monochromator; Lp correction; structure solution by direct methods (SHELXS), refined by the full-matrix least-squares method (SHELXL-97). Final R_1 and wR_2 values on all data 0.0910, 0.1248; [$I > 2\sigma(I)$] data 0.0484, 0.1093; reflex/parameter ratio 18.04; max./min. residual electron density $+1.168/-1.364$ e Å^{-3}.

CCDC reference number 167897. See http://www.rsc.org/suppdata/nj/b1/b104787f/ for crystallographic data in CIF or other electronic format.

1 A. Fürstner, M. Picquet, C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1998, 1315.

2 Representative articles: E. L. Dias and R. H. Grubbs, *Organometallics*, 1998, **17**, 2758; S. Chang, L. Jones, C. Wang, L. M. Henling and R. H. Grubbs, *Organometallics*, 1998, **17**, 3460; M. S. Sanford, L. M. Henling and R. H. Grubbs, *Organometallics*, 1998, **17**, 5384; S. M. Hansen, M. A. O. Volland, F. Rominger, F. Eisenträger and P. Hofmann, *Angew. Chem.*, 1999, **111**, 1360; S. M. Hansen, M. A. O. Volland, F. Rominger, F. Eisenträger and P. Hofmann, *Angew. Chem., Int. Ed.*, 1999, **38**, 1273; S. M. Hansen, F. Rominger, M. Metz and P. Hofmann, *Chem. Eur. J.*, 1999, **5**, 557; T. Weskamp, F. J. Kohl and W. A. Herrmann, *J. Organomet. Chem.*, 1999, **582**, 362; L. Ackermann, A. Fürstner, T. Weskamp, F. J. Kohl and W. A. Herrmann, *Tetrahedron Lett.*, 1999, **40**, 4787; J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, Jr. and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1999, **121**, 791; J. Huang, E. D. Stevens, S. P. Nolan and J. L. Petersen, *J. Am. Chem. Soc.*, 1999, **121**, 2674; A. Fürstner, A. F. Hill, M. Liebl and J. D. E. T. Wilton-Ely, *Chem. Commun.*, 1999, 601; C. W. Bielawski and R. H. Grubbs, *Angew. Chem.*, 2000, **112**, 3025; C. W. Bielawski and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2000, **39**, 2903; D. M. Lynn, B. Mohr, R. H. Grubbs, L. M. Henling and M. W. Day, *J. Am. Chem. Soc.*, 2000, **122**, 6601.

3 E. Lindner, U. Schober, R. Fawzi, W. Hiller, U. Englert and P. Wegner, *Chem. Ber.*, 1987, **120**, 1621.

4 E. Lindner, M. Geprägs, K. Gierling, R. Fawzi and M. Steimann, *Inorg. Chem.*, 1995, **34**, 6106.

5 J. Wolf, W. Stüer, C. Grünwald, H. Werner, P. Schwab and M. Schulz, *Angew. Chem.*, 1998, **110**, 1165; J. Wolf, W. Stüer, C. Grünwald, H. Werner, P. Schwab and M. Schulz, *Angew. Chem., Int. Ed.*, 1998, **37**, 1124.

6 L. Porri, M. C. Gallazzi, A. Colombo and G. Allegra, *Tetrahedron Lett.*, 1965, 4187; D. N. Cox and R. Roulet, *Inorg. Chem.*, 1990, **29**, 1360.

7 D. Touchard, N. Pirio and P. H. Dixneuf, *Organometallics*, 1995, **14**, 4920.

8 Reviews: M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197; M. I. Bruce, *Chem. Rev.*, 1998, **98**, 2797; V. Cadierno, M. P. Gamasa and J. Gimeno, *Eur. J. Inorg. Chem.*, 2001, 571.

9 Recent papers: M. I. Bruce, P. Hinterding, P. J. Low, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 1009; M. Martin, O. Gevert and H. Werner, *J. Chem. Soc., Dalton Trans.*, 1996, 2275; M. P. Gamasa, J. Gimeno, C. Gonzalez-Bernardo, J. Borge and S. Garcia-Granda, *Organometallics*, 1997, **16**, 2483; H. P. Xia, W. F. Wu, W. S. Ng, I. D. Williams and G. Jia, *Organometallics*, 1997, **16**, 2940; R. F. Winter and F. M. Hornung, *Organometallics*, 1997, **16**, 4248; I. de los Rios, M. J. Tenorio, M. C. Puerta and P. Valerga, *J. Organomet. Chem.*, 1997, **549**, 221; W.-H. Leung, E. Y. Y. Chan and W.-T. Wong, *Organometallics*, 1998, **17**, 1245; M. C. B. Colbert, J. Lewis, N. J. Long, P. R. Raithby, M. Younus, A. J. P. White, D. J. Williams, N. N. Payne, L. Yellowlees, D. Beljonne, N. Chawdhury and R. H. Friend, *Organometallics*, 1998, **17**, 3034.

10 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976; G. M. Sheldrick, SHELXS-86, Program for Crystal Structure Determination, University of Göttingen, Germany, 1986; G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

11 H. Werner, A. Stark, P. Steinert, C. Grünwald and J. Wolf, *Chem. Ber.*, 1995, **128**, 49.

12 V. Cadierno, M. P. Gamasa, J. Gimeno, M. Gonzalez-Cueva, E. Lastra, J. Borge, S. Garcia-Granda and E. Perez-Carreno, *Organometallics*, 1996, **15**, 2137.

13 W. Stüer, J. Wolf, H. Werner, P. Schwab and M. Schulz, *Angew. Chem.*, 1998, **110**, 3603; W. Stüer, J. Wolf, H. Werner, P. Schwab and M. Schulz, *Angew. Chem., Int. Ed.*, 1998, **37**, 3421.

14 K. Ilg and H. Werner, *Chem. Eur. J.*, in press.

15 E. Lindner, S. Meyer, P. Wegner, D. Karle, A. Sickinger and B. Steger, *J. Organomet. Chem.*, 1987, **335**, 59.