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Synthesis and coordination behaviour of the new (8-quinolyl)cyclopentadienyl ligand

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Dedicated to Professor Günter Helmchen on the occasion of his 60th birthday.

Abstract

8-Bromoquinoline reacts with zincated cyclopentadienyl derivatives of Fe, Mn, and Re in the presence of bis(triphenylphosphine)palladium(0) to yield the corresponding 8-quinolylcyclopentadienyl metal complexes. Tricarbonyl[η^5-(8-quinolyl)-cyclopentadienyl]manganese(I) (**5**) and tricarbonyl[η^5-(8-quinolyl)cyclopentadienyl]rhenium(I) (**6**) eliminate CO upon irradiation to form dicarbonyl[η^5-(8-quinolyl)cyclopentadienyl]manganese(I) (**7**) and dicarbonyl[η^5-(8-quinolyl)cyclopentadienyl]rhenium(I) (**8**), respectively. The intensely coloured complexes **7** and **8** show solvatochromism, which has been investigated in more detail. Coordination of the quinolyl moiety in **7** and **8** could be proved by spectroscopy and by crystal structure determination.

Keywords: *N*-functionalized cyclopentadienyl ligands; Zincated cyclopentadienyl compounds; Palladium-catalyzed cross-coupling; Hemilabile ligands; Solvatochromism

1. Introduction

The cyclopentadienyl ligand, C_5H_5 (Cp), is a very versatile ligand and complexes are known with most metals of the periodic table. Functionalised Cp ligands where a donor group is connected to the Cp ring by a suitable spacer have been investigated intensively in the last decade [1]. In most cases the five-membered cycle binds strongly whereas the donor atom (e.g. N, O, P) interacts only if necessary. This concept of so-called hemilabile ligands [2] has been used for stabilisation of reactive intermediates or for catalytic applications. We have synthesized *N*-functionalised cyclopentadienes like **1a**, where the C_2 spacer and the nitrogen atom are embedded in an aromatic system [3]. This ligand has a predefined geometry and prefers to form half-sandwich chelate complexes. Whereas the synthetic route shown in Scheme 1 yields the tetramethylcyclopentadiene derivative **1a** as a pure compound in large quantity, it was not possible to obtain the cyclopentadiene derivative **2a** in good yield and sufficient purity by this route.

Therefore we tried to synthesize the desired cyclopentadienyl ligand **2b** directly in a metal complex. Due to the absence of any methyl groups in **2b**, rotation about the C–C single bond is easier and the ligand is less electron rich, compared to the tetramethyl derivative **1b**. These changes in steric and electronic situation should influence the properties of the resulting complexes.

2. Results and discussion

The reaction of 8-lithioquinoline with cyclopent-2-enone according to the procedure in Scheme 1 led to the formation of up to 50% yield of **2a** as could be shown by GC/MS analysis. However, the isolation of **2a** is difficult, and neither distillation nor column chromatography led to pure **2a** in acceptable yield.

Palladium-catalyzed cross-coupling is described to be an effective method in the synthesis of ring substituted cyclopentadienyl complexes [4] and should also be applicable to the formation of the desired ligand **2b**.

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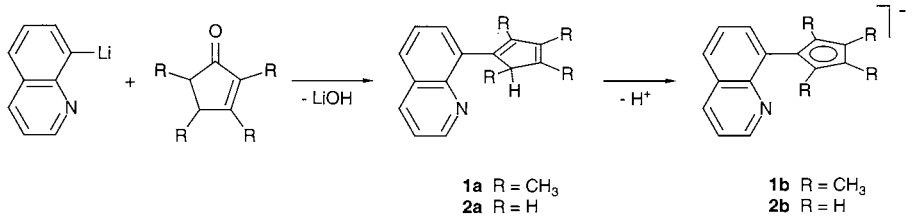


Scheme 1. Synthesis of quinolyl substituted cyclopentadienes and -dienids.

2.1. Quinolyl substituted ferrocenes

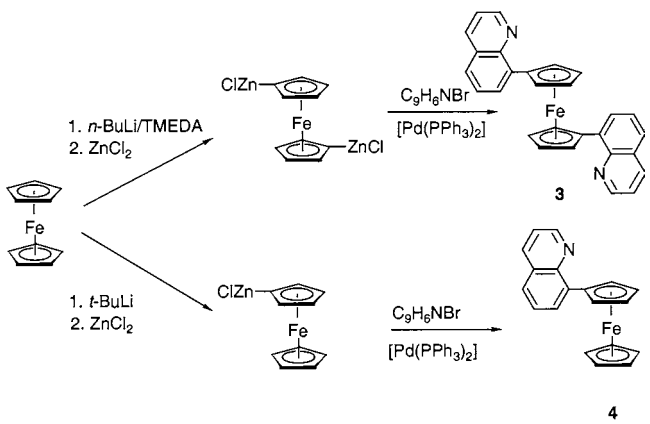
Ferrocene can easily be dimetallated by treatment with *n*-BuLi–TMEDA [5]. Reaction of the resulting 1,1′-dilithioferrocene with zinc chloride yields dizincated ferrocene which was then directly coupled with 8-bromoquinoline in the presence of 2.5 mol% of $Pd(PPh_3)_2$. The latter was prepared from $Pd(PPh_3)_2Cl_2$ by reduction using two equivalents of $(iso\text{-}C_4H_9)_2AlH$ (Dibal-H) [4c]. After 3 days at room temperature the reaction mixture was quenched with aqueous NaOH and bis-[η^5-(8-quinolyl)cyclopentadienyl]iron(II) (**3**) could be obtained as a red, crystalline product in 62% yield (Scheme 2).

The ^{1}H-NMR spectrum of **3** shows for the Cp protons two pseudotriplets which are typical for the AA′BB′ spin systems in monosubstituted cyclopentadienyl derivatives. Therefore the quinolyl moieties are lying in one mirror plane orthogonal to the Cp rings (C_{2v} or C_{2h} symmetry for **3**) or they are rotating so fast, that the NMR experiment shows only two resonances for the eight ring protons. This is still the case at –110°C in a 500 MHz ^{1}H-NMR spectrum. However, a different arrangement is found in the solid state. Crystals of **3** could be obtained from a CH_2Cl_2 solution at room temperature. The single-crystal structure determination shows that the angles of the cyclopentadienyl and the quinoline planes are 21.0 and 24.8°, respectively. The ferrocenyl geometry is eclipsed (ca. 3.3° deviation), and the two quinoline groups lie on the same side of the molecule. They build an angle of 4.8° and the distance between the planes ranges from 3.14 to 3.55 Å.The average distance (3.358 Å) is in the same range as in the graphite lattice (3.354 Å) [6]. Related arrangements with parallel aromatic groups were found in 1,1′,3,3′-tetraphenylferrocene [7] but not in bis-1,1′-(9-antracenyl)ferrocene [8]. As expected for an 18 VE ferrocene derivative no coordination of the nitrogen atoms to the metal is observed in **3**. As the symmetry of **3** in the solid state is not observed in the NMR spectra, a rapid rotation of the quinoline moiety around the C–C single bond must take place in solution, even at low temperatures (Fig. 1).

The synthesis of a ferrocene with only one quinolyl group has also been realised. Treatment of ferrocene with 0.8 equivalents of *t*-BuLi yields the monolithiated derivative [9]. After the transformation to the chlorozinc compound we used palladium-catalyzed coupling with 8-bromoquinoline to obtain η^5-cyclopentadienyl[η^5-(8-quinolyl)cyclopentadienyl]iron(II) (**4**) in 77% yield as a red viscous oil which became solid after some time. The synthesis of a derivative of **4** [(4-methyl-8-quinolyl)ferrocene] in 28% yield by a different route has been described before [10].

2.2. Quinolyl substituted cyclopentadienyl manganese and rhenium complexes

Palladium-catalyzed cross-coupling reactions leading to substituted $CpMn(CO)_3$ or $CpRe(CO)_3$ complexes are described in the literature [11]. The halogenated



Scheme 2. Preparation of the quinolyl substituted ferrocenes **3** and **4**.

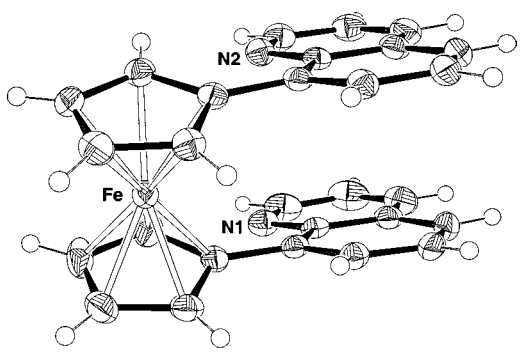
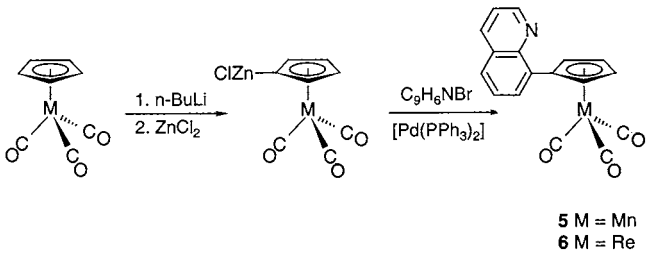


Fig. 1. Solid state structure of **3**.



Scheme 3. Preparation of the manganese and rhenium complexes **5** and **6**.

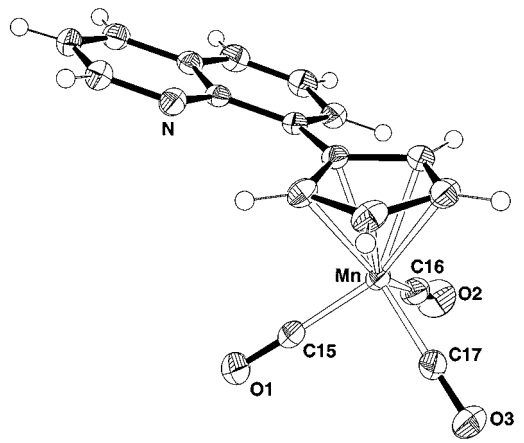
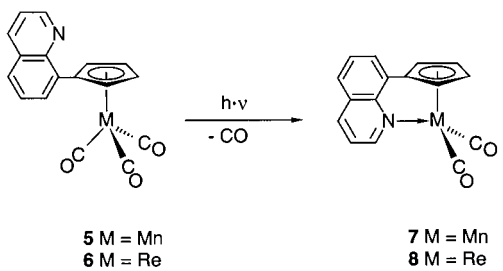


Fig. 2. Solid state structure of **5**, the structure of the Re complex **6** is very similar. Selected bond lengths (Å): (a) **5**, Mn–C_{Cp} 2.14–2.17; Mn–C_{CO} 1.79–1.80; C–O 1.14–1.15. (b) **6**, Re–C_{Cp} 2.30–2.33; Re–C_{CO} 1.91–1.92; C–O 1.14.



Scheme 4. Synthesis of **7** and **8** by photoinduced substitution of one CO ligand in **5** and **6**.

cyclopentadienyl metal compounds have been used as the aryl halide component which reacts with an organo tin molecule in a Stille coupling. However, the transformation of $CpMn(CO)_3$ and $CpRe(CO)_3$ into the cyclopentadienyl zinc derivatives in order to use them in a palladium-catalyzed cross-coupling has not been described before.

The lithiation of $CpMn(CO)_3$ and $CpRe(CO)_3$ was carried out by adding *n*-BuLi to a solution of the respective metal complex [12]. Addition of one equivalent of $ZnCl_2$ leads to the zincated complexes, which were coupled with 8-bromoquinoline yielding the half-sandwich complexes **5** and **6**, respectively (Scheme 3).

The ^{1}H-NMR spectra of **5** and **6** show for the Cp protons two pseudotriplets as in the spectra of **3** or **4** indicating a C_s symmetry on the NMR time scale. The FT-IR spectra in the carbonyl region are very similar to those of the educt complexes $CpMn(CO)_3$ and $CpRe(CO)_3$, showing two intensive absorptions.

Crystals of **5** could be obtained from a toluene solution at −28°C, those of **6** from a 1:1 mixture of hexane and toluene at −28°C. As expected no coordination of the nitrogen atom to the metal is found in both complexes. The dihedral angle between the quinolyl moiety (max. deviation from planarity 0.013 Å for **5** and 0.016 Å for **6**) and the Cp ring is ca. 23°. This allows a good conjugation of the π-systems. The distances between the metal and the Cp carbon atoms are very similar to the values found for the corresponding $CpMn(CO)_3$ and $CpRe(CO)_3$ [13] (Fig. 2).

Photoinduced substitution of CO in metalcarbonyl complexes is an effective route for the synthesis of new and sometimes reactive compounds. Photolability of one CO ligand is described for $CpMn(CO)_3$ and $CpRe(CO)_3$ [14]. Therefore, CO elimination should also take place by irradiation of **5** and **6** with visible or ultraviolet light. The saturation of the resulting 16 valence electrons fragments should occur by intramolecular coordination of the *N*-function of the quinolyl moiety. Indeed irradiation of **5** in a hexane/toluene mixture with visible light leads to a colour change from yellow to deep blue and dicarbonyl[η^5-(8-quinolyl)cyclopentadienyl]manganese(I) (**7**) can be isolated in 97% yield as a brown-red solid.

Rhenium carbonyl complexes normally are more stable towards photochemical replacement of a CO ligand [14]. Hence, visible light does not induce carbonyl elimination. However, the synthesis of dicarbonyl[η^5-(8-quinolyl)cyclopentadienyl]rhenium(I) (**8**) is possible by irradiation of **6** with a high pressure mercury lamp in a quartz schlenk tube. Red crystals of **8** deposit from the red reaction solution if a solvent mixture hexane: toluene (30:1) is used. By this procedure **8** can be isolated in 75% yield (Scheme 4).

The FT-IR spectra of **7** and **8** show a significant shift of the two CO streching frequencies to lower wavenumbers compared to the tricarbonylcomplexes **5** and **6**. Due to the strong donor ability of the coordinating quinoline, the metal to CO back-bonding is increased which results in a weakening of the C–O bonds. The ^{1}H-NMR spectra show the two pseudotriplets for the cyclopentadienyl protons as in the other complexes of **2b**. The signals of the quinolyl protons in the dicarbonyl complexes (**7**, **8**) and in the tricarbonyl complexes (**5**, **6**) are very similar. Hence, NMR spectroscopy gives no evidence for the interaction of the nitrogen atom with the metal centre.

The coordination of the quinolyl moiety in **7** and **8** is obvious because of the dramatic change of colour when

going from the tricarbonyl compounds **5** and **6** to the dicarbonyl complexes **7** and **8**. Whereas solutions of **5** and **6** are only weakly yellow, those of **7** and **8** show intensive colours. In addition we observed solvatochromism, e.g. **7** is blue in hexane or CCl_4 but purple in CH_2Cl_2. Therefore, we examined the visible spectra in solvents of different polarity (Table 1).

The complexes **7** and **8** show high extinction coefficients in all solvents and hypsochromic (blue) shifts when going to solvents of higher polarity. If the direction of the dipole moment in the ground state is different from the excited state, the transition energy becomes larger in polar solvents leading to the observed solvatochromism [15]. This behaviour is typical for a MLCT $d \rightarrow \pi^*$ exitation. The relation of the transition energy and the solution polarity is described for non-specific interactions by the equation:

$$\Delta\chi = S'P + W$$

where $\Delta\chi$ is the transition energy; S' is a measure of the solvent polarity; P describes the magnitude of solvatochromic shifts; and W is the value of $\Delta\chi$ when S' is zero [16–18]. Values of S' have been established by Drago et al. [17]. We determined the parameters $P = 1.16$, $W = 15.4$ cm^{-1} (corresponding to 650 nm) for **7** and $P = 1.79$, $W = 15.6$ cm^{-1} (corresponding to 641 nm) for **8** by plotting $\Delta\chi$ against S' and approximation of the experimental values by linear regression. The values of P are similar to those found for CpMn(CO)$_2$(pyridine) and CpRe(CO)$_2$(pyridine), whereas the values of W are lower than those of the corresponding pyridine complexes indicating a lower excitation energy in **7** and **8** [18,19].

Table 1
Visible absorption bands of **7** and **8** in dependence of the used solvent [a]

Solvent	7	8
CCl_4	596 (5421)	563 (4421); 515 (4054)
Toluene	575 (4657)	538 (5052); shoulder at 500 (4759)
CH_2Cl_2	549 (4283)	498 (4758)
Acetone	544 (4145)	494 (4541)
CH_3CN	535 (3835)	484 (4221)

[a] λ_{max} [nm] (ε [l mol^{-1} cm^{-1}]).

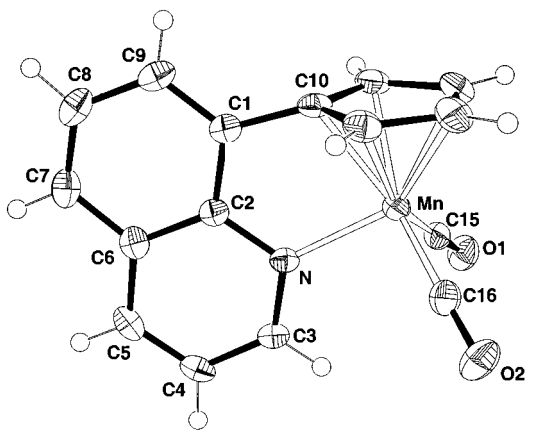


Fig. 3. Solid state structure of **7**, the structure of the Re complex **8** is very similar. Selected bond lengths (Å) and angles (°): (a) **7**, Mn–N 2.014(1); Mn–C_{Cp} 2.12–2.14; Mn–C_{CO} 1.78; C–O 1.16; C3–N–Mn 125.8(1); C2–N–C3 117.1(2); C2–N–Mn 117.0(1); C2–C1–C10 114.7(2); C9–C1–C10 126.2(2). (b) **8**, Re–N 2.123(3); Re–Ccp 2.26–2.30; Re–C_{CO} 1.89–1.90; C–O 1.15–1.18; C3–N–Re 125.6(3); C2–N–C3 117.7(3); C2–N–Re 116.7(2); C2–C1–C10 117.5(3); C9–C1–C10 123.4(4).

The chelating binding of the ligand **2b** was finally proved by two single-crystal structure determinations. Crystals of **7** were obtained from a saturated hexane solution at room temperature. Those of **8** developed during the irradiation of a solution of **6** in toluene. The metal-nitrogen distances are with 2.014(1) Å (for **7**) and 2.123(3) Å (for **8**) about 0.1 Å shorter then those found for related compounds with alkylamino donors and flexible C_2 spacers [20]. The metal atoms are placed 1.759 Å (for **7**) and 1.932 Å (for **8**) below the five-membered ring, a little bit closer than in the related tricarbonyl complexes **5** (1.772 Å) and **6** (1.965 Å). The nearly planar quinolyl moiety (max. deviation from planarity 0.033 Å for **7** and 0.043 Å for **8**) forms a dihedral angle of ca. 64° with the Cp ring. The C1 atom in **7** and **8** lies not in the cyclopentadienyl plane but is shifted to the metal centre by 0.34 Å. The angles around the nitrogen atom in both complexes sum up to 360°, which indicates that the lone pair of the nitrogen atom is pointing directly to the metal centre (Fig. 3).

3. Conclusion

The reliable route for the synthesis of quinolyl functionalised cyclopentadienes like **1a** is not applicable for the less substituted derivative **2a**. However, we showed that the desired cyclopentadienyl ligand **2b** can be built up in high yields by palladium-catalyzed cross-coupling reactions of zincated Cp complexes with 8-bromoquinoline. In the resulting metal complexes **3**, **4**, **5** and **6** the non-coordinating quinoline groups have the tendency to lie coplanar to the bonded Cp rings. The manganese and rhenium tricarbonyl complexes **5** and **6** eliminate CO upon irradiation, the resulting 16 valence electrons compounds are stabilised by intramolecular coordination after rotation of the quinolyl moiety. The interaction of the nitrogen donor with the metal centre in **7** and **8** leads to strong charge transfer absorptions. In our present investigations we try to bind a second metal atom to the non-coordinating nitrogen atom in compounds like **3** and **4**.

4. Experimental

4.1. General remarks

All experiments were carried out under an atmosphere of dry argon. Solvents were dried by using standard procedures and distilled prior to use. 1,1′-dilithioferrocene-2/3-TMEDA [21], 8-bromoquinoline [22], and tricarbonylcyclopentadienylrhenium [23] were prepared according to the literature procedures. $ZnCl_2$ was dried by refluxing in thionylchloride until no evolution of gas was observed [24]. All other reagents were used as purchased. — NMR: Bruker DRX 200 (200.1 and 50.3 MHz for ^{1}H- and ^{13}C-NMR, respectively), the ^{1}H-NMR spectra were calibrated using signals of residual protons from the solvent referenced to $SiMe_4$. The ^{13}C spectral chemical shifts are reported relative to the ^{13}C triplet ($CDCl_3$) at 77.0 ppm. — IR: Bruker IFS 28. — UV–vis: Perkin Elmer Lambda 12. — MS: VG Micromass 7070 H.

4.2. bis-[η^5-(8-Quinolyl)cyclopentadienyl]iron(II) (**3**)

A suspension of 5.18 g (18.8 mmol) of 1,1′-dilithioferrocene-2/3-TMEDA in 100 ml THF was cooled to 0°C and a solution of 5.13 g (37.6 mmol) of $ZnCl_2$ in 80 ml THF was added. The resulting orange slurry was allowed to stir over 1.5 h at room temperature (r.t.). In a separate flask 0.66 g (0.94 mmol) of $(PPh_3)_2PdCl_2$ were suspended in 30 ml THF, to which were added dropwise 1.9 ml (1.9 mmol) of a 1.0 M solution of Dibal-H in THF. This gave a homogeneous dark solution of $(PPh_3)_2Pd$ which was added to the 1,1′-bis(chlorozinc)ferrocene via cannula. 7.8 g (37.5 mmol) of 8-bromoquinoline were added tropwise and the resulting suspension was stirred for 3 days in which its colour changed from brown to red. The reaction mixture was quenched by adding a solution of 30 g (0.75 mol) of NaOH in 100 ml water. After 2 h of stirring the organic layer was separated from the water fraction, which was extracted twice with 100 ml of CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated until precipitation of fine red crystals occurred. The crystals were collected by filtration, washed twice with 100 ml hexane, and dried in vacuum; yield 5.09 g (11.6 mmol, 62%), m.p. 175°C. ^{1}H-NMR ($CDCl_3$): $\delta = 4.35$ (pt, 2H, Cp CH); 5.15 (pt, 2H, Cp CH); 7.12 (dd, ^3J(H, H) = 7.5 Hz, ^3J(H, H) = 8.0 Hz, 1H, H^6); 7.24 (dd, ^3J(H^3, H^2) = 4.1 Hz, ^3J(H^3, H^4) = 8.3 Hz, 1H, H^3); 7.48 (dd, ^3J(H, H) = 8.1 Hz, ^4J(H, H) = 1.4 Hz, 1H, H^5 or H^7); 7.70 (dd, ^3J(H, H) = 7.3 Hz, ^3J(H, H) = 1.5 Hz, 1H, H^5 or H^7); 7.98 (dd, ^3J(H^4, H^3) = 8.3 Hz, ^3J(H^4, H^2) = 1.9 Hz, 1H, H^4); 8.78 (dd, ^3J(H^2, H^3) = 4.1 Hz, ^3J(H^2, H^4) = 1.9 Hz, 1H, H^2). ^{13}C {^{1}H}-NMR ($CDCl_3$): $\delta = 70.4$, 72.1 (CH_{Cp}); 84.3 (quart. C_{Cp}); 120.4, 125.3, 125.6, 128.8, 135.9, 148.7 ($CH_{quinoline}$); 128.4, 136.7, 146.1 (quart. $C_{quinoline}$). MS (EI), m/z (%): 440 (100) [M$^+$]; 248 (98) [M$^+$ − Cp^Q]; 192 (30) [Cp^{Q+}]. $C_{28}H_{20}N_2Fe$ (440.33): Calc. C 76.37, H 4.57, N 6.36; Found C 75.90, H 4.71, N 6.37.

4.3. η^5-Cyclopentadienyl[η^5-(8-quinolyl)-cyclopentadienyl]iron(II) (**4**)

To a solution of 1.50 g (8.1 mmol) of ferrocene in 30 ml THF at −40°C were added 5.5 ml (6.7 mmol) of a 1.26 M solution of *t*-BuLi in pentane. After stirring for 2 h at r.t. a solution of 884 mg (6.5 mmol) of $ZnCl_2$ chloride was added via cannula and the resulting solution of ferrocenylzinc chloride was stirred for an additional hour. A solution of $(PPh_3)_2Pd$ (prepared from 235 mg (0.35 mmol) of $(PPh_3)_2PdCl_2$ and 0.70 mmol of Dibal-H as described above) was added to the red solution of ferrocenylzinc chloride via cannula. A total of 1.25 g (6.9 mmol) of 8-bromoquinoline was added dropwise and the dark solution was stirred for 5 days. The reaction mixture was quenched by adding a solution of 5 g (0.13 mol) of NaOH in 30 ml water. After 1 h of stirring the organic layer was separated from the water fraction, which was extracted once with 100 ml of CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to give a red oil. This oil was chromatographed on Al_2O_3/5% H_2O with hexane to give 0.78 g (4.2 mmol) of ferrocene, followed by toluene as eluent to give **4** as a red viscous oil which became solid after stored at room temperature for some weeks; yield 0.93 g (3.0 mmol, 77% based on reacted ferrocene (3.9 mmol)). ^{1}H-NMR ($CDCl_3$): $\delta = 4.07$ (s, 5H, C_5H_5); 4.43 (pt, 2H, quinoline-Cp CH); 5.19 (pt, 2H, quinoline-Cp CH); 7.38 (dd, ^3J(H^3, H^2) = 4.1 Hz, ^3J(H^3, H^4) = 8.3 Hz, 1H, H^3); 7.51 (dd, ^3J(H, H) = 7.3 Hz, ^3J(H, H) = 8.1 Hz, 1H, H^6); 7.69 (dd, ^3J(H, H) = 8.1 Hz, ^4J(H, H) = 1.5 Hz, 1H, H^5 or H^7); 8.06 (dd, ^3J(H, H) = 7.3 Hz, ^3J(H, H) = 1.5 Hz, 1H, H^5 or H^7); 8.15 (dd, ^3J(H^4, H^3) = 8.3 Hz, ^3J(H^4, H^2) = 1.8 Hz, 1H, H^4); 8.98 (dd, ^3J(H^2, H^3) = 4.1 Hz, ^3J(H^2, H^4) = 1.8 Hz, 1H, H^2). ^{13}C {^{1}H}-NMR ($CDCl_3$): $\delta = 69.6$ (CH_{Cp}); 68.8, 70.9 ($CH_{Cp\text{-}quinoline}$); 83.4 (quart. $C_{Cp\text{-}quinoline}$); 120.7, 125.8, 126.0, 129.0, 136.2, 149.3 ($CH_{quinoline}$); 128.7, 138.2, 146.2 (quart. $C_{quinoline}$). MS (EI), m/z (%): 313 (66) [M$^+$]; 248 (100) [M$^+$ − Cp]; 192 (44) [Cp^{Q+}]; 121 (38) [M$^+$ − Cp^Q]. $C_{19}H_{15}NFe$ (313.18): Calc. C 72.87, H 4.83, N 4.47; Found C 72.85, H 4.89, N 4.51.

4.4. Tricarbonyl[η^5-(8-quinolyl)cyclopentadienyl]-manganese(I) (**5**)

All manipulations were carried out with protection against light. To a solution of 1.00 g (4.9 mmol) of tricarbonylcyclopentadienylmanganese(I) in 50 ml THF at −78°C were added 2.2 ml (5.5 mmol) of a 2.5 M solution of *n*-BuLi in hexane. After stirring for 1 h a

solution of 685 mg (5.0 mmol) of $ZnCl_2$ in 25 ml THF was added via cannula and the resulting solution of $(C_5H_4ZnCl)Mn(CO)_3$ was stirred for an additional hour. A solution of $(PPh_3)_2Pd$ (prepared from 175 mg (0.25 mmol) of $(PPh_3)_2PdCl_2$ and 0.50 mmol of Dibal-H as described above) was added to the yellow solution of $(C_5H_4ZnCl)Mn(CO)_3$ via cannula. A total of 1.04 g (5.0 mmol) of 8-bromoquinoline was added dropwise and the dark solution was allowed to warm to r.t. and stirred for 5 days. The reaction mixture was quenched by adding a solution of 10 g (0.25 mol) of NaOH in 50 ml water. After 1.5 h of stirring the organic layer was separated from the water fraction, which was extracted twice with THF. The combined organic fractions were dried over $MgSO_4$, filtered, and evaporated. Column chromatography on Al_2O_3/5% H_2O using toluene as eluent yielded 1.49 g (4.50 mmol, 92%) of **5** as a yellow, lightsensitive solid. IR (toluene): $\tilde{\nu}$(CO) = 1934 (s), 2018 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 4.88 (pt, 2H, Cp CH); 5.86 (pt, 2H, Cp CH); 7.44 (dd, $^3J(H^3, H^2)$ = 4.1 Hz, $^3J(H^3, H^4)$ = 8.3 Hz, 1H, H^3); 7.52 (dd, ^3J(H, H) = 7.4 Hz, ^3J(H, H) = 8.1 Hz, 1H, H^6); 7.77 (dd, ^3J(H, H) = 8.2 Hz, ^4J(H, H) = 1.4 Hz, 1H, H^5 or H^7); 7.87 (dd, ^3J(H, H) = 7.3 Hz, ^3J(H, H) = 1.5 Hz, 1H, H^5 or H^7); 8.17 (dd, $^3J(H^4, H^3)$ = 8.3 Hz, $^3J(H^4, H^2)$ = 1.8 Hz, 1H, H^4); 8.98 (dd, $^3J(H^2, H^3)$ = 4.1 Hz, $^3J(H^2, H^4)$ = 1.8 Hz, 1H, H^2). ^{13}C {^{1}H}-NMR ($CDCl_3$, 50 MHz) δ = 81.5, 86.7 (CH_{Cp}); 99.5 (quart. C_{Cp}); 121.2, 125.9, 128.1, 128.7, 136.3, 149.5 ($CH_{quinoline}$); 128.6, 131.5, 145.7 (quart. $C_{quinoline}$); 225.3 (CO). MS (EI), m/z (%): 331 (0.4) [M^+]; 303 (21) [$M^+ - CO$]; 247 (100) [$M^+ - 3$ CO]; 191 (27) [$M^+ - Mn - 3$ CO–H]; 123.5 (14) [$M^{2+} - 3$ CO], 55 (42) [Mn^+]. $C_{17}H_{10}NO_3Mn$ (331.21): Calc. C 61.65, H 3.04, N 4.23; Found C 61.91, H 3.44, N 4.00.

4.5. Tricarbonyl[η^5-(8-quinolyl)cyclopentadienyl]-rhenium(I) (6)

The procedure is analogous to that for **5** except that protection against light is not necessary. Scale: 1.2 g (3.6 mmol) of tricarbonylcyclopentadienylrhenium(I), 1.6 ml (4.0 mmol) of a 2.5 M solution of *n*-BuLi in hexane, 0.5 g (3.7 mmol) of $ZnCl_2$, 140 mg (0.2 mmol) of $(PPh_3)_2PdCl_2$, 0.4 mmol of Dibal-H, 0.75 g (3.6 mmol) of 8-bromoquinoline.

The reaction mixture was quenched with 8 g (0.2 mol) of NaOH in 40 ml water, the water fraction was extracted twice with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, concentrated and filtered over Al_2O_3/5% H_2O. Unreacted $CpRe(CO)_3$ was removed by sublimation at 100°C and 10^{-2} mbar. Column chromatography on Al_2O_3/5% H_2O using toluene as eluent yielded 1.29 g (2.79 mmol, 78%) of **6** as a pale yellow solid, m.p. 97°C. IR (toluene): $\tilde{\nu}$(CO) = 1926 (s), 2021 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 5.47 (pt, 2H, Cp CH); 6.39 (pt, 2H, Cp CH); 7.44 (dd, $^3J(H^3, H^2)$ = 4.2 Hz, $^3J(H^3, H^4)$ = 8.3 Hz, 1H, H^3); 7.50 (dd, ^3J(H, H) = 7.2 Hz, ^3J(H, H) = 8.1 Hz, 1H, H^6); 7.78 (dd, ^3J(H, H) = 8.2 Hz, ^4J(H, H) = 1.4 Hz, 1H, H^5 or H^7); 7.86 (dd, ^3J(H, H) = 7.2 Hz, ^3J(H, H) = 1.4 Hz, 1H, H^5 or H^7); 8.16 (dd, $^3J(H^4, H^3)$ = 8.3 Hz, $^3J(H^4, H^2)$ = 1.8 Hz, 1H, H^4); 8.98 (dd, $^3J(H^2, H^3)$ = 4.2 Hz, $^3J(H^2, H^4)$ = 1.8 Hz, 1H, H^2). ^{13}C {^{1}H}-NMR ($CDCl_3$): δ = 83.3, 88.3, (CH_{Cp}); 103.5 (quart. C_{Cp}); 121.3, 126.0, 128.4, 129.2, 136.3, 149.9 ($CH_{quinoline}$); 128.6, 130.8, 145.4 (quart. $C_{quinoline}$); 194.7 (CO). MS (EI), m/z (%): 463 (10) [M^+]; 435 (73) [$M^+ - CO$]; 407 (100) [$M^+ - 2$ CO]; 379 (72) [$M^+ - 3$ CO]; 353 (30); 189.5 (15) [$M^{2+} - 3$ CO]. $C_{17}H_{10}NO_3Re$ (462.48): Calc. C 44.06; H 2.18; N 3.02; Found C 44.47; H 2.56; N 3.07.

4.6. Dicarbonyl[η^5-(8-quinolyl)cyclopentadienyl]-manganese(I) (7)

A total of 210 mg (0.63 mmol) of tricarbonyl[η^5-(8-chinolyl)cyclopentadienyl]manganese(I) (**5**) was dissolved in a mixture of 25 ml of hexane and 25 ml of toluene. The yellow solution was irridiated for 4 h in which the colour changed to dark blue. The solution was concentrated in vacuum and purified by column chromatography on Al_2O_3/5% H_2O using toluene as eluent. Removal of the solvent yielded 186 mg (0.61 mmol, 97%) of **7** as a brown–red powder, m.p. 220°C. IR (toluene): $\tilde{\nu}$(CO) = 1864 (s), 1928 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 3.98 (pt, 2H, Cp CH); 5.59 (pt, 2H, Cp CH); 6.94 (dd, $^3J(H^3, H^2)$ = 5.2 Hz, $^3J(H^3, H^4)$ = 8.4 Hz, 1H, H^3); 7.48 (dd, ^3J(H, H) = 6.9 Hz, ^3J(H, H) = 8.1 Hz, 1H, H^6); 7.60 (dd, ^3J(H, H) = 8.1 Hz, ^4J(H, H) = 1.4 Hz, 1H, H^5 or H^7); 7.73 (dd, ^3J(H, H) = 6.8 Hz, ^3J(H, H) = 1.4 Hz, 1H, H^5 or H^7); 7.80 (dd, $^3J(H^4, H^3)$ = 8.4 Hz, $^3J(H^4, H^2)$ = 1.2 Hz, 1H, H^4); 8.58 (dd, $^3J(H^2, H^3)$ = 5.2 Hz, $^3J(H^2, H^4)$ = 1.2 Hz, 1H, H^2). ^{13}C {^{1}H}-NMR ($CDCl_3$): δ = 78.2, 83.2 (CH_{Cp}); 117.3 (quart. C_{Cp}); 121.6, 127.1 (2C), 128.3, 134.4, 157.4 ($CH_{quinoline}$); 128.1, 134.7, 158.6 (quart. $C_{quinoline}$); 234.8 (CO). MS (EI), m/z (%): 303 (10) [M^+]; 247 (100) [$M^+ - 2$ CO]; 191 (15) [$Cp^{Q+} - H$]; 55 (29) [Mn^+]. $C_{16}H_{10}NO_2Mn$ (303.20): Calc. C 63.38; H 3.32; N 4.62; Found C 63.59; H 3.56; N 4.56.

4.7. Dicarbonyl[η^5-(8-quinolyl)cyclopentadienyl]-rhenium(I) (8)

In a quartz-Schlenktube 110 mg (0.25 mmol) of tricarbonyl[η^5-(8-chinolyl)cyclopentadienyl]rhenium(I) (**6**) were dissolved in 2 ml of toluene. To this mixture 60 ml of hexane were added and the resulting colourless solution was irradiated for 5 days (150 W high-pressure mercury lamp). The colour turned to red and small red

Table 2
Crystal data and experimental details of the X-ray structure determinations

Compound	**3**	**5**	**6**	**7**	**8**
Empirical formula	$C_{28}H_{20}FeN_2$	$C_{17}H_{10}MnNO_3$	$C_{17}H_{10}NO_3Re$	$C_{16}H_{10}MnNO_2$	$C_{16}H_{10}NO_2Re$
Formula weight	440.31	331.20	462.46	303.19	434.45
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions					
a (Å)	13.6189(9)	7.0772(1)	6.7908(7)	9.2835(7)	9.3386(2)
b (Å)	9.8659(6)	9.6861(1)	18.1739(19)	14.2568(10)	14.5863(3)
c (Å)	14.5812(10)	10.2255(1)	11.2443(12)	9.6322(7)	9.5749(2)
α (°)	90	95.440(1)	90	90	90
β (°)	96.016(1)	93.963(1)	101.422(2)	96.409(1)	97.210(2)
γ (°)	90	99.222(1)	90	90	90
V (Å^3)	1948.4(2)	686.247(14)	1360.2(2)	1266.88(16)	1293.94(5)
Z	4	2	4	4	4
D_{calc} (mg m^{-3})	1.501	1.603	2.258	1.590	2.230
Absorption coefficient (mm^{-1})	0.793	0.973	8.945	1.040	9.390
F(000)	912	336	872	616	816
Crystal size (mm)	$0.22\times0.22\times0.05$	$0.41\times0.32\times0.25$	$0.45\times0.45\times0.25$	$0.22\times0.22\times0.16$	$0.29\times0.25\times0.03$
Theta range for data collection (°)	1.50–26.39	2.01–28.30	2.16–28.37	2.56–28.31	2.56–28.31
Index ranges	$-17\le h\le16$, $0\le k\le12$, $0\le l\le18$	$-9\le h\le9$, $-12\le k\le12$, $0\le l\le13$	$-8\le h\le8$, $0\le k\le23$, $0\le l\le14$	$-12\le h\le12$, $0\le k\le18$, $0\le l\le12$	$-12\le h\le12$, $0\le k\le19$, $0\le l\le12$
Reflections collected	12002	9126	9141	8621	20829
Independent reflections	3978 ($R_{int}=0.039$)	3328 ($R_{int}=0.025$)	3264 ($R_{int}=0.033$)	3039 ($R_{int}=0.027$)	3225 ($R_{int}=0.062$)
Max. and min. transmission	0.908 and 0.794	0.7930 and 0.6911	0.215 and 0.115	0.928 and 0.695	0.928 and 0.570
Refined parameters	360	239	239	221	221
Goodness-of-fit on F^2	0.954	1.087	1.145	1.031	1.070
Final R indices [I$>2\sigma$(I)]	$R_1=0.0368$	$R_1=0.0281$	$R_1=0.0285$	$R_1=0.0329$	$R_1=0.0286$
R indices (all data)	$wR_2=0.0926$	$wR_2=0.0813$	$wR_2=0.0758$	$wR_2=0.0942$	$wR_2=0.0862$
Largest difference peak and hole (e Å^{-3})	0.531 and −0.295	0.501 and −0.191	3.063 and −1.094	0.591 and −0.310	2.289 and −2.154

crystals precipitated. The solution was removed with a syringe and the red solid was purified by column chromatography on Al_2O_3/5% H_2O using toluene as eluent. Removal of the solvent yielded 78 mg (0.18 mmol, 75%) of **8** as a red powder, m.p. 285°C. IR (toluene) (CO) = 1849 (s), 1913 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 5.19 (pt, 2H, Cp CH); 5.71 (pt, 2H, Cp CH); 7.01 (dd, $^3J(H^3, H^2)$ = 5.2 Hz, $^3J(H^3, H^4)$ = 8.4 Hz, 1H, H^3); 7.50 (dd, ^3J(H, H) = 7.0 Hz, ^3J(H, H) = 8.2 Hz, 1H, H^6); 7.63 (dd, ^3J(H, H) = 8.3 Hz, ^4J(H, H) = 1.5 Hz, 1H, H^5 or H^7); 7.75 (dd, ^3J(H, H) = 6.9 Hz, ^3J(H, H) = 1.5 Hz, 1H, H^5 or H^7); 7.95 (dd, $^3J(H^4, H^3)$ = 8.5 Hz, $^3J(H^4, H^2)$ = 1.4 Hz, 1H, H^4); 9.33 (dd, $^3J(H^2, H^3)$ = 5.2 Hz, $^3J(H^2, H^4)$ = 1.4 Hz, 1H, H^2). ^{13}C {^{1}H}-NMR ($CDCl_3$): δ = 76.8, 82.3 (CH_{Cp}); 117.2 (quart. C_{Cp}); 123.3, 127.6, 127.8, 130.6, 134.7, 160.6 ($CH_{quinoline}$); 130.0, 133.0, 162.0 (quart. $C_{quinoline}$); 204.4 (CO). MS (EI), m/z (%): 435 (85) [M^+]; 407 (97) [M^+ − CO]; 379 (100) [M^+ − 2 CO]; 353 (33) [M^+ − 2 CO–C_2H_2]; 189.5 (27) [M^{2+} − 2 CO]. $C_{16}H_{10}NO_2Re$ (434.47): Calc. C 44.23; H 2.32; N 3.22; Found C 44.95; H 2.63; N 3.23.

5. Crystal structure determination of 3, 5, 6, 7 and 8

Data for the crystal structure determinations were collected on a Bruker AXS CCD area detector (Mo–K_α radiation, λ = 0.71073 Å) at −100°C. Crystal data and experimental details are listed in Table 2. Absorption corrections were applied using SADABS [25]. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data using SHELXTL programs [26]. All non-hydrogen atoms were refined an isotropically. Hydrogen atoms were located and refined isotropically.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 145424 to 145428. Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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