Oxygen as Oxidant in Palladium-Catalyzed Inter- and Intramolecular Coupling Reactions

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Dedicated to Professor Ivar Ugi on the occasion of his 65th birthday

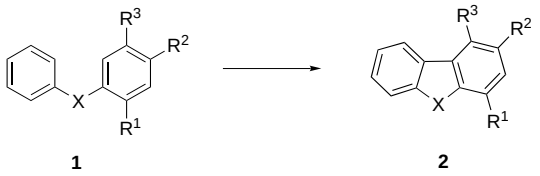
Abstract: Facile palladium-catalyzed cyclizations of arylaminoquinones giving biologically important carbazoloquinones in high yields have been performed with oxygen as the single oxidant. By a slight modification of the catalyst, diphenylamine, diphenyl ether, and related compounds can be cyclized. The system could also be used in intermolecular couplings between naphthoquinones and benzene or naphthalene.

Keywords: alkaloids · C–H activation · catalysis · cyclizations · palladium

Introduction

Aromatic compounds may be oxidatively coupled inter- or intramolecularly to biaryls, polyaryls, or ring-closed compounds with stoichiometric amounts of palladium.[1–3] Differently substituted carbazoles (**2**) may be prepared from diphenylamine derivatives (**1**) with palladium acetate (1.0 equiv) in refluxing acetic acid (Scheme 1).[2, 4]

Procedures for the facile synthesis of carbazole and carbazoloquinones are of interest since a number of biologically active alkaloids contain these units.[5] The synthesis



	R^1	R^2	R^3	X
a	H	H	H	NH
b	H	H	H	O
c	NO_2	H	H	NH
d	H			NH
e	OEt	H	H	NMe
f	H	H	H	CO NH

Scheme 1. Cyclization of aryl amines, aryl ethers, and benzanilide.

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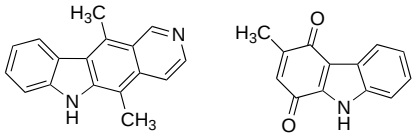
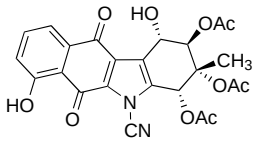
of ellipticine, a compound with promising activity against some forms of cancer, is an example where palladium-mediated cyclization of diphenylamine structures is a crucial step.[6] Use of this type of cyclization also leads to a



Ellipticine

Murrayaquinone A



Kinamycin A

simple route for the preparation of carbazoloquinones (**4**) (Scheme 2) such as different kinamycins[7] and murrayaquinones,[8] which exhibit interesting biological activity.[9]

However, as these reactions use stoichiometric amounts of palladium, a catalytic system would be highly desirable.[4] Although such systems have been developed with copper acetate[10] or *tert*-butyl hydroperoxide[11] as oxidants, oxygen would clearly be preferred.[12] The well-known Wacker industrial process uses a $PdCl_2/CuCl_2/O_2$ catalytic system for the oxidation of ethylene to acetaldehyde or acetic anhydride,[13] but in aromatic coupling reactions chloride ions effectively poison the catalyst. An alternative catalyst, consisting of palladium trifluoroacetate in combination with a bispyrazole ligand, has recently been used in catalytic Wacker type reactions with a combination of benzoquinone and oxygen as the oxidant.[14] However, the presence of nitrogen

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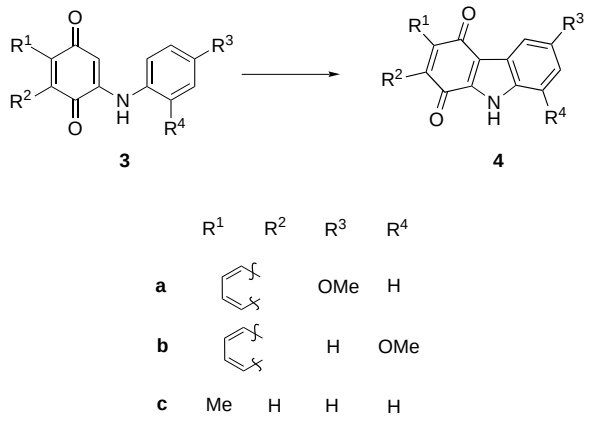


Scheme 2. Cyclization of 2-arylamino-1,4-quinones.

Table 1. Palladium-catalyzed oxidative aromatic ring closure.

Entry	Product	Catalyst system[a]	T[°C]	Yield[%][b]	t/h
1	**2a**	A	90	61	14
2	**2a**	B	87	66	14
3	**2b**	B	116	60	48
4	**2c**	B	116	80	50
5	**2d**	B	85	30	12
6	**2e**	B	25	-[c]	10
7	**2f**	B	116	60	60
8	**4a**	A	95	89	48
9	**4b**	A	95	87	48
10	**4c**	A	95	86	48
11	**5**	B	80	54	12

[a] Catalyst system: A) 5 mol% $Pd(OAc)_2$ in acetic acid under oxygen atmosphere. B) 5 mol% $Pd(OTFA)_2$ and 10 mol% $Sn(OAc)_2$ in acetic acid under oxygen atmosphere. [b] Yields of isolated product. [c] The product was unstable under these conditions.

ligands also effectively inhibits the cyclization reactions. A system for aromatic coupling has been reported that uses neat palladium acetate as the catalyst and a mixture of nitrogen and oxygen (1:1) as the oxidant at a pressure of 50 kg cm^{-2}.[15] This reaction produced a 1:1 mixture of dibenzofuran and dimers of diphenyl ether from intra- and intermolecular coupling, respectively. Addition of 2,4-pentanedione reduced the amount of dimerized product, but it was still significant.[16] Furthermore, transition metal-catalyzed reactions with oxygen at high pressure are hazardous, and explosions have been reported in reactions related to aromatic coupling.[1c, 17] We would therefore like to report a procedure that uses oxygen at atmospheric pressure.

Results and Discussion

We have shown earlier that 2-arylamino-1,4-quinones (**3**) can be cyclized to carbazoloquinones (**4**) (Scheme 2) in good-to-fair yields with palladium(II) acetate as catalyst and *tert*-butyl hydroperoxide as oxidant.[11] Hydrogen peroxide can also be used as oxidant in these reactions, but the yields are lower. A hydrogen peroxide and benzoquinone system did not improve the yields, perhaps because this system is not stable under the reaction conditions. The use of a Wacker type oxidation system, $Pd(OAc)_2/Cu(OAc)_2/O_2$, gave lower yields than those obtained with *tert*-butyl hydroperoxide. We have now found that efficient cyclization of carbazoloquinones is possible under similar conditions with molecular oxygen at atmospheric pressure as the oxidant (entries 8–10, Table 1). In fact, the yields were distinctly higher with oxygen as oxidant. For instance, the yields of **4a** and **4c** were higher than 85% with oxygen, but only around 65% with *tert*-butyl hydroperoxide.[11] With H_2O_2 as oxidant, the yield was even lower at about 30%.

The successful use of oxygen in the oxidative aromatic cyclizations of 2-arylamino-1,4-quinones prompted us to test whether this simple oxidation system could be applied to other related reactions. Although carbazole (**2a**) could be obtained in decent yield (61%) from diphenylamine, diphenyl ether could not be cyclized to dibenzofuran (**2b**). One major problem in the reaction of diphenyl ether seemed to be the formation of metallic palladium. It has been reported previously that addition of cocatalysts such as tin(II) acetate, $Sn(OAc)_2$, increases the yields in palladium(II)-catalyzed reactions.[18] Addition of $Sn(OAc)_2$ together with the use of a more electrophilic catalyst, palladium trifluoroacetate ($Pd(OTFA)_2$), was found to effect cyclization of diphenyl ether to dibenzofuran in reasonable yield (60%, entry 3, Table 1). This dramatic increase in activity in going from $Pd(OAc)_2$ to $Pd(OTFA)_2$ was the first indication that the reaction is very sensitive to the conditions. Because of problems with reproducibility in the formation of dibenzofuran, we decided to investigate this reaction in more detail.

For diphenyl ether, the yield increased with increasing temperature. With the more reactive substrates, such as the substituted diphenylamines and the 2-arylamino-1,4-quinones, lower temperatures were necessary to avoid intermolecular side reactions. Addition of activated charcoal to disperse the precipitated palladium(0)[18] had a positive effect on the reaction, but this was not enough to assure reproducibility. Most interestingly, addition of a small amount of diphenylamine to the reaction of diphenyl ether improved the yield of dibenzofuran, while addition of carbazole or amines such as pyrrolidine or diisopropylamine did not have any effect. This indicates that diphenylamine has a special ability to promote cyclizations, perhaps by keeping the palladium(0) from being precipitated in these systems, by formation of arylpalladium species.[19]

The high yields in the reactions of 2-arylamino-1,4-quinones may be because of the quinone moiety. Benzoquinone is known to coordinate to palladium(0),[20] and is therefore expected to prevent the formation of metallic palladium. Furthermore, the coordination of a quinone moiety to palladium(II) activates the catalyst and may facilitate the reoxidation of palladium(0).[21, 22] However, addition of benzoquinone to the reaction of diphenyl ether did not improve the results.

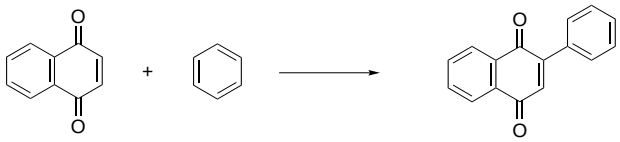
Acetic acid seems to be the best solvent, but propionic acid can also be used. Ethanol, ethyl acetate, and dimethyl sulfoxide were also tried, but in these solvents no ring closure was observed. The quality of the acetic acid is of primary importance, but the reason for this is not known. The reaction was not very sensitive to small differences in water concen-

0947-6539/99/0508-2414 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 8

tration, but acetic anhydride had a negative influence on the reactivity. One explanation may be that acetic acid generally contains some anhydride, but addition of a small amount of water to hydrolyze any anhydride present did not improve the efficiency of the reaction. Halide ions also have an adverse effect on the cyclization reaction. In order to remove any small amount of halide that might be present as residues from the manufacturing process of acetic acid, silver acetate was added but this also failed to improve the efficiency of the reaction. Addition of trifluoroacetic acid resulted in a more reactive catalytic system and led not only to faster reactions, but also to intermolecularly coupled by-products unless the concentration was lowered. With a 1:10 ratio of trifluoroacetic acid and acetic acid the concentration had to be decreased by one half to minimize the intermolecular side reactions.

With the more effective $Pd(OTFA)_2/Sn(OAc)_2/O_2$ system it was possible to effect ring closure of some substrates related to diphenylamine (Scheme 1; entries 4–7, Table 1). The substrate **1e** reacted very rapidly, but the product **2e** was further oxidized under the given conditions and no product could be isolated (entry 6). The ring closure of benzanilide (**1f**, entry 7) shows that it is possible to prepare six-membered rings by this procedure.

In order to study whether selective intermolecular coupling would be possible, the reaction between naphthoquinone and naphthalene or benzene was also investigated. The reaction with naphthalene turned out to be quite complicated, perhaps because of the high reactivity of naphthalene, and a complex mixture of products was obtained. Mass spectrometry showed that two major products were formed, both in low yields. One was the desired product from the coupling of naphthalene with one molecule of naphthoquinone. The other came from coupling with two molecules of naphthoquinone. In contrast, benzene (Scheme 3) gave the anticipated product **5** in reasonable yield (entry 11, Table 1).



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Scheme 3. Intermolecular coupling of naphthoquinone and benzene.

Conclusion

Aromatic systems can be efficiently coupled, inter- and intramolecularly, with palladium(II) as the catalyst and oxygen (1 atm) as the oxidant. Intramolecular coupling yields both five- and six-membered rings. The cyclization of very reactive systems, such as diphenylamine, requires only palladium acetate as the catalyst, while a more electrophilic catalyst, such as palladium trifluoroacetate together with tin acetate, is necessary for less reactive systems like diphenyl ether and benzanilide. The positive effect of additives such as tin acetate and diphenylamine shows that minor modifications can lead to substantial improvements in the efficiency of the reaction. This suggests that the palladium-catalyzed coupling has potential for even wider application than described in the present work and further studies are in progress.

Efficient catalytic methods have recently been developed for the preparation of unsymmetric diarylamines and diaryl ethers.[23] In combination with these methods, the palladium-catalyzed coupling described here by us offers a facile route to condensed aromatic heterocyclic systems.

Experimental Section

All solvents and reagents were purchased from Aldrich. $Pd(OAc)_2$ was recrystallized from acetic acid before use. $Pd(OTFA)_2$ was prepared from $Pd(OAc)_2$ by a literature procedure.[24] Purification by medium-pressure liquid chromatography (MPLC) was performed as described by Baeckström et al.[25] The gel used was Merck Silica gel 60. TLC analyses were performed on Merck aluminum plates coated with silica; UV light and phosphomolybdic acid in ethanol (5%) were used for visualization. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz (Bruker Model AM 400) and 250 MHz (Bruker Model ACF 250) spectrometers. ^{1}H NMR chemical shifts are reported in δ (ppm) relative to Me_4Si as the internal standard. ^{13}C chemical shifts are given in δ values relative to the solvent ($CDCl_3$ 77.00 ppm or [D_6]DMSO 128.0 ppm). The abbreviation app = apparent is used in descriptions of NMR multiplicities. ^{1}H NMR integrations are reported as the relative number of hydrogens (H). GLC analyses were performed on a Varian 3700 instrument fitted with a BP-1 (methylsilicone, 25 m) capillary column. C_8–C_{16} *n*-alkanes were used as internal standards for GLC analyses. The Analytische Laboratorien, Engelskirchen, Germany performed all the elemental analyses.

Procedure for oxidative coupling with oxygen as oxidant: The substrate (1–5 mmol, 100 mol%) together with $Pd(OAc)_2$, or $Pd(OTFA)_2$, (5 mol%) and $Sn(OAc)_2$ (10 mol%) were dissolved in acetic acid (5–25 mL). The atmosphere was changed to oxygen and the mixture was stirred at the reported temperature for the time stated. When the reaction was complete the acetic acid was removed under reduced pressure, and the residue was purified by MPLC. Optimizations were achieved by following the reactions by TLC until no starting material could be detected or by capillary GLC with internal standards. The ^{1}H NMR spectra of **2a** and **2b** were in accordance with those of commercially available samples. The ^{13}C NMR spectra obtained for **2c** and **2d**[26] and the ^{1}H NMR spectrum for **2f**[27] were as reported in the literature.

Preparation of compound 5: Naphthoquinone (3 mmol) was dissolved in benzene (5 mL); reaction time 12 h, temperature 80 °C; yield: 54%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (m, 1H), 8.11 (m, 1H), 7.77 (m, 2H), 7.57 (m, 2H), 7.47 (m, 3H), 7.07 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 185.2, 184.4, 148.2, 135.3, 134.0, 133.9, 133.4, 132.5, 132.1, 130.1, 129.5, 128.5, 127.1, 126.0. $C_{16}H_{10}O_2$: calcd C 82.04, H 4.30; found C 81.92, H 4.44.

Preparation of 2-arylamino-1,4-quinones: The 2-arylamino-1,4-quinones **3a**–**c** were prepared according to a literature procedure.[28]

Compound 3a: yield: 60%; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.12 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 1.3 Hz, 1H), 8.10 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 1.3 Hz, 1H), 7.76 (app dt, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 1.3 Hz, 1H), 7.66 (app dt, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 1.3 Hz, 1H), 7.43 (br s, 1H), 7.20 (AB app d, ^3J(H,H) = 8.9 Hz, 2H), 6.95 (AB app d, ^3J(H,H) = 9.0 Hz, 2H), 6.23 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (400 MHz, [D_6]DMSO): δ = 182.1, 181.6, 156.9, 146.8, 134.8, 132.7, 132.4, 130.5, 130.3, 126.0, 125.5, 125.2, 114.4, 101.0, 55.2. $C_{17}H_{13}NO_3$: calcd C 73.11, H 4.69; found C 73.22, H 4.78.

Compound 3b: yield: 59%; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.13 (dd, ^3J(H,H) = 7.4 Hz, ^3J(H,H) = 1.5 Hz, 1H), 8.11 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 1.5 Hz, 1H), 7.90 (br s, 1H), 7.76 (app dt, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 1.5 Hz, 1H), 7.67 (app dt, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 1.5 Hz, 1H), 7.44 (dd, ^3J(H,H) = 7.8 Hz, ^3J(H,H) = 1.6 Hz, 1H), 7.15 (app dt, ^3J(H,H) = 7.9 Hz, ^3J(H,H) = 1.6 Hz, 1H), 7.03 (dd, ^3J(H,H) = 7.7 Hz, ^3J(H,H) = 1.5 Hz, 1H), 6.97 (dd, ^3J(H,H) = 8.1 Hz, ^3J(H,H) = 1.3 Hz, 1H), 6.50 (s, 1H), 3.92 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 184.0, 182.2,

151.2, 144.0, 134.8, 133.3, 132.3, 130.6, 127.0, 126.6, 125.5, 121.1, 120.9, 111.2, 103.6, 55.8. $C_{17}H_{13}NO_3$: calcd C 73.11, H 4.69; found C 73.16, H 4.80.

Compound 3c: yield: 60%; The ^{1}H NMR spectrum was in full accordance with that reported in reference [28].

Cyclization of 2-aryl-1,4-quinones

Compound 4a: The substrate (2 mmol, 100 mol%) and $Pd(OAc)_2$ (22.4 mg, 0.1 mmol) were dissolved in glacial acetic acid (25 mL) and the atmosphere was changed to oxygen. The mixture was stirred at 95 °C until no starting material could be detected by TLC (approximately after 48 h). Then the acetic acid was removed under reduced pressure and the residue was purified by MPLC to give an 89% yield. The ^{1}H NMR spectrum of **4a** was in full agreement with that reported in the literature.[29]

Compound 4b: Compound **4b** was prepared according to the procedure described above for **4a**. 87% yield; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 9.49$ (brs, 1H), 8.26 (dd, $^3J(H,H) = 7.4$ Hz, $^3J(H,H) = 1.4$ Hz, 1H), 8.20 (dd, $^3J(H,H) = 7.4$ Hz, $^3J(H,H) = 1.4$ Hz, 1H), 7.96 (d, $^3J(H,H) = 8.0$ Hz, 1H), 7.76 (td, $^3J(H,H) = 7.4$ Hz, $^3J(H,H) = 1.4$ Hz, 1H), 7.70 (td, $^3J(H,H) = 7.4$ Hz, $^3J(H,H) = 1.4$ Hz, 1H),7.31 (d, $^3J(H,H) = 8.0$ Hz, 1H), 6.86 (d, $^3J(H,H) = 8.2$ Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (400 MHz, $[D_6]$DMSO): $\delta =$ 180.4, 177.1, 147.4, 136.9, 134.0, 133.9, 133.1, 132.7, 129.1, 125.9, 125.9, 125.4, 124.9, 117.8, 114.2, 106.6, 55.5. $C_{17}H_{11}NO_3$: calcd C 73.64, H 4.00; found C 73.45, H 4.15.

Compound 4c: The same procedure was used as for compound **4a**, such that 86% of **4c** was isolated. The ^{1}H NMR spectrum was in full accordance with that reported in reference [28].

Acknowledgments

This work was supported by the Swedish Research Council for Engineering Sciences and the Carl Trygger Foundation. H.H. and J.D.O. wish to thank the Royal Institute of Technology for their scholarships.

[1] a) R. van Helden, G. Verberg, B. Balder, *Recl. Trav. Chim. Pays-Bas*, **1965**, *84*, 1263; b) J. M. Davidson, C. Triggs, *J. Chem. Soc. A*, **1968**, 1324 – 1330; c) H. Iataaki, H. Yoshimoto, *J. Org. Chem.* **1973**, *38*, 76 – 79; d) F. R. S. Clarke, R. P. C. Norman, C. B. Thomas, J. S. Willson, *J. Chem. Soc. Perkin Trans 1*, **1974**, *38*, 1289.

[2] B. Åkermark, L. Eberson, E. Jonsson, E. Petterson, *J. Org. Chem.* **1975**, *40*, 1365 – 1367.

[3] For a general reviews of palladium-assisted reactions see: a) R. F. Heck, *Palladium Reagents in Organic Syntheses*, Academic Press, London, **1985**; b) B. M. Trost, T. R. Verhoeven in *Comprehensive Organometallic Chemistry, Vol. 8* (Ed.: G. Wilkinson, F. G. A. Stone, E. Abel), Pergamon, Oxford, **1982**, 799 – 938.

[4] L. S. Hegedus, *Angew. Chem.* **1988**, *100*, 1147 – 1161; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1113 – 1226.

[5] For a review of carbazole alkaloids see for example: J. Bergman, B. Pelcman in *Studies in Natural Products Chemistry* (Eds.: Atta-ur-Rhaman, P. W. Le Quesne), Springer, Berlin, Heidelberg, **1988**.

[6] a) B. R. Miller, T. Moock, *Tetrahedron Lett.* **1980**, *21*, 3319 – 3322; b) R. J. Hall, J. Marchant, A. M. F. Oliveira-Campos, M.-J. R. P. Queiroz, P. V. R. Shannon, *J. Chem. Soc. Perkin Trans. 1*, **1992**, 3439 – 3450.

[7] H.-J. Knölker, N. O'Sullivan, *Tetrahedron Lett.* **1994**, *35*, 1695 – 1698.

[8] M. Yogo, C. Ito, H. Furukawa, *Chem. Pharm. Bull.* **1991**, *39*, 328 – 334.

[9] K. Takeya, M. Itoigawa, H. Furukawa, *Eur. J. Pharmacol.* **1989**, *169*, 137.

[10] H.-J. Knölker, N. O'Sullivan, *Tetrahedron*, **1994**, *50*, 10893 – 10908.

[11] B. Åkermark, J. D. Oslob, U. Heuschert, *Tetrahedron Lett.* **1995**, *36*, 1325 – 1326.

[12] R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**.

[13] K. Weissermel, H.-J. Arpe, *Industrial Organic Chemistry, Third Completely Revised Edition*, VCH Publishers, New York, **1997**, pp. 164 – 167, 181 – 182.

[14] a) Y. Uozumi, K. Kato, T. Hayashi, *J. Org. Chem.* **1998**, *63*, 5071 – 5075; b) Y. Uozumi, K. Kato, T. Hayashi, *J. Am. Chem. Soc.* **1997**, *119*, 5063 – 5064.

[15] H. Yoshimoto, H. Itatani, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2490 – 2492.

[16] A. Shiotani, H. Itatani, *Angew. Chem.* **1974**, *86*, 478 – 479; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 471 – 472.

[17] H. Itatani, H, Yoshimoto, *Chem. Ind. (Düsseldorf)* **1971**, 674 – 675.

[18] a) D. R. Bryant, J. E. McKeon, B. C. Ream, *J. Org. Chem.* **1968**, *33*, 4123 – 4127; b) T. Ohishi, J. Yamada, Y. Inui, T. Sakaguchi, M. Yamashita, *J. Org. Chem.* **1994**, *59*, 7521 – 7522.

[19] a) W. A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem.* **1995**, *107*, 1989 – 1992; *Angew. Chem. Int. Ed Engl.* **1995**, *34*, 1844 – 1848; b) M. Ohff, A. Ohff, M. E. van der Boom, D. Milstein, *J. Am. Chem. Soc.* **1997**, *119*, 11687 – 11688.

[20] H. Grennberg, A. Gogoll, J.-E. Bäckvall, *Organometallics*, **1993**, *12*, 1790 – 1793.

[21] See, for example, J.-E. Bäckvall in *Advances in Metal-Organic Chemistry, Vol. 1* (Ed.: L. S. Liebeskind), JAI Press, London, **1989**, pp. 135 – 175.

[22] a) J.-E. Bäckvall, R. B. Hopkins, H. Grennberg, M. M. Mader, A. K. Awasthi, *J. Am. Chem. Soc.* **1990**, *112*, 5160 – 5166; b) J.-E. Bäckvall, *Pure Appl. Chem.* **1992**, *64*, 429 – 437; c) J.-E. Bäckvall, A. Gogoll, *J. Chem. Soc. Chem. Commun.* **1987**, 1236 – 1238.

[23] See for example: a) J.-F. Marcoux, S. Doye, S. L. Buchwald, *J. Am. Chem. Soc.* **1997**, *119*, 10539 – 10540; b) G. Mann, J. F. Hartwig, *Tetrahedron Lett.* **1997**, *38*, 8005 – 8008, and references therein.

[24] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, G. Wilkinson, *J. Chem. Soc.* **1965**, 3632 – 3640.

[25] P. Baeckström, K. Stridh, L. Li, T. Norin, *Acta Chem. Scand. Ser. B* **1987**, *41*, 442 – 447.

[26] A. R. Katritzky, G. W. Rewcastle, W. Gordon, L. M. V. Miguel, Z. Wang, *Magn. Reson. Chem.* **1988**, *26*, 347 – 350.

[27] A. M. Andrievskii, A. N. Poplavskii, K. M. Dyumaev, S. Bogachev, Y. Yu, S. S. Berestova, *Chem. Heterocycl. Compd. (USSR) (Engl. Transl.)* **1985**, *21*, 924 – 931.

[28] M. Yogo, C. Ito, H. Furukawa, *Chem. Pharm. Bull.* **1991**, *39*, 328 – 334.

[29] S. Bittner, P. Krief, T. Massil, *Synthesis*, **1991**, 215 – 216.

Received: October 7, 1998
Revised version: February 25, 1999 [F1382]

  0947-6539/99/0508-2416 $ 17.50+.50/0