ELSEVIER

Journal of Organometallic Chemistry 532 (1997) 261–265

Journal of Organometallic Chemistry

Preliminary Communication

Heterocyclic carbenes [1]. One-pot synthesis of rhodium and iridium carbene complexes

Christian Köcher, Wolfgang A. Herrmann *

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

Received 17 July 1996; revised 27 July 1996

Abstract

Rhodium carbene complexes of the type $Rh(X)(\eta^4\text{-}1,5\text{-cod})(L_{carbene})$ (X = halide anion, $L_{carbene}$ = imidazole, triazole, pyrazole and benzimidazole carbene) are directly accessible from $[Rh(\eta^4\text{-}1,5\text{-cod})Cl]_2$ following a simple new one-pot synthesis. A slurry of this complex in ethanol is successively treated with an excess of both sodium ethoxide and heteroaromatic azolium salt. An in situ formed rhodium ethoxide complex acts as deprotonating agent. Cyclooctadiene may be displaced by two molecules of carbon monoxide yielding complexes of the type $Rh(CO)_2X(L_{carbene})$, and one carbon monoxide ligand may again be replaced by phosphines or phosphites to yield *trans*-$Rh(CO)X(L_{carbene})(L_p)$. The described method also works for analogous iridium complexes. The σ-donor/π-acceptor characteristics of imidazole carbenes are compared with those of phosphines.

Keywords: Carbenes; Heterocycles; Heterocyclic carbenes; Rhodium; Iridium

1. Introduction

In 1968 Wanzlick and Öfele found that heterocyclic carbenes derived from imidazolium and pyrazolium salts form extraordinarily stable transition metal complexes [1,2]. Free carbenes of the imidazoline- and imidazolidine-2-ylidene type were isolated much later by Arduengo and coworkers [3,4]. We found that imidazoline-2-ylidenes are advantageously synthesized from azolium salts in mixtures containing liquid ammonia, often within a few minutes at −35 °C. We were thus able to synthesize temperature-sensitive, functionalized and chiral free carbenes in excellent yields [5,6]. We also reported on carbene complexes of high and low oxidation state transition metals [7], the latter being extremly stable [6]. Finally, transition Group 8–10 carbene complexes are excellent catalysts in a number of coupling reactions [8].

2. Results and discussion

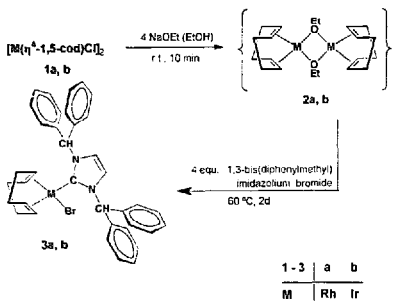
The principle of the new synthesis is based on the conversion of an organometallic halide precursor into a corresponding alkoxide, which latter species – possibly generated only in situ – has a sufficient basicity to deprotonate the N-heterocyclic azolium salt. At the same time, the alkoxide ligand is replaced by the carbene ligand thus generated.

An illustrative example for the new procedure is presented in Scheme 1. Here, the chlororhodium and -iridium complexes **1a** and **1b**, respectively, are suspended in ethanol and treated with four equivalents of a 1 M solution of sodium ethoxide in the same solvent. The formation of alkoxy complexes, e.g. **2a,b**, is indicated by a colour change of the orange slurry into bright yellow within 5 min. In the next step, four equivalents of 1,3-bis(diphenylmethyl)imidazolium bromide are added in one portion. The reaction mixture is then allowed to react at 60 °C for two days. After washing with methanol, the rhodium and iridium complexes **3a,b** are obtained in 94 and 95% yield respectively. These compounds are stable to air and moisture, even in solution.

* Corresponding author.

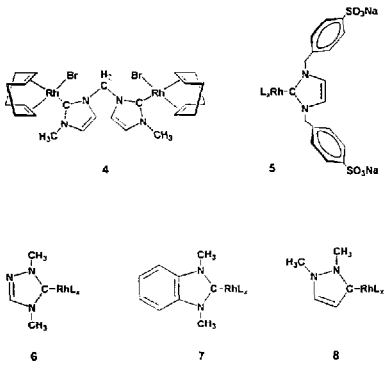
[1] Heterocyclic carbenes Part 11. For Part 10 see W.A. Herrmann, C. Köcher, L. Gooßen and G. Artus, *Chem. Eur. J.*, 2 (12) (1996) 229.

PII S0022-328X(96)06732-0



Scheme 1.

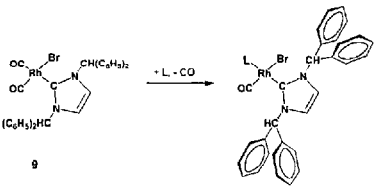
Quite a number of new carbene complexes has thus become available. Examples are the imidazol-derived rhodium complexes **4** and **5**, but also the triazole-, benzimidazole- and pyrazole-derived rhodium carbenes **6–8**.



Further acidic protons like in the methylene group of complex **4** do not interfere with carbene complex formation. The triazole carbone complex **6** was synthesized as described above for the imidazole carbone complexes. In the case of **7**, a stoichiometric amount of *N,N*-dimethylbenzimidazolium iodide is required, otherwise dicarbene complexes are formed as well. A more laborious synthesis of benzimidazole-type carbene complexes was previously reported by Lappert and coworkers [9]. In contrast, pyrazole carbene complex **8** requires a higher excess of *N,N*-dimethylpyrazolium iodide as well as longer reaction times. The reaction rate decreases in the order benzimidazole > triazole > imidazole > pyrazole with decreasing acidity of the corresponding azolium salt. In every case square-planar mono-carbene complexes of the type $RhX(\eta^4\text{-}1,5\text{-cod})(L_{carbene})$ were obtained, with X representing the heaviest halide anion present in the reaction mixture.

Although an excess of sodium ethoxide and azolium salt was used in the synthesis of imidazole, triazole and pyrazole carbene complexes, we never observed the formation of cationic dicarbene complexes of the type $[Rh(\eta^4\text{-}1,5\text{-cod})(L_{carbene})_2]^+X^-$. However, imidazole carbene complexes of this kind are formed quantitatively when $[Rh(\eta^4\text{-}1,5\text{-cod})Cl]_2$ is treated with two equivalents of a sterically not very demanding free carbene such as 1,3-dimethylimidazoline-2-ylidene [6]. Thus, the intermediate formation of free carbenes can be ruled out, at least in the case of imidazole carbene complexes.

From $Rh(X)(\eta^4\text{-cod})(L_{carbene})$, e.g. **3a**, cyclooctadiene may be displaced by two molecules of carbon monoxide to yield compound **9** with $\nu(CO) = 2078$, 2015 [cm^{-1}], indicating a *cis*-configuration. One carbon monoxide ligand may again be replaced to give the *trans*-carbene/phosphine or phosphite complexes **10a** and **10b** (r.t., $CHCl_3$):



(1)

The donor/acceptor characteristics of different ligands **L** can be qualified with the example of *trans*-

Table 1
CO stretching frequencies of complexes of the type *trans*-$RhL_2(CO)X$ (* in KBr, otherwise in benzene [10])

$L_{1,2}$		X	$\nu(CO)$ (cm^{-1})
carbene^{Me}	*	Cl	1924
carbene^{Cy}	*	Cl	1929
PCy_3		Cl	1939
PMe_3		Cl, Br, I	1957, 1958, 1960
carbene$^{CH(C_6H_5)_2}$/**PPh**$_3$	*	Br	1968
PPh_3		Cl	1983
carbene$^{CH(C_6H_5)_2}$/**P(OPh)**$_3$	*	Br	1994
$P(C_6F_5)_3$		Cl	2003
$P(OPh)_3$		Cl, Br	2018, 2020

Rh(CO)X(L)$_2$: the CO stretching frequencies are sensitive to the electron density at the metal. It can be seen that imidazole carbenes induce a significantly higher electron density at the rhodium centre than the standard phosphine ligands PMe_3 and PCy_3 (Table 1).

3. Spectroscopic and analytical data

3.1. Bromo(η⁴-1,5-cyclooctadiene)(1,3-bis(diphenylmethyl)imidazoline-2-ylidene)rhodium(I) (3a)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] 1.40 (br, 2H, COD_{ally}), 1.76 (br, 4H, COD_{ally}), 2.23 (br, 2H, COD_{ally}), 2.76 (br, 2H, COD_{vinyl}), 5.17 (br, 2H, COD_{vinyl}), 6.71 (s, 2H, NC*HCH*N), 7.27–7.41 (m, 20H, C_6H_5), 8.25 (s, 2H, NC*H*(C_6H_5)).

^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 25 °C): δ [ppm] 28.84, 32.22 (s each, COD_{ally}), 67.23 (s, NCH(Ph)$_2$), 70.15 (d, ^1J(C–Rh) = 13.8 Hz, COD_{vinyl}), 97.60 (d, ^1J(C–Rh) = 6.4 Hz, COD_{vinyl}), 97.72 (d, ^1J(C–Rh) = 6.4 Hz, COD_{vinyl}), 120.44 (s, N*CHCH*N), 126.89, 127.58, 128.05, 128.46, 128.71, 129.66, 139.98, 140.21 (s each, NCH(C_6H_5)$_2$, Ph groups not equivalent), 185.30 (d, ^1J(C–Rh) = 51.5 Hz, NC_{carb}N).

IR (KBr): ν [cm^{-1}] 3164, 3136, 3061, 3052, 3025, 2937, 2914, 2871, 2828, 2822, 1494, 1453, 1411, 1397, 1278, 1236, 1208, 1181, 1078, 1028, 750, 725, 717, 697.

Anal. Found: C, 64.16; H, 5.18; N, 3.99. $C_{37}H_{36}N_2BrRh$ (691.52) Calc.: C, 64.27; H, 5.25; N, 4.05%.

3.2. Bromo(η⁴-1,5-cyclooctadiene)(1,3-bis(diphenylmethyl)imidazoline-2-ylidene)iridium(I) (3b)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] 1.09 (br, 2H, COD_{ally}), 1.63 (br, 4H, COD_{ally}), 2.12 (br, 2H, COD_{ally}), 2.42 (br, 2H, COD_{vinyl}), 4.79 (br, 2H, COD_{vinyl}), 6.78 (s, 2H, NC*HCH*N), 7.29–7.45 (m, 20H, C_6H_5), 8.12 (s, 2H, NC*H*(C_6H_5)).

^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 25 °C): δ [ppm] 29.53, 32.91 (s each, COD_{ally}), 53.75 (s, COD_{vinyl}), 66.87 (s, NCH(Ph)$_2$), 84.10 (s, COD_{vinyl}), 120.07 (s, N*CHCH*N), 126.92, 127.58, 128.07, 128.49, 128.71, 129.50, 139.98, 140.12 (s each, NCH(C_6H_5)$_2$, Ph groups not equivalent), 182.20 (s, NC_{carb}N).

IR (KBr): ν [cm^{-1}] 3062, 3027, 2915, 2869, 2827, 1979, 1933, 1903, 1495, 1451, 1413, 1403, 1382, 1323, 1277, 1236, 1208, 1182, 1077, 1031, 751, 721, 695, 603, 469.

3.3. Bromodicarbonyl(1,3-bis(diphenylmethyl)imidazoline-2-ylidene)rhodium(I) (9)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] 6.79 (s, 2H, NC*HCH*N), 7.13 (d, 4H, ^3J(H–H) = 7.3 Hz, NCH(C_6H_5)$_2$), 7.33–7.41 (m, 16H, NCH(C_6H_5)$_2$), 7.59 (s, 2H, NC*H*(C_6H_5)$_2$).

^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 25 °C): δ [ppm] 68.02 (s, NCH(C_6H_5)$_2$), 120.58 (s, N*CHCH*N), 127.38, 128.01, 128.58, 128.75, 129.61, 138.26, 138.82 (s each, NCH(C_6H_5)$_2$, Ph groups not equivalent), 176.99 (d, ^1J(C–Rh) = 43.2 Hz, *CO*), 180.64 (d, ^1J(C–Rh) = 78.1 Hz, *CO*), 186.15 (d, ^1J(C–Rh) = 54.2 Hz, NC_{carb}N).

IR (KBr): ν [cm^{-1}] 3165, 3135, 3058, 3027, 2923, 2078, 2015, 1495, 1451, 1418, 1385, 1277, 1203, 1187, 1164, 1077, 1031, 751, 720, 697.

Anal. Found: C, 58.73; H, 4.06; N, 4.34. $C_{31}H_{24}N_2O_2BrRh$ (639.35) Calc.: C, 58.24; H, 3.78; N, 4.38%.

3.4. Bromocarbonyl-trans-(triphenylphosphine)(1,3-bis(diphenylmethyl)imidazoline-2-ylidene)rhodium(I) (10a)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] 6.81 (s, 2H, NC*HCH*N), 7.23–7.65 (m, 35H, NCH(C_6H_5)$_2$, P(C_6H_5)$_3$), 8.14 (s, 2H, NC*H*(C_6H_5)$_2$).

^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 25 °C): δ [ppm] 67.73 (s, NCH(C_6H_5)$_2$), 119.87 (s, N*CHCH*N), 127.51, 127.68, 127.78, 128.11, 128.43, 128.52, 129.48, 129.74, 134.04, 134.48, 139.21, 139.69 (NCH(C_6H_5)$_2$, P(C_6H_5)$_3$), 183.46 (dd, ^1J(C_{carb}–Rh) = 45.0 Hz, ^1J(C_{carb}–P) = 119.0 Hz), 184.35 (dd, ^1J(CO–Rh) = 80.0 Hz, ^1J(CO–P) = 15.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ [ppm] 32.2 (d, ^1J(P–Rh) = 115.5 Hz).

IR (KBr): ν [cm^{-1}] 3162, 3135, 3058, 3027, 3004, 1968, 1495, 1480, 1449, 1433, 1415, 1205, 1185, 1159, 1092, 1028, 751, 726, 695, 564, 523.

Anal. Found: C, 65.94; H, 4.50; N, 3.16; P, 3.49. $C_{48}H_{39}N_2POBrRh$ (873.63) Calc.: C, 65.99; H, 4.50; N, 3.21; P, 3.55%.

3.5. Bromocarbonyl-trans-(triphenylphosphite)(1,3-bis(diphenylmethyl)imidazoline-2-ylidene)rhodium(I) (10b)

^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ [ppm] 6.43 (s, 2H, NC*HCH*N), 6.73–7.57 (m, 35H, NCH(C_6H_5)$_2$, P(OC_6H_5)$_3$), 7.78 (s, 2H, NC*H*(C_6H_5)$_2$).

^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ [ppm] 67.95 (s, NCH(C_6H_5)$_2$), 120.14 (s, N*CHCH*N), 122.23, 124.66, 125.64, 128.41, 128.51, 128.73, 128.84, 129.28, 129.60, 129.83, 130.08, 130.78, 139.60, 139.73, 152.28, 152.32 (NCH(C_6H_5)$_2$, P(OC_6H_5)$_3$).

^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ [ppm] 126.9 (d, ^1J(P–Rh) = 200.7 Hz).

IR (KBr): ν [cm^{-1}] 3166, 3138, 3061, 3027, 1994, 1587, 1487, 1451, 1413, 1382, 1187, 1162, 1023, 908, 885, 785, 749, 733, 721, 690, 659, 618, 600, 559, 495, 467.

Anal. Found: C, 62.66; H, 4.30; N, 2.88. $C_{48}H_{39}N_2P_1O_4BrRh$ (921.63) Calc.: C, 62.56; H, 4.27; N, 3.04%.

3.6. (1,1'-Methylene-3,3'-dimethyldiimidazoline-2-ylidene)dibromo(η⁴-1,5-cyclooctadiene)rhodium(I)] (4)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] 1.8–2.4 (m, 16H, COD_{ally}), 3.33 (br, 4H, COD_{vinyl}), 4.01 (s, 6H, NCH_3). 5.11 (br, 4H, COD_{vinyl}), 6.75 (s, 2H, NCH_2N), 7.38, 7.70 (s each, 2H each, NC*H*C*H*N).

^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 25 °C): δ [ppm] 28.69, 29.31, 32.14, 33.24 (s each, COD_{ally}), 37.81 (s, NCH_3), 62.61 (s, NCH_2N), 69.20 (d, ^1J(C–Rh) = 13.8 Hz, COD_{vinyl}), 70.18 (d, ^1J(C–Rh) = 14.7 Hz, COD_{vinyl}), 98.63 (d, ^1J(C–Rh) = 6.4 Hz, COD_{vinyl}), 99.31 (d, ^1J(C–Rh) = 6.4 Hz, COD_{vinyl}), 121.04, 123.46 (s each, NC*H*C*H*N), 183.11 (d, ^1J(C–Rh) = 50.6 Hz, $NC_{carb}N$).

IR (KBr): ν [cm^{-1}] 3156, 3101, 3087, 2985, 2930, 2913, 2875, 2827, 1444, 1383, 1225, 1119, 958, 760, 751, 696, 674, 482, 440.

Anal. Found: C, 39.86; H, 4.65; N, 7.20; Rh, 27.8. $C_{25}H_{36}N_4Br_2Rh_2$ (758.21) Calc.: C, 39.60; H, 4.79; N, 7.39; Rh, 27.1%.

3.7. Bromo(η⁴-1,5-cyclooctadiene)[1,3-di(4-sulfonatobenzyl-sodium)imidazoline-2-ylidene)]rhodium(I) (5)

1H NMR (400 MHz, $CDCl_3$, 25°C) δ [ppm]: 2.0–2.7 (m, COD_{allyl}), 3.44, 5.14 (COD_{vinyl}), 5.74 (s, 2H, NCH_2Ar), 6.06 (dd, ^2J(H,H) = 12 Hz, 2H, NCH_2Ar), 7.44, 8.14 (s, 1H, NCH), 7.0 (d, 4H, ^3J(H,H) = 8 Hz), 7.9 (d, 4H, ^3J(H,H) = 8 Hz).

^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 25 °C): δ [ppm] 28.33, 32.35 (s each, COD_{ally}), 53.08, 56.00 (s each, $NCHC_6H_4R$), 68.06 (d, ^1J(C–Rh) = 12.9 Hz, COD_{vinyl}), 96.82 (s, COD_{vinyl}), 121.87, 122.83 (s each, NC*H*C*H*N), 125.72, 125.93, 126.11, 127.23, 134.93, 136.37, 147.37, 148.33 (s each, $NCHC_6H_4R$ groups not equivalent), 181.80 (d, ^1J(C–Rh) = 51.5 Hz, $NC_{carb}N$).

3.8. Iodo(η⁴-1,5-cyclooctadiene)[1,4-dimethyl-4,5-dihydro-1H-1,2,4-triazole-5-ylidene)rhodium(I) (6)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] 1.80–2.31 (br, 8H, COD_{ally}), 3.45 (m, 2H, COD_{vinyl}), 3.96, 4.09, 4.17, 4.20 (s each, 6H, NCH_3), 5.24 (s, 2H, COD_{vinyl}), 7.88 (s, 1H, NC*H*N).

^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 25 °C): δ [ppm] 29.33, 29.46, 32.09, 32.26 (s each, COD_{ally}), 35.11, 35.56, 39.64, 39.80 (s each, NCH_3), 71.52 (d, ^1J(C–Rh) = 13.8 Hz, COD_{vinyl}), 72.06 (d, ^1J(C–Rh) = 13.8 Hz, COD_{vinyl}), 97.43 (d, ^1J(C–Rh) = 6.4 Hz, COD_{vinyl}), 92.52 (d, ^1J(C–Rh) = 7.4 Hz, COD_{vinyl}), 142.86 (s, NCHN), 144.17 (s, NCHN), 186.11 (d, ^1J(C–Rh) = 42.6 Hz, $NC_{carb}N$).

IR (KBr): ν [cm^{-1}] 3125, 2988, 2923, 2875, 2824, 1541, 1469, 1382, 1341, 1215, 1108, 1041, 959, 859, 764, 692, 677, 641, 480, 459, 441.

Anal. Found: C, 32.66; H, 4.21; N, 9.61; Rh, 23.5; I, 29.25. $C_{12}H_{19}N_3IRh$ (435.11) Calc.: C, 33.13; H, 4.40; N, 9.66; Rh, 23.7; I, 29.17%.

3.9. Iodo(η⁴-1,5-cyclooctadiene)[1,3-(dimethyl)benzimidazoline-2-ylidene]rhodium(I) (7)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] 1.85 (m, 2H, COD_{ally}), 2.03 (m, 2H, COD_{ally}), 2.37 (m, 4H, COD_{ally}), 3.51 (br, 2H, COD_{vinyl}), 4.18 (s, 6H, NCH_3), 5.33 (br, 2H, COD_{vinyl}), 7.24 (m, 4H, C_6H_4).

^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 25 °C): δ [ppm] 29.43, 32.26 (s each, COD_{ally}), 34.64 (s, NCH_3), 71.73 (d, ^1J(C–Rh) = 13.8 Hz, COD_{vinyl}), 98.03 (d, ^1J(C–Rh) = 6.4 Hz, COD_{vinyl}), 109.05, 122.14, 135.43 (s each, C_6H_4), 196.43 (d, ^1J(C–Rh) = 47.8 Hz, $NC_{carb}N$).

Anal. Found: C, 42.50; H, 4.84; N, 5.50; I, 24.72. $C_{17}H_{22}N_2IRh$ (484.19) Calc.: C, 42.17; H, 4.58; N, 5.79; I, 26.21%.

3.10. Iodo(η⁴-1,5-cyclooctadiene)[1,2-(dimethyl)pyrazoline-5-ylidene]rhodium(I) (8)

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ [ppm] 1.23–2.34 (br, COD_{ally}), 3.43 (m, 2H, COD_{vinyl}), 3.82, 4.28 (s each, 6H, NCH_3), 5.08 (s, 2H, COD_{vinyl}), 6.25, 7.23 (d each, 2H, ^3J(H,H) = 3.1 Hz, C*H*C*H*).

^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, 25 °C): δ [ppm] 29.95, 32.81 (s each, COD_{ally}), 36.41, 39.88 (s, NCH_3), 72.34 (br, COD_{vinyl}), 94.89 (d, ^1J(C–Rh) = 6.4 Hz, COD_{vinyl}), 114.15 (s, CH), 133.70 (s, CH), 187.50 (d, ^1J(C–Rh) = 43.2 Hz, $NC_{carb}N$), [DMSO-d_6]: 182.60 (d, ^1J(C–Rh) = 43.2 Hz, $NC_{carb}N$).

IR (KBr): ν [cm^{-1}] 3119, 3104, 2977, 2927, 2869, 2819, 1556, 1541, 1520, 1474, 1425, 1382, 1359, 1297, 1277, 1156, 1077, 926, 795, 780, 439.

Acknowledgements

This work received generous support from the Bundesministerium für Bildung und Forschung (Bonn), Hoechst AG and Degussa AG. We are especially indebted to Dr. Karl Öfele for continued interest, regular discussions and experimental assistance.

References

[1] H.-W. Wanzlick and H.-J. Schönherr, *Angew. Chem., 80* (1968) 154.
[2] K. Öfele, *J. Organomet. Chem., 12* (1968) P42.
[3] A.J. Arduengo III, R.L. Harlow and M. Kline, *J. Am. Chem.*

Soc., 113 (1991) 361; A.J. Arduengo III, H.V. Dias, R.L. Harlow and M. Kline, *J. Am. Chem. Soc., 114* (1992) 5530.

[4] A.J. Arduengo III, J.R. Goerlich and W.J. Marshall, *J. Am. Chem. Soc., 117* (1995) 11027.

[5] W.A. Herrmann, C. Köcher, L.J. Gooßen and G.R.J. Artus, *Chem. Eur. J., 2* (12) (1996) 229.

[6] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher and G.R.J. Artus, *Chem. Eur. J., 2*(7) (1996) 114.

[7] W.A. Herrmann, K. Öfele, M. Elison, F.E. Kühn and P.W. Roesky, *J. Organomet. Chem., 480* (1994) C7; W.A. Herrmann, G.M. Lobmaier and M. Elison, *J. Organomet. Chem., 520* (1996) 231; K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer and J. Mink, *J. Organomet. Chem., 459* (1993) 177; K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, T. Priermeier and P. Kiprof, *J. Organomet. Chem., 498* (1995) 1; W.A. Herrmann, P.W. Roesky, M. Elison, G. Artus and K. Öfele, *Organometallics, 14* (1995) 1085.

[8] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher and G.R.J. Artus, *Angew. Chem., 107* (1995) 2602; *Angew. Chem., Int. Ed. Engl., 34* (1995) 3005; W.A. Herrmann, M. Elison, J. Fischer and C. Köcher, *DE-4447068*, Hoechst AG, 1994; *DE-447066*, Hoechst AG, 1994; J. Fischer, *Ph.D. Thesis*, Technische Universität München, 1996; W.A. Herrmann, L.J. Gooßen, C. Köcher and G.R.J. Artus, *Angew. Chem.*, in press.

[9] E. Cetinkaya, P.B. Hitchcock, H. Kücükbay, M.F. Lappert and S. Al-Juaid, *J. Organomet. Chem., 481* (1994) 89.

[10] D.K. Dutta and M.M. Singh, *Trans. Met. Chem., 5* (1980) 244.