8-Quinolylcyclopentadienyl, a Ligand with a Tailored Fit for Chelate Complexes

Markus Enders*, Ralph Rudolph, and Hans Pritzkow

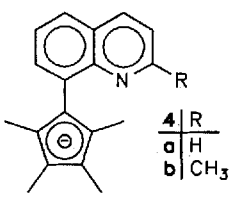
Anorganisch-Chemisches Institut der Universität,
Im Neuenheimer Feld 270, D-69120 Heidelberg (Germany)
Telefax: (internat.) +49(0)6221-545609
E-mail: gn1@ix.urz.uni-heidelberg.de

Received November 13, 1995

Key Words: Cyclopentadienes / Half-sandwich complexes / Intramolecular nitrogen donors

8-Lithioquinoline reacts with 2,3,4,5-tetramethylcyclopentenone to give 8-quinolylcyclopentadiene (**1/2**) after acidic workup and treatment with ammonia. Two of the possible three isomers are formed; the acidic protons on the Cp rings show unusual downfield shifts in the ^{1}H-NMR spectra. Treatment with strong bases led to the intensely coloured anionic **4** which was converted into the trimethylsilyl derivative **5**. This is a suitable starting compound for the trihalotitanium and -zirconium compounds **6** and **7**. The two complexes were investigated by crystal structure analyses. In both cases the quinolyl nitrogen atom is coordinated to the metal.

Among the enormous number of cyclopentadienyl ligands, there are a few systems where an additional ligand is fixed to the five-membered ring by a side chain[1]. If the second functionality interacts only weakly with the metal centre, this system is a so-called semilabile ligand. This type of compound is of great current interest since it is possible to modify the properties of organometallic catalysts or reagents for stereoselective synthesis[2]. Amines can serve only as donor units; in many cases they interact only weakly or not at all with transition metal centres. The coordination can be improved by using aromatic amines, especially when they are part of a chelating system. There are several examples where an amine or a pyridyl unit is fixed to a cyclopentadiene[3]. To ensure good chelating properties, a C_2 or a C_3 moiety between the nitrogen atom and the ring carbon atom is required. If the spacer is an alkyl chain, several conformations are possible due to its flexibility. The molecule can only act as a chelating ligand when it adopts a suitable conformation. If the donor group does not interact with the metal, the "side arm" moves freely and the compounds are often obtained as liquids or non-crystalline solids. We synthesised a more rigid system, a quinoline which bears a cyclopentadienide at the 8-position[4].

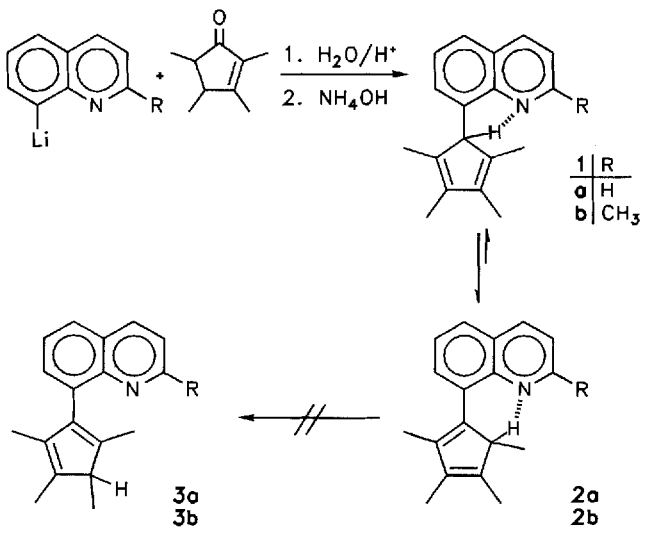


The interesting feature of this system is the fact that the C_2 spacer between the nitrogen atom and the cyclopentadienyl is fixed in the planar heterocyclic ring system. Therefore only rotation about one carbon–carbon bond is possible.

Results and Discussion

1a/2a and **1b/2b** were synthesised according to the procedure, for the preparation of C_5Me_5H[5]. 8-Lithioquinoline was allowed to react with 2,3,4,5-tetramethylcyclopentenone and the formed lithium enolate was converted into the corresponding cyclopentadiene by hydrolysis and dehydratation under acidic conditions.

Scheme 1



The products were distilled under vacuum. If necessary they were further purified by chromatography on silica gel. Two of the possible three isomers are formed. Immediately after distillation the isomer with the acidic Cp proton in

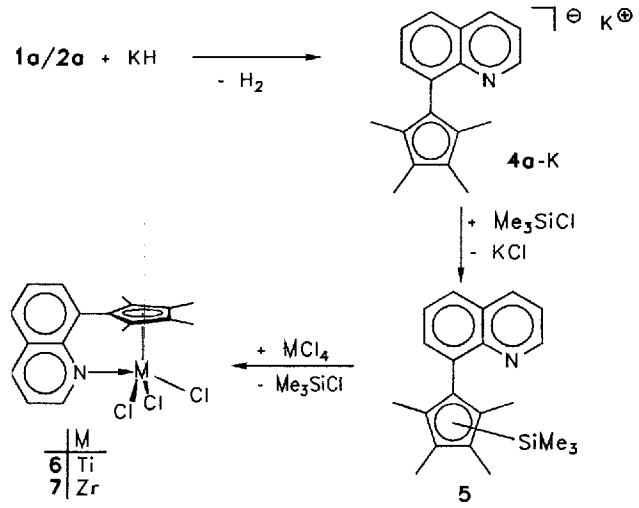
  0009–2940/96/0404–0459 $ 15.00+.25/0

position 1 (**1a** and **1b**) is the major one with up to 70% abundance. It isomerises partially to **2a** (**2b**) where the Cp-double bond is in conjugation with the heterocycle. Formation of the third isomer **3a** (**3b**) was not observed. After distillation and storing for several days at room temperature, **1a** (**1b**) and **2a** (**2b**) were obtained in a ratio of 30:70.

All isomers show interesting NMR shifts for the acidic Cp proton. The quartet for the isomer **2a** (**2b**) is found at $\delta = 4.00$ (4.20), the singlet originating from **1a** (**1b**) appears at even lower field at $\delta = 5.57$ (5.53). These unusual NMR shifts indicate a hydrogen bond to the quinoline nitrogen atom. For **3a** (**3b**) the allylic Cp proton cannot interact with the nitrogen atom because it is too far away. This might be the reason why this isomer is not formed. The mass spectra show intense peaks for the molecular ion (M^+), for $M^+ - H$ and for $M^+ - CH_3$. Besides these peaks, only low intensity fragments are detected.

The cyclopentadienes can be deprotonated with butyllithium or with potassium hydride to form the lithium or potassium salts which are red in the solid state and intensely violet in solutions of THF, acetonitrile, or toluene. Until now we have no plausible explanation for the formation of the colours. The colourless solution of Cp* lithium remains colourless upon addition of quinoline.

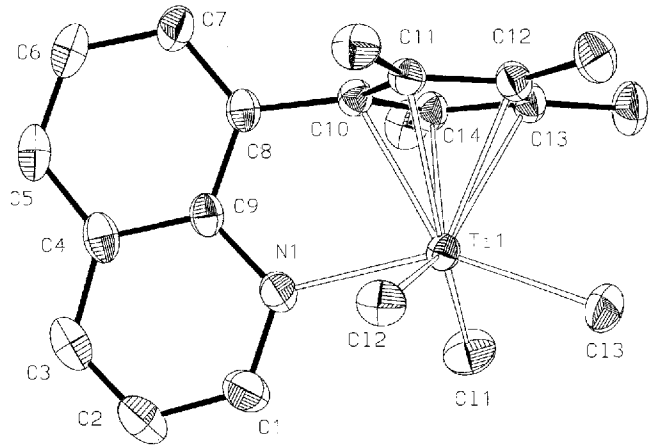
Scheme 2



The anion **4a**-K was treated with trimethylsilyl chloride to yield **5** as a yellow liquid. It shows dynamic behaviour on the NMR time-scale due to the trimethylsilyl group[7]. Reaction of **5** with $TiCl_4$ or $ZrCl_4$ in toluene leads to the formation of the complexes **6** and **7**, respectively. The titanium compound **6** is formed as a red powder in 76% yield. In the case of the zirconium complex **7**, recrystallisation from dichloromethane is necessary to obtain 72% of pale yellow crystals. Both compounds are nearly insoluble in unpolar solvents, such as hexane or toluene, but soluble in polar aprotic solvents such as chloroform, dichloromethane, or DMSO. In protic solvents like water or methanol, **7** dissolves without decomposition. However, in the presence of aqueous bases the compound is hydrolysed and the protonated ligand **1/2** is obtained. The titanium compound **6** is not stable in water. The mass spectrum of **6** does not show a molecular peak, but rather the abstraction of one chlorine atom. A second chlorine atom is lost together with a hydrogen atom. In the case of **7** the molecular peak is observed. The base peak is due to a fragment generated by loss of hydrogen chloride. The NMR spectra which contain two signals each for the four Cp-CH_3 groups show that the molecules have a mirror plane orthogonal to the Cp ring. The ^{1}H-NMR signal of the hydrogen adjacent to the quinoline nitrogen is a probe for coordination to the nitrogen atom. Whereas in the case of free quinoline this ^{1}H-NMR signal appears at $\delta = 8.81$[6] and that of **1a** (**2a**) at about $\delta = 8.9$, it shifts to $\delta = 9.13$ for **6** and to $\delta = 9.15$ for **7**. These values indicate, that the nitrogen atom is coordinated to the metal.

To prove this, we performed two single-crystal structure analyses. Crystals of **6** and **7** were obtained from saturated chloroform solutions at room temperature.

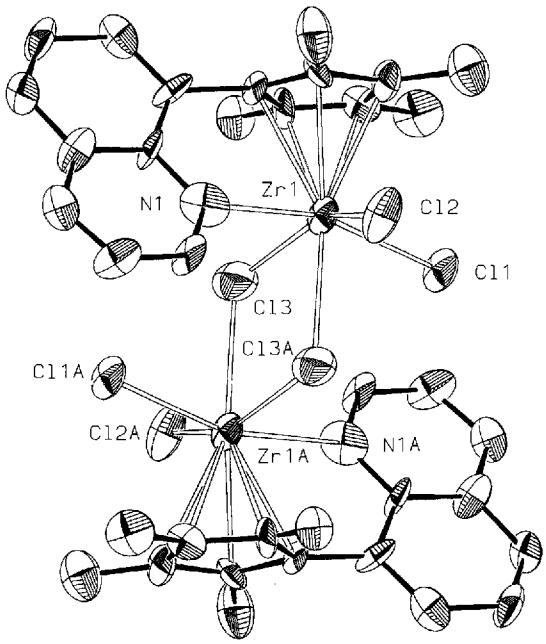
Figure 1. Crystal structure of **6**[a]



[a] Selected bond lengths [Å] and angles [°]: Ti1–N1 2.261(2); Ti1–Cl1 2.307(1); Ti1–Cl2 2.331(1); Ti1–Cl3 2.338(1), Ti1–C10 2.338(2); Ti1–C11 2.402(2); Ti1–C12 2.403(2); Ti1–C13 2.386(2); Ti1–C14 2.359(2); C1–N1–Ti1 120.73(14); C1–N1–C9 118.09(17); C9–N1–Ti1 121.02(12); C9–C8–C10 115.3(2); C9–C8–C7 119.7(2); C7–C8–C10 124.9(2).

Compound **6** is monomeric in the solid state as $C_5H_5TiCl_3$[8]. The titanium is coordinated to the Cp ring, three chlorine atoms and the quinolyl nitrogen atom. The Ti–N distance is with 2.261(2) Å in the usual range for a donative nitrogen–titanium bond. Because of the additional nitrogen ligand, the Ti–Cl bonds [2.307(1) Å–2.338(1) Å] are elongated by ca. 0.1 Å compared to $C_5H_5TiCl_3$[8] or $C_5Me_4EtTiCl_3$[9]. All atoms of the quinoline system lie in a plane (max. deviation 0.01 Å) forming a dihedral angle of 96.96° with the Cp ring. The angles at the C8 atom indicate that the quinoline is slightly bent towards the metal centre. Thus, the C8–C9–C10 angle is reduced from the ideal angle of 120° to a value of 115.3° and the C7–C8–C10 angle increases to 124.9° whereas the C7–C8–C9 angle is not effected significantly. The angles around the nitrogen are 118.1° (C1–N1–C9), 121.0° (C9–N1–Ti1) and 120.7° (C1–N1–Ti1) with a sum of

Figure 2. Crystal structure of **7**[b]



[b] Selected bond lengths [Å]: Zr1–N1 2.405(14); Zr1–Cl1 2.444(5); Zr1–Cl2 2.466(5); Zr1–Cl3 2.524(6); Zr1–Cl3A 2.684(6); Zr1-cyclopenadienyl carbon atoms 2.44(2)–2.55(2).

359.8°. This shows, that the nitrogen atom is in a planar arrangement with the lone pair pointing directly to the metal.

Compound **7** crystallises with one molecule of chloroform in the asymmetric unit. Because of the low quality of the crystals, the bond lengths are not as reliable as in the case of the structure of **6**. However, they fall all in the expected range. While $C_5H_5ZrCl_3$[8] has a polymeric chain structure, so that each zirconium is coordinated by one Cp ring and five chlorine atoms, the bulkier C_5Me_5 ligand makes it more difficult for the compound $C_5Me_5ZrCl_3$ to be a polymer and a dimeric structure results. Although the quinoline donor in **7** occupies one coordination site of the metal, the compound is still dimeric as is $C_5Me_5ZrCl_3$[10]. The best plane of the quinoline has an angle of 110.7° to the Cp ring. Because this angle is not the ideal 90°, the nitrogen lone pair of a perfectly planar quinoline would not point directly to the metal centre. Therefore, the heterocycle is distorted with maximum deviations up to 0.07 Å from the best plane. Thus the nitrogen atom is in the proper orientation to interact with the metal centre. The structures of **6** and **7** show, that the new ligand **4** has a convenient geometry for coordination to transition metal ions. Although it is rigid, the metal-to-nitrogen bond distance can be varied to some extent by rotation of the quinoline moiety and by distortion. We are now investigating the binding capabilities of the ligands **4** to other transition metals. In **6** and **7** we want to substitute the chlorine atoms or to reduce the metals to obtain highly reactive species.

Experimental

2,3,4,5-Tetramethyl-1-(8-quinolyl)cyclopentadiene (**1a/2a**): A solution of 20.8 g (100 mmol) of 8-bromoquinoline in 300 ml of THF was cooled to −78 °C and 38.5 ml of a 2.6 M solution of *n*-butyllithium in hexane (100 mmol) was added with stirring within 10 min. After stirring for another 10 min at this temperature, 13.82 g (100 mmol) of 2,3,4,5-tetramethylcyclopent-2-enone was added dropwise. The mixture was allowed to warm to room temp. and was then heated at reflux for 1 h. After cooling down, 100 g of ice and 20 ml of hydrochloric acid were added and the mixture was stirred for 30 min. It was subsequently alkalised with aqueous ammonia, then 200 ml of diethyl ether was added and the organic layer was isolated. All volatile components were removed under vacuum and the product was distilled at 93–97 °C/10^{-3} mbar to give 14.2 g of a crude oil. Further purification by chromatography on silica gel (solvent cyclohexane/ethylacetate, 3:1) yielded 12.2 g (48.9%) of the two isomers **1a** and **2a** in a 40:60 ratio. – ^{1}H NMR ($CDCl_3$): δ = 0.86 (d, ^3J = 7.7 Hz, 3H); 1.66 (s, 6H), 1.89–1.93 (m, 12H); 1.97 (s, 3H); 4.00 (q, ^3J = 7.5 Hz, 1H); 5.57 (s, 1H); 6.99–7.03 (m, 1H); 7.30–7.70 (m, 7H); 8.09–8.14 (m, 2H); 8.90–9.00 (m, 2H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.1, 11.2, 11.9, 12.0, 12.7, 14.0 (CH_3); 52.0, 56.2 (allyl. CH); 120.4, 120.6, 125.7, 125.9, 126.1, 126.5, 126.6, 130.3, 135.9, 136.2, 149.0, 149.5 (quinoline CH); 128.5, 128.6, 134.5, 135.6, 137.2, 138.7, 139.0, 139.5, 141.5, 141.8, 147.3, 147.4 (quat. C). – MS (EI), *m/z* (%): 249 (88) [M^+], 248 (81) [M^+ – H], 234 (100) [M^+ – CH_3], 218 (30) [M^+ – H – 2 CH_3]. – $C_{18}H_{19}N$ (249.36): calcd. C 86.70, H 7.68, N 5.62; found C 85.90, H 7.69, N 5.59.

2,3,4,5-Tetramethyl-1-(2-methyl-8-quinolyl)cyclopentadiene (**1b/2b**): A solution of 4.4 g (20 mmol) of 8-bromoquinoline in 50 ml of THF was cooled to −78 °C and 11.0 ml of a 2.0 M solution of *n*-butyllithium in pentane (22 mmol) was added with stirring within 10 min. After stirring at this temperature for another 10 min, 3.5 g (25 mmol) of 2,3,4,5-tetramethylcyclopent-2-enone was added dropwise. The mixture was allowed to warm to room temp. and heated at reflux for 1 h. After cooling down, 50 g of ice and 5 ml of hydrochloric acid were added and the mixture was stirred for 30 min. It was then alkalised with aqueous ammonia, 100 ml of pentane was added and the organic layer was separated. All volatile components were removed under vacuum and the product was distilled at 115–125 °C/10^{-2} mbar to give 3.2 g (60%) of a crude oil. The product was purified by chromatography on silica gel (solvent cyclohexane/ethylacetate, 3:1) to yield **1b** and **2b**. – ^{1}H NMR ($CDCl_3$): **1b** δ = 1.55 (s, 6H); 1.78 (s, 6H); 2.64 (s, 3H); 5.53 (s, 1H); 6.84 (dd, 1H); 7.12–7.50 (m, 3H); 7.90 (d, 1H). **2b** δ = 0.71 (d, ^3J = 7.6 Hz, 3H); 1.82 (s, 3H); 1.87–1.88 (m, 6H); 2.58 (s, 3H); 4.20 (q, ^3J = 7.6 Hz, 1H); 7.09–7.55 (m, 4H); 7.89 (d, 1H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): **1b** δ = 11.2, 11.3 (CH_3); 25.6 (quinoline CH_3); 56.3 (allyl. CH); 121.3, 125.7, 126.4, 130.5, 136.2 (quinoline CH); 135.6, 138.9, 139.0, 141.8, 147.0, 157.4 (quat. C). **2b** δ = 12.0, 12.2, 13.0, 14.2 (CH_3); 25.7 (quinoline CH_3); 52.1 (allyl. CH); 121.4, 125.0, 125.3, 125.8, 136.0 (quinoline CH); 126.7, 126.8, 131.2, 134.6, 138.4, 142.7, 146.7, 157.8 (quat. C). – MS (EI), *m/z* (%): 263 (85) [M^+], 262 (100) [M^+ – H], 248 (98) [M^+ – CH_3], 232 (20) [M^+ – H – 2 CH_3], 218 (10) [M^+ – 3 CH_3]. – $C_{19}H_{21}N$: calcd. 263.1674, found 263.1647 (MS).

2,3,4,5-Tetramethyl-1-(8-quinolyl)trimethylsilylcyclopentadiene (**5**): 4.99 g (20 mmol) of **1a/2a** was added to a suspension of 0.88 g of potassium hydride (22 mmol) in 200 ml of THF. After 6 h 2.61 g (24 mmol) of trimethylsilyl chloride was added and the mixture was heated at reflux for 1 h. The solution was concentrated under vacuum to 50 ml, and 200 ml of pentane was added. The precipi-

tated potassium chloride was filtered off, the solvent was removed under vacuum and the product distilled at 101–103 °C/10^{-3} mbar to yield 5.53 g (86%) of yellow **5**. – ^{1}H NMR ($CDCl_3$, 335 K): δ = 0.19 (s, 9H, $SiMe_3$), 1.68 (s, 12H, 4 × CH_3); 7.28–7.34 (m, 1H), 7.49–7.55 (m, 2H), 7.70–7.75 (m, 1H), 8.08–8.13 (m, 1H), 8.86–8.91 (m, 1H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = –2.6 ($SiMe_3$); 12.0–13.5 (broad, CH_3); 120.6, 125.9, 126.7, 128.6, 131.1, 136.0, 149.9. – MS (EI), *m/z* (%): 321 (19) [M^+], 306 (100) [$M^+ - CH_3$], 248 (53) [$M^+ - SiMe_3$], 73 (28) [$SiMe_3^+$]. – $C_{21}H_{27}NSi$ (321.54): calcd. C 78.45, H 8.46, N 4.36; found C 78.27, H 8.44, N 4.35.

Trichloro[2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]-titanium(IV) (**6**): 1.12 g (5.9 mmol) of titanium(IV) chloride was dissolved in 50 ml of toluene. To the obtained solution, a solution of 1.90 (5.9 mmol) of **5** in 20 ml of toluene was added at –10 °C during 1 h. The reaction mixture was warmed up to room temp. and stirred for 15 h to give a red precipitate. The solid was filtered and dried under vacuum to yield 1.81 g (76%) of **6**. – ^{1}H NMR ($CDCl_3$): δ = 2.17 (s, 6H); 2.52 (s, 6H); 7.57–7.63 (m, 2H); 7.71–7.79 (m, 1H); 7.96–8.01 (m, 1H); 8.37–8.41 (m, 1H); 9.12–9.15 (m, 1H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 14.7, 15.4 (CH_3); 122.2, 127.9, 128.1, 130.7, 138.6, 152.0 (quinoline CH); 129.0, 131.8, 137.0, 137.3, 142.1, 151.6 (quat. C). – MS (EI), *m/z* (%): 366 (100) [$M^+ - Cl$]; 330 (42) [$M^+ - 2\,Cl - H$]; 248 (30) [$M^+ - TiCl_3$]. – $C_{18}H_{18}NTiCl_3$ (402.59): calcd. C 53.70, H 4.51, N 3.48; found C 53.51, H 4.69, N 3.27.

Trichloro[2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]-zirconium(IV) (**7**): 1.05 g (4.5 mmol) of zirconium(IV) chloride was suspended in 40 ml of toluene and at –10 °C a solution of 1.45 g (4.5 mmol) of **5** in 20 ml of toluene was added during 1 h to the suspension. It was subsequently warmed up to room temp. and stirred for 15 h. The solvent was removed under vacuum and the residue was extracted with 2 × 50 ml of CH_2Cl_2. Upon cooling **7** precipitated as pale yellow crystals (0.90 g). Concentration of the mother liquor gave another 0.54 g of **7** (total yield 72%). – ^{1}H NMR ($CDCl_3$): δ = 2.02 (s, 6H), 2.34 (s, 6H), 7.60–7.80 (m, 3H); 7.94–7.99 (m, 1H), 8.41–8.46 (m, 1H); 9.14–9.17 (m, 1H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 12.8, 13.5 (CH_3); 121.9, 127.9, 128.1, 132.2, 139.7, 151.7 (quinoline CH); 128.6, 129.1, 129.3, 131.4, 132.1, 151.4 (quat. C). – MS (EI), *m/z* (%): 445 (11) [M^+]; 409 (100) [$M^+ - HCl$]; 372 (10) [$M^+ - 2\,Cl - H$]; 248 (22) [$M^+ - ZrCl_3$]. – $C_{18}H_{18}Cl_3NZr$ (445.93): calcd. C 48.48, H 4.07, N 3.14; found C 47.91, H 4.22, N 3.05.

Table 1. Crystallographic data and parameters of the crystal structure determinations

compound	**6**	**7** · $CHCl_3$
formula	$C_{18}H_{18}Cl_3NTi$	$C_{19}H_{19}Cl_6NZr$
formula weight	402.6	564.3
crystal system	orthorhombic	monoclinic
space group	$P2_1nb$	$P2_1/c$
cell constants		
a [Å]	8.327 (4)	11.33 (1)
b [Å]	14.260 (7)	12.02 (1)
c [Å]	14.737 (7)	17.04 (2)
β [°]	90	108.38 (8)
V [Å^3]	1750	2201
Z	4	4
μ [cm^{-1}]	9.4	12.3
d [g cm^{-3}]	1.53	1.71
crystal size [mm]	0.3×0.3×0.8	0.2×0.3×0.5
$2\theta_{max}$; hkl range	65°; 0/+12, 0/+21, 0/+22 50°; -9/0, -16/0, -17/0	40°; 0/+10, 0/+11, -16/+15
no. of reflections measured	4780	2065
no. of unique reflections	4665	2065
no. of observed reflections	4377	1392
no. of parameters	281	251
R1	0.026	0.082
wR2	0.065	0.206
Δρ [e Å^{-3}]	-0.34/+0.34	-0.9/+1.0
temperature [°C]	-70	ambient

Crystal Structure Determination of **6** *and* **7**[11]: X-ray data of **6** were collected with a Siemens-Stoe AED2 diffractometer, those of **7** with a Syntex R3 diffractometer by using Mo-K_α radiation and the ω-scan technique. Additionally for **6**, Friedel pairs ($\bar{h}\bar{k}\bar{l}$) were collected up to 2Θ = 50°. The data of **6** were corrected for absorption (Ψ-scans, 0.93 < *T* < 1.00). An empirical absorption correction for **7** was not possible as the crystal quality was very poor.

The structures were solved by direct methods (SHELXS 86)[12] and refined by full-matrix least-squares techniques of all reflections based on F^2 (SHELXL 93)[12]. Non-hydrogen atoms were refined anisotropically. For **6** all hydrogen atoms were located in a difference Fourier map and refined isotropically. For **7** hydrogen atoms were included in calculated positions and only common isotropic temperature factors were refined. Crystallographic data are given in Table 1.

[1] J. Okuda, *Comments Inorg. Chem.* **1994**, *16*, 185–205.

[2] G. Erker, R. Aul, *Organometallics* **1988**, *7*, 2070–2072; J. C. Flores, J. C. W. Chien, M. D. Rausch, *Organometallics* **1994**, *13*, 4140–4142; R. L. Halterman, *Chem. Rev.* **1992**, *92*, 965; J. Christoffers, R. G. Bergman, *Angew. Chem.* **1995**, *107*, 2423–2425.

[3] J. W. Patasina, F. von Bolhuis, J. H. Teuben, *Angew. Chem.* **1987**, *99*, 342–343, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 330–331; G. Paolucci, R. D'Ippolito, C. Ye, C. Quin, J. Gräper, D. R. Fischer, *J. Organomet. Chem.* **1994**, *471*, 97–104; G. Paolucci, F. Ossola, M. Bettinelli, R. Sessoli, F. Benetollo, G. Bombieri, *Organometallics* **1994**, *13*, 1746–1750; G. Paolucci, R. D. Fischer, F. Benetollo, R. Seraglia, G. Bombieri, *J. Organomet. Chem.* **1991**, *412*, 327–342; J. R. van den Hende, P. B. Hitchcock, M. F. Lappert, T. A. Nile, *J. Organomet. Chem.* **1994**, *472*, 79–85; T. F. Wang, T. Y. Lee, Y. S. Wen, L. K. Liu, *J. Organomet. Chem.* **1991**, *403*, 353–358; T. F. Wang, T. Y. Lee, J. W. Chou, C. W. Ong, *J. Organomet. Chem.* **1991**, *423*, 31–38; T. F. Wang, Y. S. Wen, *J. Organomet. Chem.* **1992**, *439*, 155–162; W. A. Herrmann, R. Anwander, F. C. Munck, W. Scherer, *Chem. Ber.* **1993**, *126*, 331–337; P. Jutzi, J. Dahlhaus, M. O. Kristen, *J. Organomet. Chem.* **1993**, *450*, C1–C3; P. Jutzi, J. Dahlhaus, *Synthesis* **1993**, 684–686; P. Jutzi, M. O. Kristen, B. Neumann, H. G. Stammler, *Organometallics* **1994**, *13*, 3854–3861; P. Jutzi, M. Bangel, *J. Organomet. Chem.* **1994**, *480*, C18–C19; P. Jutzi, J. Kleimeier, *J. Organomet. Chem.* **1995**, *486*, 287–289; U. Siemeling, U. Vorfeld, B. Neumann, H. G. Stammler, *Chem. Ber.* **1995**, *128*, 481–485; U. Siemeling, B. Neumann, H. G. Stammler, *Z. Naturforsch., B: Chem. Sci.* **1994**, *49*, 683–686; K. Jonas, P. Klusmann, R. Goddard, *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 394–404.

[4] A tetraphenyl derivative of **1** was yielded in a triphenylphosphine induced depalladation reaction of a η^3-tetraphenylpentadienylquinoline–palladium complex see: M. Pfeffer, J. P. Sutter, *Organometallics* **1993**, *12*, 1167–1173.

[5] F. X. Kohl, P. Jutzi, *J. Organomet. Chem.* **1983**, *243*, 119–121.

[6] P. J. Black, M. C. Hefferman, *Austr. J. Chem.* **1964**, *17*, 558.

[7] A. Davison, P. E. Rakita, *Inorg. Chem.* **1970**, *9*, 289–294; A. Davison, P. E. Rakita, *J. Am. Chem. Soc.* **1968**, *90*, 4479–4480.

[8] L. M. Engelhardt, R. I. Papasergio, C. L. Raston, A. H. White, *Organometallics* **1984**, *3*, 18.

[9] N. W. Alcock, G. E. Toogood, M. G. H. Wallbridge, *Acta Cryst., C (Cr. Str. Comm.)* **1984**, *40*, 598.
[10] A. Martin, M. Mena, F. Palacios, *J. Organomet. Chem.* **1994**, *480*, C10–C11.
[11] Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-404751 for **6** and -404750 for **7**.
[12] G. M. Sheldrick, *SHELXS 86*, Univ. Göttingen **1986**; G. M. Sheldrick, *SHELXL 93*, Univ. Göttingen **1993**.

[95181]