ELSEVIER

Journal of Organometallic Chemistry 572 (1999) 239–247

Journal of Organo metallic Chemistry

Dicationic chelating *N*-heterocyclic carbene complexes of palladium: new catalysts for the copolymerisation of C_2H_4 and CO[☆,☆☆]

Michael G. Gardiner, Wolfgang A. Herrmann *, Claus-Peter Reisinger [1], Jürgen Schwarz, Michael Spiegler

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-85747, Germany

Received 14 July 1998; received in revised form 27 August 1998

Abstract

Dicationic *N*-heterocyclic carbene chelates of formula $[cis\text{-}CH_2\{\overline{N(H)C{=}C(H)N(R)C}\}_2Pd(NCCH_3)_2]^{2+}$ (R = Me, 2,4,6-Me_3–C_6H_2) have been prepared via high yielding, air-stable procedures and structurally characterized in the former case as a $2[BF_4]^-$ salt. The complexes catalyze the copolymerisation of C_2H_4 and CO to give high molecular weight, strictly alternating poly(C_2H_4-*alt*-CO) under mild conditions and low pressures. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Homogeneous catalysis; Copolymerisation; Polymers; Heterocyclic carbene

---

1. Introduction

N-Heterocyclic based carbene complexes have long been the subject of both synthetic and catalytic studies in our group, and a review has appeared recently [1]. Of note in these past endeavours has been the discovery that di(carbene)palladium(II)dihalide complexes are efficient catalysts for various C–C and C–N coupling reactions involving redox-active palladium transformations (Pd(0)–Pd(II)), in particular the activation of chloro-arenes in the Heck reaction [2,3]. In these fields of catalysis metal–phosphine complexes had achieved initial success.

From the work of E. Drent et al. monocationic alkyl and dicationic *cis*-chelating (usually phosphine, L_2) complexes of palladium, $[L_2Pd(solvent)Me]^+$ and $[L_2Pd(solvent)_2]^{2+}$, respectively are known to yield copolymers of ethene and CO which have such industrial importance as to warrant the establishment of the large-scale production by Shell. The subject has been reviewed by E. Drent and other authors in recent times with emphasis on both mechanistic and catalyst structural detail [4].

In the present paper, we report on extensions of our synthetic studies of palladium–carbene complexes to include a number of mono- and dicationic *cis*-chelating di(carbene) complexes. Beyond that, our preliminary catalytic results for the copolymerisation of C_2H_4 and CO are reported.

2. Experimental section

2.1. General procedures

All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or nitrogen. Methanol was dried over Mg, dichloromethane over CaH_2 and acetonitrile over P_2O_5 and

---

[☆] Communication 19 of the series '*N*-Heterocyclic Carbenes'; Preceeding paper: W.A. Herrmann, L.J. Gooßen, M. Spiegler, J. Organomet. Chem. 547 (1997) 357.

* Corresponding author. Tel.: +49-89-289-13080; fax: +49-89-289-13473; e-mail: lit@arthur.anorg.chemie.tu–muenchen.de.

[☆☆] Dedicated to my friend Hans Bock, Universität Frankfurt, on the occasion of his 70th birthday.

[1] Present address: Bayer AG, Central Research, Geb. R 79, 47812 Krefeld.

0022-328X/99/$ - see front matter © 1999 Elsevier Science S.A. All rights reserved.

PII: S0022-328X(98)00960-7

distilled prior to use using conventional procedures. Other solvents were used as received as technical grade solvents. [*cis*-$CH_2\{\overline{N(H)C{=}C(H)N(Me)C}\}_2PdBr_2$] **4** was prepared according to our literature procedure for the iodide analogue [3]. 1-(Mesityl)imidazole **1** was prepared according to a variation of the literature procedure for the preparation of 1-alkylimidazoles which gave higher yields of the product by solubilizing the intermediate imine compounds by the addition of 1,4-dioxane [5]. The compound $(CF_3)_2CHOH$ was obtained from Merck. Other chemicals were obtained from Aldrich and used as received. ^1H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a JOEL JNM-GX 400 spectrometer in $CDCl_3$, d_6-DMSO, $(CF_3)_2CHOH/C_6D_6$ and D_2O and referenced to the residual ^1H resonances of the solvents. Elemental analyses were performed by the microanalytical laboratory in our institute. Melting points were determined in glass capillaries under air. IR spectra were recorded on a FT-IR PERKIN ELMER 1680 spectrometer. Mass spectra were recorded on a Varian MAT 311a spectrometer using FAB ionisation (xenon/*p*-nitrobenzylalcohol matrix). GC/MS were obtained on a Hewlett-Packard 5890 instrument.

2.2. Synthesis of 1-(mesityl)imidazole **1**

An ammonium chloride solution (5.35 g, 0.10 mol, 20 ml H_2O) was added dropwise over 30 min to a rapidly stirred solution of 100 ml H_2O and 100 ml 1,4-dioxane at 100°C containing paraformaldehyde (3.00 g, 0.10 mol), mesitylammonium salt (prepared from the addition of phosphoric acid to mesitylamine (13.5 g, 0.10 mol) in 50 ml H_2O until a pH of ca. 2 was reached) and glyoxal (11.5 ml of 40% aqueous solution, 0.10 mol). During the addition the solution turns yellow and then rapidly black. The solution is maintained at 100°C for a further 1 h (all mesitylamine consumed by GC/MS analysis) and then chilled in an ice bath. Solid NaOH was added at 0°C until a $pH > 12$ was obtained and a dark organic layer separated. H_2O (150 ml) was added to the reaction mixture and the product was extracted with 3 × 500 ml hexane. The combined hexane extracts were dried over $MgSO_4$ and evaporated to yield the product as a light brown solid which was recrystallised from ethyl acetate as a colourless crystalline solid in three crops (7.36 g, 40%). M.p. 112–113°C; ^1H-NMR (400 MHz, $CDCl_3$) δ 1.98 (6 H, s, *o*-Me), 2.34 (3 H, s, *p*-Me), 6.89 (1 H, bs, CH(imid.)), 6.97 (2 H, s, *m*-CH(*mes.*)), 7.23, 7.43 (2×1 H, bs, CH(imid.)); ^{13}C-NMR (100.53 MHz, $CDCl_3$) δ 17.3 (*o*-Me), 21.0 (*p*-Me), 120.0, 128.9, 129.5, 133.4, 135.4, 137.4, 138.8 ($3 \times$ CH(imid.), *ipso*-, *o*-, *m*-, *p*-C(*mes.*)); MS *m*/*z* 186 (M^+, 32%); found C 77.37, H 7.56, N 14.97%, calc. (for $C_{12}H_{14}N_2$) C 77.38, H 7.58, N 15.04%.

2.3. Synthesis of 1,1′-di(mesityl)-3,3′-methylene-diimidazolium dibromide **2**

A stirred toluene solution (10 ml) of 1-(mesityl)imidazole **1** (1.50 g, 8.06 mmol) and CH_2Br_2 (1.40 g, 8.06 mmol) was heated at 150°C for 2 days to yield a white powder of the product which was collected, washed with THF and dried in vacuo (2.00 g, 69%). M.p. 303°C (with dec.); ^1H-NMR (400 MHz, d_6-DMSO) δ 2.07 (12 H, s, *o*-Me), 2.34 (6 H, s, *p*-Me), 7.04 (2 H, s, CH_2), 7.18 (4 H, s, *m*-CH(*mes.*)), 8.13 (2 H d, $^3J_{HH} = 1.2$ Hz, CH(imid.)), 8.61 (2 H d, $^3J_{HH} = 1.2$ Hz, CH(imid.)), 10.22 (2 H, s, CH(imid.)); ^{13}C-NMR (100.53 MHz, d_6-DMSO) δ 18.9 (*o*-Me), 22.5 (*p*-Me), 60.5 (CH_2), 124.6, 126.5, 130.8, 132.7, 136.4, 141.1, 142.4 ($3 \times$ CH(imid.), *ipso*-, *o*-, *m*-, *p*-C(*mes.*)).

2.4. Synthesis of [{1,1′-di(mesityl)-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II)dibromide] **3**

A stirred DMSO solution (5 ml) of 1,1′-di(mesityl)-3,3′-methylenediimidazolium dibromide **2** (506 mg, 0.927 mmol) and $Pd(OAc)_2$ (208 mg, 0.929 mol) was heated at 50°C for 3 h and then at 110°C for a further 2 h, during which time the reaction solution had turned to a pale yellow solution from being initially orange. The remaining DMSO was then removed in vacuo to give a yellow solid which was washed with DCM to give the product as a very pale yellow solid. Recrystallisation from acetonitrile gave the product as very fine pale yellow needles (450 mg, 75%). M.p. 310°C (dec.); ^1H-NMR (400 MHz, 80°C, d_6-DMSO) δ 2.04 (12 H, bs, *o*-Me), 2.31 (6 H, bs, *p*-Me), 6.54 (2 H, bs, CH_2), 6.97 (4 H, bs, *m*-CH(*mes.*)), 7.31 (2 H, bs, CH(imid.)), 7.86 (2 H, bs, CH(imid.)); FAB-MS *m*/*z* 1221 ((2M−Br)$^+$, 5%); found C 46.01, H 4.35, N 8.60%, calc. (for $C_{25}H_{28}N_4Br_2Pd$) C 46.14, H 4.34, N 8.61%.

2.5. Synthesis of [{1,1′-di(mesityl)-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II)-diiodide] **5**

An acetonitrile:H_2O (10:10 ml) solution of [{1,1′-di(mesityl)-3,3′-methylenediimidazolin-2,2′-diylidene}-palladium(II)dibromide] **3** (30 mg, 0.046 mmol) and NaI (160 mg, 1.07 mmol) was heated at 80°C for 10 min before removing the acetonitrile in vacuo to precipitate the product as a yellow oil which solidified on cooling to room temperature. The solid was collected, washed with H_2O and dried in vacuo. The product was recrystallised as fine yellow needles by layering Et_2O onto a saturated acetonitrile solution (29 mg, 84%). M.p. 285–300°C (dec.); ^1H-NMR (400 MHz, d_6-DMSO) δ 2.03 (12 H, s, *o*-Me), 2.30 (6 H, s, *p*-Me), 6.56 (2 H, bs, CH_2), 7.02 (4 H, s, *m*-CH(*mes.*)), 7.48 (2 H, bs, CH(imid.)), 7.90 (2 H, bs, CH(imid.)); FAB-MS *m/z* 1363 ($(2M-I)^+$, 8%); found C 40.53, H 4.05, N 7.41%, calc. (for $C_{25}H_{28}N_4I_2Pd$) C 40.32, H 3.97, N 7.53%.

2.6. Synthesis of [{1,1′-di(mesityl)-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II)-bis(acetonitrile)][PF_6]$_2$ **6**

An acetonitrile:H_2O (30:30 ml) solution of [{1,1′-di(mesityl)-3,3′-methylenediimidazolin-2,2′-diylidene}-palladium(II)dibromide] **3** (200 mg, 0.31 mmol) and Na[PF_6] (2.00 g, 119 mmol) was heated at 80°C for 10 min before removing the acetonitrile in vacuo to precipitate the product as a white solid which was collected, washed with H_2O and dried in vacuo. The product was recrystallised as colourless rods by layering Et_2O onto a saturated acetonitrile solution (244 mg, 92%). M.p. 215°C (dec.); ^{1}H-NMR (400 MHz, d_6-DMSO) δ 2.09 (12 H, s, *o*-Me), 2.09 (6 H, s, *p*-Me), 2.35 (6 H, s, MeCN), 6.65 (2 H, s, CH_2), 7.14 (4 H, s, *m*-CH(*mes.*)), 7.61 (2 H, d, $^3J_{HH} = 1.84$ Hz, CH(imid.)), 8.02 (2 H, d, $^3J_{HH} = 1.84$ Hz, CH(imid.)); ^{13}C-NMR (100.53 MHz, d_6-DMSO) δ 1.6 (MeCN), 18.7 (*o*-Me), 21.0 (*p*-Me), 62.8 (CH_2), 118.6 (MeCN), 123.4, 126.1, 129.6, 134.7, 135.0, 139.7, 145.5 ($2 \times$ CH(imid.), *ipso*-, *o*-, *m*-, *p*-C(*mes.*), carbene); ^{31}P-NMR (161.85 MHz, d_6-DMSO) δ 56.78 (sept., $^1J_{PF} = 711.1$ Hz, PF_6); FAB-MS *m/z* 489 (((dicarbene)Pd−H)$^+$, 11%); IR (KBr disc) 2327 (s, MeCN), 2301 (s, MeCN); found C 40.58, H 4.06, N 10.02, P 7.12%, calc. (for $C_{29}H_{34}N_6F_{12}P_2Pd$) C 40.36, H 3.97, N 9.74, P 7.17%.

2.7. Synthesis of [{1,1′-dimethyl-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II)-(acetonitrile)bromide] [PF_6] **7**

An acetonitrile:H_2O (20:15 ml) solution of [{1,1′-dimethyl-3,3′-methylenediimidazolin-2,2′-diylidene}-palladium(II)dibromide] **4** (200 mg, 0.45 mmol) and K[PF_6] (1.50 g, 8.15 mmol) was refluxed for 12 h before removing the acetonitrile in vacuo to precipitate the product as a white solid which was collected, washed with H_2O and dried in vacuo. The product was recrystallised as fine needles by layering Et_2O onto a saturated acetonitrile solution (237 mg, 96%). M.p. 223°C (dec.); ^{1}H-NMR (400 MHz, d_6-DMSO) δ 3.85, 3.95 (2×3 H, s, Me), 1.99 (3 H, s, MeCN), 6.02 (1 H, AB $^2J_{HH} = 13.52$ Hz, CH_2), 6.24 (1 H, AB $^2J_{HH} = 13.52$ Hz, CH_2), 7.11 (2 H, bs, CH(imid.)), 7.38 (2 H, bs, CH(imid.)); ^{13}C-NMR (100.53 MHz, d_6-DMSO) δ 0.6 (MeCN), 37.2, 39.0 ($2 \times$ Me), 62.6 (CH_2), 117.5 (MeCN), 117.5 (CH(imid.)), 121.4 (CH(imid.)), 121.9 (CH(imid.)), 122.9 (CH(imid.)), 142.3 (carbene), 145.5 (carbene); FAB-MS *m/z* 363 ((dicarbene)PdBr$^+$, 63%); found C 24.52, H 3.37, N 13.18%, calc. (for $C_{11}H_{15}N_5BrF_6PPd$) C 24.14, H 2.76, N 12.80%.

2.8. Synthesis of [{1,1′-dimethyl-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II)-bis(acetonitrile)] [BF_4]$_2$ **8**

An acetonitrile solution (15 ml) of [{1,1′-dimethyl-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II) dibromide] **4** (300 mg, 0.68 mmol) and Ag[BF_4] (265 mg, 1.36 mmol) was heated at 60°C for 8 h. The solution was then filtered from the precipitated AgBr and the acetonitrile removed in vacuo to give a white solid. The product was recrystallised as colourless rods by layering Et_2O onto a saturated acetonitrile solution (358 mg, 98%). M.p. 235°C; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 2.08 (6 H, s, MeCN), 3.85 (6 H, s, Me), 6.35 (1 H, bs, CH_2), 6.48 (1 H, bs, CH_2), 7.44 (2 H, bs, CH(imid.)), 7.68 (2 H, bs, CH(imid.)); ^{13}C-NMR (100.53 MHz, d_6-DMSO) δ 1.6 (MeCN), 38.5 (Me), 62.5 (CH_2), 118.6 (MeCN), 122.9 (CH(imid.)), 124.4 (CH(imid.)), 146.4 (carbene); FAB-MS *m/z* 536 (M$^+$, 58%); found C 29.39, H 3.75, N 15.16%, calc. (for $C_{13}H_{18}N_6B_2F_8Pd$) C 29.00, H 3.37, N 15.61%.

2.9. Structure determination for compound **8**

$C_{13}H_{18}N_6B_2F_8Pd.CH_3CN$, $M = 579.41$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 11.1502(2)$ Å, $b = 12.3449(2)$ Å, $c = 16.7746(2)$ Å, $U = 2308.99(6)$ Å^3, $Z = 4$, $D_{calc.} = 1.667$ g cm^{-3}, $F(000) = 1152$. Monochromated Mo–K$_\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu = 8.8$ cm^{-1}.

A crystal of **8**, $0.25 \times 0.20 \times 0.13$ mm, suitable for X-ray structure determination was grown by vapour diffusion of diethyl ether into a concentrated acetonitrile solution and mounted in a glass capillary. Data were collected on a Nonius KappaCCD detection system at 193K ($\theta_{min} - \theta_{max} = 4.7$–$26.4°$). A total of 23 879 reflections were measured and 4656 unique reflections ($R_{int} = 0.044$) were used in the full matrix least squares refinement. Preliminary positions of heavy atoms were found by direct methods [6], and the positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with initial isotropic least squares refinement [7]. The PLATON program was used for the molecular projection diagram [8]. Anisotropic thermal parameters were refined for all non-hydrogen atoms in the structure determination. Hydrogen atom positions were calculated and constrained at estimated values (C–H 0.93, 0.96 and 0.97 Å for the sp^2, methylene and methyl hydrogens, respectively). Temperature factors for hydrogen atoms were estimated at $1.2 \times U_{ii}$(average) of the attached carbon atom. The final residuals were $R_1 = 0.0250$ and $wR_2 = 0.0656$ for 298 parameters, $s = 1.038$, and a final difference map had extreme values of $+0.39$ and -0.56 e Å^{-3}. Non-hydrogen atom coordinates and isotropic thermal parameters are presented in Table 1, and selected structural parameters are given in Table 2. Further details of the crystal structure determination can be obtained from the Cambridge Crystallographic Data Centre.

2.10. Copolymerisation catalysis studies

The solutions for copolymerisation studies were typically prepared as follows; dissolving the catalyst and *p*-benzoquinone in the solvent mixture by gentle heating which was then allowed to cool and transferred directly under a flow of nitrogen into a vacuum dried 40 ml Parr autoclave fitted with a glass liner and equipped with a stirring bar. The stirred solutions were charged in turn with C_2H_4 and then CO and heated to the appropriate temperature of the experiment. The copolymerisation rates were monitored by the reduction in pressure of the sealed autoclave, which typically commenced after ca. 30 min and were complete after ca. 2–4 h for reactions at 50°C. The vessels were then cooled to room temperature, vented of remaining C_2H_4 and CO, and the resulting grey poly(C_2H_4-*alt*-CO) powders collected, washed with methanol, vacuum dried and weighed, while the pale yellow methanol solutions were filtered and analysised by GC/MS for the formation of oligomeric products. In selected cases, the polymers had their melting points determined and were characterized by ^{1}H- and ^{13}C-NMR spectroscopy in ca. 50:50% C_6D_6: 1,1,1,3,3,3-hexafluoro-*iso*-propanol which were filtered to remove the suspended palladium. Table 3 shows results from pertinent copolymerisation experiments.

3. Results and discussion

The use of late transition metal complexes as alternative alkene polymerisation catalysts to the established Ziegler–Natta and metallocene systems is attracting increasing interest in the literature due to the high activity of the catalysts and the high molecular weight polymers which can thus be produced [9].

The initial discovery that extremely bulky cationic β-diimine complexes of palladium and nickel were necessary to block chain transfer and termination mechanisms, known to thwat the production of high molecular weight polymers of olefins, was the key to opening this field and it is now a highly researched area by both experimentalists [10] and theoreticians [11].

Prior to these breakthroughs, it was known that high molecular weight alternating copolymers of ethene and CO can be produced using dicationic *cis*-chelating diphosphine complexes of palladium since the structure of the growing polymeric chain affords protection against termination mechanisms owing to a chelation stabilisation of the γ-carbonyl group of the polymer to the metal centre [4]. Further, the alternation of the monomeric units of the polymer is assured due to both thermodynamic and kinetic considerations of the coordination, and then insertion, of the respective monomers into the growing polyketone chain. More recent studies based on the copolymerisation of CO with α-olefins have provided further mechanistic detail for the catalytic processes [12] and other, non-phosphine ligand systems have been reported to catalyse the production of poly(C_2H_4-*alt*-CO) with varying success [13]. Complexes arising from the insertion of C_2H_4, α-olefins and CO into both Pd–Me and Pd–CO bonds

Table 1
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms of **8**

Atom	x	y	z	U_{eq}[a] (Å^2)
Pd	0.42030(2)	0.38586(1)	0.15113(1)	0.0264(1)
N(2)	0.5166(2)	0.15774(19)	0.16579(15)	0.0417(8)
N(5)	0.6543(2)	0.2788(2)	0.16820(14)	0.0383(7)
N(8)	0.6619(2)	0.4424(2)	0.09632(16)	0.0389(8)
N(10)	0.5337(3)	0.49467(19)	0.00847(15)	0.0446(8)
N(21)	0.3045(2)	0.32274(19)	0.23433(15)	0.0358(7)
N(31)	0.3066(2)	0.51617(19)	0.13582(14)	0.0360(7)
C(1)	0.5342(2)	0.2654(2)	0.16337(16)	0.0312(7)
C(3)	0.6250(3)	0.1047(3)	0.1733(2)	0.0549(11)
C(4)	0.7110(3)	0.1794(3)	0.17512(19)	0.0521(11)
C(6)	0.4005(4)	0.1030(3)	0.1617(3)	0.0635(13)
C(7)	0.7096(2)	0.3849(3)	0.16491(19)	0.0448(9)
C(9)	0.5436(3)	0.4456(2)	0.07925(16)	0.0325(8)
C(11)	0.7270(4)	0.4921(3)	0.0363(2)	0.0538(11)
C(12)	0.6472(4)	0.5246(3)	−0.0178(2)	0.0599(13)
C(13)	0.4237(4)	0.5158(3)	−0.03413(18)	0.0592(13)
C(22)	0.2503(3)	0.2892(2)	0.28573(16)	0.0331(8)
C(23)	0.1821(3)	0.2442(2)	0.3511(2)	0.0446(9)
C(32)	0.2452(3)	0.5881(2)	0.12752(16)	0.0362(8)
C(33)	0.1674(3)	0.6810(3)	0.1159(2)	0.0494(10)
N(41)	−0.1111(3)	0.2682(3)	0.0281(2)	0.0603(11)
C(42)	−0.0145(3)	0.2776(3)	0.0458(2)	0.0570(12)
C(43)	0.1091(4)	0.2874(7)	0.0695(5)	0.142(4)
F(1)	0.03558(19)	0.99747(18)	0.33378(12)	0.0571(7)
F(2)	0.1212(3)	1.0481(3)	0.22091(19)	0.1070(15)
F(3)	−0.0795(3)	1.0269(3)	0.22732(15)	0.1106(12)
F(4)	0.0431(3)	0.8868(2)	0.2268(2)	0.1026(11)
B(1)	0.0293(3)	0.9917(3)	0.2515(2)	0.0444(11)
F(5)	0.5914(3)	0.3369(2)	0.34905(16)	0.0845(10)
F(6)	0.4265(2)	0.3751(2)	0.41977(15)	0.0789(9)
F(7)	0.4685(3)	0.2037(2)	0.3827(2)	0.1009(12)
F(8)	0.5824(3)	0.2834(3)	0.47597(16)	0.1068(13)
B(2)	0.5184(4)	0.3012(4)	0.4083(2)	0.0510(12)

[a] U_{eq} is 1/3 of the trace of the orthogonalized U.

Table 2
Structural parameters of **8**

Bond distances (Å)			
Pd–N(21)	2.055(2)	N(8)–C(9)	1.350(4)
Pd–N(31)	2.064(2)	N(8)–C(11)	1.385(5)
Pd–C(1)	1.966(2)	N(10)–C(9)	1.337(4)
Pd–C(9)	1.972(3)	N(10)–C(12)	1.390(5)
N(2)–C(1)	1.344(3)	N(10)–C(13)	1.443(5)
N(2)–C(3)	1.380(4)	N(21)–C(22)	1.131(4)
N(2)–C(6)	1.462(5)	N(31)–C(32)	1.130(4)
N(5)–C(1)	1.352(3)	C(3)–C(4)	1.331(5)
N(5)–C(4)	1.385(4)	C(11)–C(12)	1.333(6)
N(5)–C(7)	1.449(4)	C(22)–C(23)	1.445(4)
N(8)–C(7)	1.453(4)	C(32)–C(33)	1.451(5)
Bond angles (°)			
N(21)–Pd–N(31)	89.66(9)	C(12)–N(10)–C(13)	124.7(3)
N(21)–Pd–C(1)	92.76(10)	Pd–N(21)–C(22)	172.8(2)
N(21)–Pd–C(9)	174.46(11)	Pd–N(31)–C(32)	179.4(2)
N(31)–Pd–C(1)	177.48(9)	Pd–C(1)–N(2)	131.05(18)
N(31)–Pd–C(9)	93.48(10)	Pd–C(1)–N(5)	123.61(19)
C(1)–Pd–C(9)	84.05(11)	N(2)–C(1)–N(5)	105.3(2)
C(1)–N(2)–C(3)	110.1(2)	N(2)–C(3)–C(4)	107.7(3)
C(1)–N(2)–C(6)	125.8(2)	N(5)–C(4)–C(3)	106.4(3)
C(3)–N(2)–C(6)	124.1(3)	N(5)–C(7)–N(8)	108.4(2)
C(1)–N(5)–C(4)	110.4(2)	Pd–C(9)–N(8)	122.7(2)
C(1)–N(5)–C(7)	122.0(2)	Pd–C(9)–N(10)	130.9(3)
C(4)–N(5)–C(7)	127.6(2)	N(8)–C(9)–N(10)	106.4(3)
C(7)–N(8)–C(9)	122.7(2)	N(8)–C(11)–C(12)	106.2(4)
C(7)–N(8)–C(11)	126.9(3)	N(10)–C(12)–C(11)	108.2(3)
C(9)–N(8)–C(11)	110.2(3)	N(21)–C(22)–C(23)	178.8(3)
C(9)–N(10)–C(12)	109.1(3)	N(31)–C(32)–C(33)	179.2(3)
C(9)–N(10)–C(13)	126.3(3)		

have been structurally and/or spectroscopically characterised as reaction intermediates in less reactive catalyst systems [14].

3.1. Synthesis of carbene complexes

Whilst not being potentially as important for ethene/CO copolymerisation studies, in analogy with the previous olefin polymerisation studies using cationic β-diimine complexes of palladium, it was seen to us as necessary to incorporate bulky (aryl) substituents into our *cis*-chelating dicarbene ligands for olefin polymerisation and olefin/CO copolymerisation studies. The mesityl substituent has proven to be the only such group that we have thus far been able to incorporate into our synthetic approaches. The neutral di(carbene)palladium(II)dibromide complex **3** was prepared via an adaptation of our straightforward in situ carbene generation procedure [3] which utilized longer reaction times and milder temperatures to give increased yields of complexes (particularly when bulky alkyl substituents are present in the methylene bridged diimidazolium salt precursors [15]), (Scheme 1). The diiodide analogue was most easily prepared via halide exchange of **3** rather than direct reaction of the diimidazolium diiodide salt precursor with $Pd(OAc)_2$. In both the cases of the halide exchange reactions involving **3** with NaI and $Na[PF_6]$ (vide infra), the isolation of the dibromide was not necessary. The dihalide complexes both crystallise as very fine needles unsuitable for X-ray structure determination, have excellent solubility in DMSO, good solubility in hot acetonitrile, are sparingly soluble in DCM and THF and have no solubility in diethyl ether and hydrocarbon solvents.

The preparation of the cationic species **6**–**8** was achieved by exchange reactions involving $Na[PF_6]$ or $K[PF_6]$, or $Ag[BF_4]$ in cases where alkali metal salts were effective in only replacing one halide ion, and isolated as air stable acetonitrile adducts. The Ag^+ salts were necessary mainly in the case of halide exchanges with {1,1′-dimethyl-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II)dihalides. Complex **8** crystallises as colourless rods suitable for X-ray structure determination, whereas the fine needles and rods obtained for complexes **6** and **7** were unfortunately unsuitable for X-ray structure determinations. All have excellent solubility in DMSO, acetonitrile and nitromethane, have good solubility in methanol and are insoluble in Et_2O, DCM, THF and hydrocarbons. All the dicarbene complexes **3**–**8** are air and moisture stable for periods of months in the solid state and in solution, and the yields of the reactions are not reduced by using wet solvents/reactants at any point. The complexes display high thermal stability, decomposing only at temperatures in excess of 215°C in the solid, and are stable in refluxing DMSO for varying periods.

3.2. Structural and spectroscopic characterisation

The chelating mode of the dicarbene complexes were confirmed by an X-ray structure determination only of the dimethyl substituted dicationic complex **8** [16]. The presence of ion fragments corresponding to dimeric as well as monomeric species in the FAB mass spectra of the mesityl substituted dihalides **3** and **5** does not discount the possibility of metal bridging coordination modes for the dicarbene ligands in these cases. We note though that related methylene bridged dicarbene complexes which have exhibited dimeric ion fragments in their FAB mass spectra have without exception been shown to be monomeric species with a chelating coordination mode of the dicarbene [17]. Related to these complexes, the CN bidentate chiral oxazoline substituted carbene ligand $\{\overline{OCH_2CH(i\text{-Pr})N{=}C}CH_2\overline{N(H)C{=}C(H)N(t\text{-Bu})C}\}$, L, was found to form a monomeric cationic complex with rhodium, $[(COD)Rh(L)]^+$, with the formation of a six-membered chelate ring and bridge metal centres [18] in the dimeric neutral palladium complex $[\{PdI_2(\mu\text{-}L)\}_2]$. Furthermore, the use of either a methylene or an ethylene linkage in related dicarbene ligands to those used in this study results in the isolation of dimetallic complexes in which the dicarbene bridges two metal centres, $[\{(COD)Rh(Cl)\}_2(\mu\text{-dicarbene})]$ [19]. In this study, the attempted preparation of ethylene and propylene linked analogues of complexes **3**–**8** resulted only in the formation of unidentified decomposition products at reaction temperatures above ca. 70°C.

^{1}H- and ^{13}C-NMR spectra of the complexes **3**–**8** are in agreement with their assigned structures. The appearance of inequivalent methylene proton resonances for **8** indicates the retention of a conformationally restrained boat shaped six-membered chelate ring for the complex as was determined in the X-ray crystal structure of the dicationic complex **8** and its neutral diiodide analogue $[cis\text{-}CH_2\{\overline{NC{=}CN(Me)C}\}_2PdI_2]$ [3]. Such conformationally rigid ring systems have been noted by us and other groups in related complexes as have examples which were fluxional at room temperature [20,21]. The variable temperature ^{1}H-NMR spectra for **8** reveals a coalescence temperature of 95°C for the methylene protons equilibrating presumably via a ring flipping mechanism. For the mesityl substituted complexes **3**, **5** and **6** a single resonance was observed for the methylene protons in the ^{1}H-NMR spectra at r.t., indicating that the ring conformation is not fixed at this temperature, despite the far greater steric bulk of the mesityl group relative to the methyl group, or indeed these complexes do not possess the ascribed monomeric chelating structures in solution. In addition, equilibria/fluxional processes were observed for the mesityl substituted dihalides **3** and **5** which broadened their ^{1}H-NMR resonances at r.t. and remains unaccounted for at this stage. At higher temperatures in d_6-DMSO the ^{1}H-NMR spectra of the dihalides **3** and **5** are consistent with single species being present and at above 80°C the resonances for all protons appear as relatively sharp singlets. The low solubility of the complexes in suitable solvents prevented low temperature ^{1}H-NMR spectra being measured for complexes **3** and **5**. This fluxionality prevented the obtaining of ^{13}C-NMR spectra for complexes **3** and **5** at or above r.t., as again did the low solubility of the complexes at lower temperatures in suitable solvents.

Crystals of complex **8** suitable for X-ray crystal structure determination were grown by vapour diffusion of diethyl ether into a concentrated acetonitrile solution of **8**. The crystal structure determination has shown the compound to be monomeric with the dicarbene ligand chelating the palladium(II) centre, the remaining two coordination sites of the distorted square planar coordinated palladium centre being occupied by molecules of acetonitrile. The dication possesses non-crystallographic C_s symmetry, the palladium and methylene carbon centres lying on this symmetry element, Fig. 1. The two $[BF_4]^-$ anions are noncoordinating and there is an additional noncoordinating molecule of acetonitrile in the crystal lattice. Summaries of important bond distances and angles appear in Table 2.

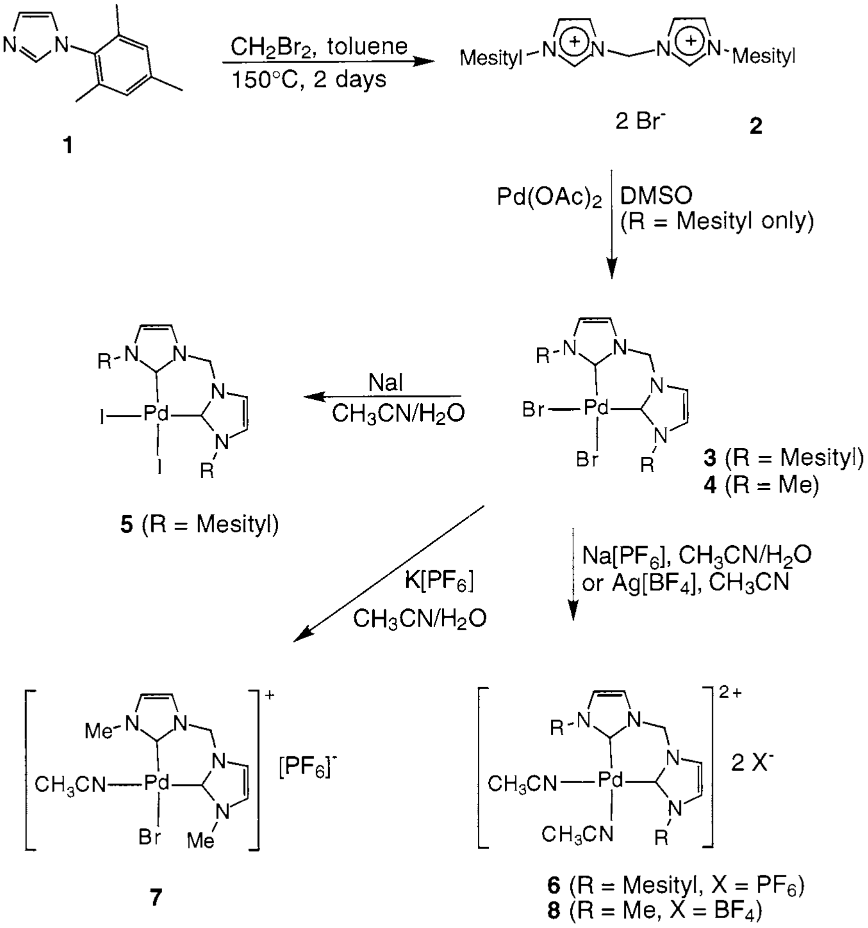
Table 3
Summary of reaction conditions for copolymerisation reactions

Run	Temperature (°C)	Pressure olefin[a]/CO(bar)	Solvent volume (ml)	p–$C_6H_4O_2$(mg)	Reaction time (min)	Yield[b] (g polymer/g Pd)
1	50	40/40	CH_3OH (5)	–	60	135
2	50	40/40	CH_3OH (2.5), CH_3CN (2.5)	–	–	0
3	50	40/40	CH_3OH (5)	3	90	210
4	50	50/20	CH_3OH (5)	–	90	256
5	50	50/20	CH_3OH (5)	3	120	432
6	50	50/20	CH_3OH (10)	3	240	810
7	80	50/20	CH_3OH (10)	3	60	260
8	50	50/20	CH_3OH (10)	20	90	200
9	50	50/20	CH_3OH (10)	40	60	62
10	50	50/20	DCM (9), CH_3OH (1)	3	60	54
11	50	2.5 g propene/35	CH_3OH (10)	3	–	0
12	50	2.5 g styrene/35	CH_3OH (10)	3	–	0
13	r.t	50/20	CH_3OH (10)	3	600	162
14	50	50/20	$(CF_3)_2CHOH$ (4), CH_3OH (1)	3	150	405
15[c]	50	50/20	CH_3OH (10)	3	90	324
16[c]	r.t	50/20	CH_3OH (10)	3	60	135
17[c]	80	50/20	CH_3OH (10)	3	60	110

[a] C_2H_4 unless otherwise stated, and then weight of olefin used.

[b] Complex **6** (20 mg) was used as the precatalyst unless otherwise noted.

[c] Complex **8** (10 mg) was used as the precatalyst.



Scheme 1.

The Pd–C distances of **8**, 1.966(2) and 1.972(3) Å, are only slightly contracted relative to those in the analogous diiodide complex [*cis*-$CH_2\{NC{=}CN(Me)C\}_2PdI_2$] at 1.988(7) and 1.989(8) Å [3] or the related non-chelating complex [*cis*-$\{MeNC{=}CN(Me)C\}_2PdI_2$] at 1.990(3) and 1.997(3) Å [2]. Both are however shortened significantly relative to the dicationic tetracarbene complex [{*cis*-$CH_2[NC{=}CN(Me)C]_2\}_2Pd]^{2+}$ and the chiral dicarbene complex [*trans*-{(*syn*-$Ph(Me)CH\{NC{=}CN(Ph)C\}_2)\}_2$-$PdI_2$] in which the Pd–C distances measure 2.137(5), 2.049(4) Å [20] and 2.018(7), 2.042(7) Å [22], respectively, in the absence of strong trans effects of the iodide and acetonitrile substituents. The Pd–N distances measure 2.055(2) and 2.064(2) Å. The formation of the six-membered chelate ring of the dicarbene distorts the coordination geometry of the palladium only slightly, with the C–Pd–C bite angle being reduced to 84.1(1)°. The *cis*- and *trans*-N–Pd–C angles are also effected by the chelate ring formation at 92.8(1), 93.5(1), 174.5(1) and 177.48(9)°, respectively, whereas the N–Pd–N angle, being free from such distortion, is close to ideal at 89.66(9)°. Further effects of the chelate ring of the dicarbene are evident in the shifting of the carbene centres out of the plane defined by the palladium centre and acetonitrile molecules by 0.156(3) and 0.024(3) Å and the angles of the imidazolin-2-ylidene based ring systems to the coordination plane of the palladium centre, 42.4(2) and 42.8(1)°, which compare to related chelating dicarbene complexes [3,21]. An angle of 90° for this last parameter is by no means a preferred coordination geometry as evidenced by the corresponding angles of 70.5–69.4° [2] and 68.7° [23] in the carbene complexes [*cis*-$\{MeNC{=}CN(Me)C\}_2PdI_2$] and [$\{MeNC{=}CN(Me)\}CPd(Me)(NC_5H_4CO_2\text{-}2)$], respectively, which are free from the influence of the chelate ring as found in complex **8** and steric effects should play minor roles. The C–C and C–N bond distances within the imidazolin-2-ylidene based ring systems and the Pd–C bond distances in complex **8** are consistent with both contributions from s- and p-donation to the metal centre and p-stabilisation of the carbene onto the adjacent nitrogen centres. Other bond angles within the molecule are unexceptional and do not require comment.

3.3. Copolymerisation studies

The dicationic complexes **6** and **8** catalyze the copolymerisation of C_2H_4 and CO (Table 3). The best results were obtained under the conditions for Entry 6 in Table 1. The addition of *p*-benzoquinone was not necessary for polymer production, though greater TONs were found in its presence, detrimental effects occurred with the increasing or decreasing of the amount from that listed in Entry 6. While we have no information at present on the initiating species ('active catalyst') in this system, we note that dried methanol (and other solvents) were used for the copolymerisation experiments and that the addition of water had a negative effect on the yield of copolymer. The copolymer end groups could not be confidently assigned on the basis of reported solution ^{13}C-NMR spectra for the copolymer [4]. No small molecular weight (co)oligomers were detected by GC/MS analysis of the methanol solutions from the copolymerisations, further not enabling conjecture on the end groups/initiation or termination mechanisms operative in the copolymer process in our system. While a reduction in the catalyst concentration reduced the polymer yield only in proportion, an increase reduced the effectiveness of the catalyst. Conducting the copolymerisations at r.t. results in an increased lifetime of the catalyst, but an overall reduction in the TON as does increased temperatures, though likely due to different decomposition pathways for the catalyst. A reaction temperature of ca. 50°C represents the most effective temperature in this case (though the catalysts are active at r.t.). Extension of the copolymerisation studies to include propene and styrene was unsuccessful and so we could not obtain information on the stereo- and regioselectivity of the copolymerisation process here. The catalysts were inactive in strongly coordinating solvents and no improvement of the catalytic activity was observed when the reactions were performed in a methanol/1,1,1,3,3,3-hexafluoro-*iso*-propanol solvent mixture in which the ethene/CO copolymer and presumably the living copolymer chain is soluble.

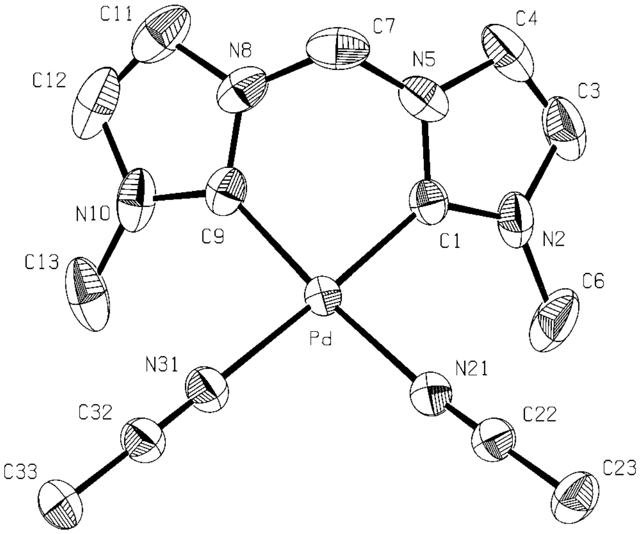


Fig. 1. Molecular Structure of the dication of [{1,1′-dimethyl-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II)bis(acetonitrile)] $[BF_4]_2$ **8**, showing atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. For clarity the hydrogens are omitted.

Samples of the ethene/CO copolymers could be obtained as white films of plastic material by the evaporation of 1,1,1,3,3,3-hexafluoro-*iso*-propanol solutions previously filtered from palladium black arising from catalyst decomposition and analyse correctly for a 1:1 copolymer. Copolymer samples having only been washed with methanol and dried in vacuo showed complete incorporation of the palladium which can be completely removed (% $Pd < 0.1$) on dissolving in 1,1,1,3,3,3-hexafluoro-*iso*-propanol followed by filtration and evaporation. The copolymers display an IR C=O stretching frequency of 1692 cm^{-1} (recorded as KBr disc). The ^{1}H-NMR spectra contain a single broad band of resonances in the region 2.40–2.55 ppm. Solution ^{13}C-NMR spectra of the copolymers show the perfect alternation of the monomers in the copolymer; single signals are observed for the methylene and carbonyl carbons at chemical shifts of 35.0 and 212.1 ppm [24], respectively, and no additional signals were observed in the region expected for a double insertion fault of C_2H_4 into the copolymer (the copolymers melt at a temperature range of 250–260°C, also suggesting a high purity for the polymer with a very small amount of alternation defects [4]). An estimation of the average molecular weight of the copolymers could not be determined from the assignment and integration of the end group resonances observed in the solution ^{13}C-NMR spectra of the copolymers due to their very low intensities. From this we presume that the average molecular weight of our copolymers greatly exceed those determined in the analyses of E. Drent et al. [4], and from this we conclude that the precentage of palladium precatalyst which is actually participating in the production of copolymer is very small given the large molecular weight of the copolymer and the relatively modest TONs that we observe for our dicarbene systems at present. For this reason, we are confident that great improvements in copolymer yield can be obtained by preparing alternative cationic (pre)catalysts which enter the catalytic process in a defined manner, monocationic methyl- or methoxy-palladium species, for example, which would enable the movement to DCM as a solvent of choice for the copolymerisations. We are also investigating various counter anion effects and the large variety of possible variations in the dicarbene ligand including the chelate ring size, terminal substituents and heterocycle choice.

Acknowledgements

We are grateful to Karl Öfele for suggestions and fruitful discussions. This work was supported by the Alexander von Humboldt-Stiftung (fellowship for M.G. Gardiner) and the Fonds der Chemischen Industrie (studentship for J. Schwarz). We would also like to thank DEGUSSA AG for generous gifts of $Pd(OAc)_2$.

References

[1] (a) W.A. Herrmann, C. Köcher, Angew. Chem. 109 (1997) 2256. (b) W.A. Herrmann, C. Köcher, Angew. Chem. Int. Ed. Engl. 36 (1997) 2162.

[2] (a) W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew. Chem. 107 (1995) 2602. (b) W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew. Chem. Int. Ed. Engl. 34 (1995) 2371. For a theoretical study on this system, see K. Albert, P. Gisdakis, N. Rösch, Organometallics 17 (1998) 1608.

[3] W.A. Herrmann, C.-P. Reisinger, M. Spiegler, J. Organomet. Chem. 557 (1998) 93.

[4] (a) E. Drent, J.A.M. van Broekhoven, M.J. Doyle, J. Organomet. Chem. 417 (1991) 235. (b) E. Drent, P.H.M. Budzelaar, Chem. Rev. 96 (1996) 663. (c) M. Sperrle, G. Consiglio, Chem. Ber. 130 (1997) 1557. (d) A. Vavasori, L. Toniolo, J. Mol. Catal. A 110 (1996) 13. B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Complexes, VCH, Weinheim, 1996.

[5] A.A. Gridnev, I.M. Mihaltseva, Synth. Commun. 24 (1994) 1547.

[6] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Cryst. 26 (1993) 343.

[7] G.M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993.

[8] A.L. Spek, Acta Crystallogr. A 46 (1990) 34.

[9] For initial papers in the field, see (a) L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414. (b) L.K. Johnson, S. Mecking, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 267. (c) C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 11664.

[10] (a) J. Feldmann, S.J. McLain, A. Parthasarathy, W.J. Marshall, J.C. Calabrese, S.D. Arthur, Organometallics 16 (1997) 1514. (b) S. Mecking, L.K. Johnson, L. Wang, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 888. (c) B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049. (d) G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849.

[11] (a) D.G. Musaev, R.D.J. Froese, M. Svensson, K. Morokuma, J. Am. Chem. Soc. 119 (1997) 367. (b) L. Deng, P. Margl, T. Ziegler, J. Am. Chem. Soc. 119 (1997) 1094. (c) L. Deng, T.K. Woo, L. Cavallo, P. Margl, T. Ziegler, J. Am. Chem. Soc. 119 (1997) 6177. (d) D.G. Musaev, R.D.J. Froese, K. Morokuma, New J. Chem. 21 (1997) 1269. (e) D.G. Musaev, M. Svensson, K. Morokuma, S. Strömberg, K. Zetterberg, P.E.M. Siegbahn, Organometallics 16 (1997) 1933. (f) D.G. Musaev, R.D.J. Froese, K. Morokuma, Organometallics 17 (1998) 1850. (g) R.D.J. Froese, D.G. Musaev, K. Morokuma, J. Am. Chem. Soc. 120 (1998) 1581.

[12] (a) A. Sen, T.-W. Lai, J. Am. Chem. Soc. 104 (1982) 3520. (b) A. Batistini, G. Consiglio, U.W. Suer, Angew. Chem. 104 (1992) 306. (c) A. Batistini, G. Consiglio, U.W. Suer, Angew. Chem. Int. Ed. Engl. 31 (1992) 303. (d) M. Brookhart, M.I. Wagner, J. Am. Chem. Soc. 116 (1994) 3641. (e) Z. Jiang, A. Sen, J. Am. Chem. Soc. 117 (1995) 4455. (f) K. Nozaki, N. Sato, H. Takaya, J. Am. Chem. Soc. 117 (1995) 9911. (g) M. Sperrle, G. Consiglio, J. Am. Chem. Soc. 117 (1995) 12130.

[13] (a) S. Bartolini, C. Carfagna, A. Musco, Macromol. Chem. Rapid Commun. 16 (1995) 9. (b) S. Brückner, C. De Rosa, P. Bolavoine, H.A. Haddou, J. Am. Chem. Soc. 116 (1994) 3641.

[14] (a) M.J. Green, G.J.P. Britovsek, K.J. Cavell, F. Gerhards, B.F. Yates, K. Frankcombe, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1998) 1137. (b) C. Carfagna, M. Formica, G. Gatti, A. Musco, A. Pierleoni, Chem. Commun. (1998) 1113.

[15] M.G. Gardiner, W.A. Herrmann, J. Schwarz, M. Spiegler (manuscript in preparation).

[16] Note added in proof: The crystal structure of complex **6** has been determined as a chelating monomeric species similar to that of complex **8**. The X-ray crystal structure will be reported elsewhere. M.G. Gardiner, W.A. Herrmann, J. Schwarz, M. Spiegler (unpublished results).

[17] M.G. Gardiner, W.A. Herrmann, J. Schwarz, M. Spiegler, (unpublished results).

[18] W.A. Herrmann, L.J. Gooßen, M. Spiegler, Organometallics 17 (1998) 2162.

[19] W.A. Herrmann, C. Köcher, J. Organomet. Chem. 532 (1997) 261.

[20] K. Öfele, W.A. Herrmann, D. Mihalios, J. Organomet. Chem. 498 (1995) 1.

[21] W.P. Fehlhammer, T. Bliss, U. Kernbach, I. Brüdgam, J. Organomet. Chem. 490 (1995) 149.

[22] D. Enders, H. Gielen, G. Raabe, J. Runsink, J.H. Teles, Chem. Ber. 129 (1996) 1483.

[23] M.J. Green, K.J. Cavell, B.W. Skelton, A.H. White, J. Organomet. Chem. 554 (1998) 175.

[24] Solid state ^{13}C-NMR resonances at 36.2 and 210.0 ppm for methylene and ketone carbons, respectively.