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Coordination chemistry of neutral quinolyl- and aminophenylcyclopentadiene derivatives

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Dedicated to Professor Rolf Gleiter on the occasion of his 65th birthday

Abstract

The cyclopentadiene and indene derivatives **1**–**4** being functionalised by a dimethylaniline and quinolyl group, respectively, were treated with metal carbonyl complexes. Whereas cyclopentadienes (C_5R_5H) normally loose one hydrogen atom prior or during metal complex formation, leading to negatively charged cyclopentadienide ligands, the compounds **1**–**4** are able to act as neutral ligands without hydrogen loss. Consequently transition metal complexes with coordination of the nitrogen donor and a C–C double bond of the five membered ring have been obtained. In some cases a hydrogen atom is eliminated and the expected η^5-(C_5R_5) complexes are formed. Reaction of $Ru_3(CO)_{12}$ with **2** leads to the binuclear η^6-fulvene complex **8**. The octahedral molybdenum complex **9** and the square planar rhodium(I) complexes **10** and **11** which were obtained from $Mo(CO)_6$ and $[Rh(CO)_2Cl]_2$, respectively, are rare examples of η^2-(C_5R_5H) coordination to metal atoms.

Keywords: N-functionalised cyclopentadienes; Olefin complexes; Carbonyl complexes

1. Introduction

Cyclopentadienide ligands, $C_5R_5^-$ are known to build stable complexes with most metals of the periodic table. The preferred ligand properties are based on the ideal geometry of the six electron π-system, paired with the negative charge of the ligand. Due to the charge, an additional stabilisation by electrostatic attraction between the metal centre and the ligand is achieved. As a result, the coordination chemistry of anionic C_5R_5-systems is much more comprehensive compared to the neutral cyclopentadienes (C_5R_5R'). However, compounds of the type (η^4-C_5R_5H)ML_n are formed as intermediates during the synthesis of some cyclopentadienyl complexes.

(η^4-C_5H_6)$Fe(CO)_3$ is very reactive and converts thermally to the dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ [1]. During the reaction of $Ru_3(CO)_{12}$ with cyclopentadiene, a metal hydride complex has been identified as an intermediate compound [2]. Heating of pentabenzylcyclopentadiene with $Fe(CO)_5$ leads to the formation of two stable products (η^4-C_5Bz_5H)$Fe(CO)_3$ as well as $[(\eta^5\text{-}C_5Bz_5)Fe(CO)_2]_2$ [3]. η^2-Complexes of neutral cyclopentadiene derivatives (C_5R_6) are very rare, only a handful compounds have been investigated structurally [4,5].

In this paper, we present the novel synthesis and molecular structures of metal complexes with functionalised cyclopentadienes or indenes where two or four carbon atoms of the five membered ring are interacting with the metal atom.

2. Results and discussion

Cyclopentadiene derivatives functionalised by a 8-quinolyl group or a *N*,*N*-dimethylanilinyl group possess a predefined geometry for the formation of chelate complexes. A metal atom bound to the nitrogen donor

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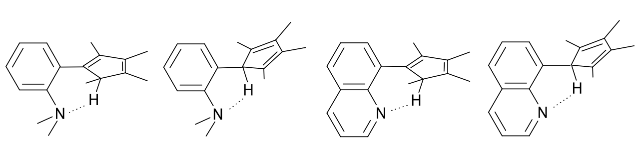
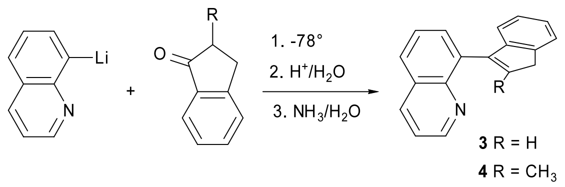
is forced to be close to the butadiene-π-system of the five membered ring. Therefore the interaction between the metal atom and a C–C double bond becomes easier. In order to study the coordination behaviour of neutral substituted cyclopentadienes (C_5R_5H), the previously reported ligands **1** [6] and **2** [7] and the new, functionalised indenes **3** and **4** were treated with metal carbonyl compounds $Fe(CO)_5$, $Ru_3(CO)_{12}$, $Mo(CO)_6$, or $[Rh(CO)_2Cl]_2$. The syntheses of **3** and **4** are accomplished by reaction of 8-lithioquinoline with 1-indanone and with 2-methyl-1-indanone, respectively. The novel compounds are formed as single isomers, with the quaternary carbon atom in the 3-position of the indene. Therefore a C–H···N hydrogen bond which is present in the cyclopentadienes **1** and **2** is not possible in **3** or **4** (Fig. 1, Scheme 1).



1a **1b** **2a** **2b**

Fig. 1. Amino substituted cyclopentadienes **1** and **2**.



Scheme 1. Preparation of the indene derivatives **3** and **4**.

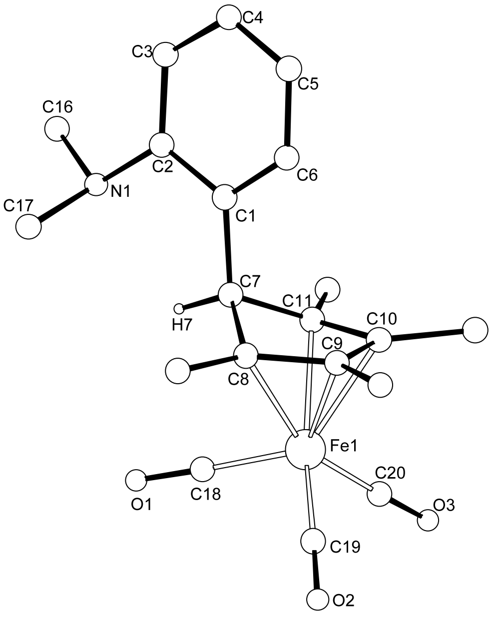
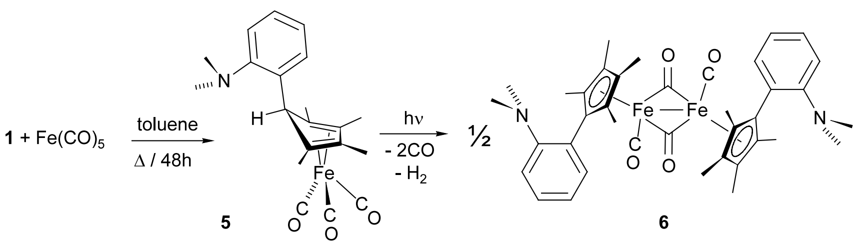


Fig. 2. Solid state structure of **5**. Selected bond lengths (Å) and angles (°): Fe–C8 2.143(2); Fe–C9 2.071(2); Fe–C_{CO} 1.785(2)–1.794(2), C–O 1.143(3)–1.148(2); C7–C8 1.529(2); C8–C9 1.432(2); C9–C10 1.428(3); C10–C11 1.437(2); C11–C7 1.529(2); C7–C1 1.534(2); C7–H7 0.97(2); N1–H7 2.38; C_{CO}–Fe–C_{CO} 93.1(1)–102.3(1).

The reaction of $Fe(CO)_5$ or $Ru_3(CO)_{12}$ with cyclopentadiene derivatives (C_5R_5H) normally leads to the formation of η^5-C_5R_5 metal complexes, although sometimes η^4-C_5R_5H complexes are isolated. The nitrogen functionalised cyclopentadiene derivative **1** (mixture of the isomers **1a** and **1b**) was treated with $Fe(CO)_5$ in boiling toluene for 48 h in order to obtain a binuclear complex comparable to $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. However, the IR-spectrum of the reaction mixture shows three bands caused by a metal tricarbonyl fragment and no signals for bridging CO groups are present. After chromatographic workup, the orange coloured, mononuclear complex **5** was isolated as the only product in 45% yield, being stable at room temperature for several weeks. The constitution is revealed by spectroscopic data, the mass spectrum shows the fragments where one or two CO ligands are lost; the third CO ligand is removed together with two hydrogen atoms leading to the base peak at $m/z = 295$. The NMR spectra indicate that the ligand isomer **1b** is incorporated in the complex leading to a molecule with an average C_s symmetry in solution. The signal for the ring hydrogen atom is observed at $\delta = 4.79$ in the ^{1}H-NMR spectrum. This value is about 2 ppm at lower field compared to other (η^4-C_5R_5H)$Fe(CO)_3$ complexes (e.g. $\delta = 2.72$ for (η^4-C_5Bz_5H)$Fe(CO)_3$) [8b]. The explanation for this ^{1}H-NMR value is the proximity of the N-lone pair of the amine substituent, leading to a C–H···N hydrogen bond. We have observed similar low-field NMR-values for the ligands **2a** ($\delta = 4.00$), **2b** ($\delta = 5.77$) [7] and **1a** ($\delta = 3.50$) [6]. The three carbonyl ligands result in one resonance in the ^{13}C-NMR spectrum at $\delta = 214.0$. Single crystals of **5** were grown from toluene at − 30 °C. The result of an X-ray analysis is shown in Fig. 2.

The iron atom is bound to four carbon atoms of the C_5R_5H ring. The ring hydrogen atom H7 lies in an endo position relative to the metal centre. The carbon atoms C8, C9, C10 and C11 build a planar diene system with nearly equidistant bond lengths (1.428–1.437 Å). This bond length equilibration is comparable to other diene $Fe(CO)_3$ complexes [8]. The nitrogen atom of the dimethylamino group is close to the atom H7 of the five-membered ring with a distance N–H7 of 2.38 Å. This is considerably smaller than the sum of the van der Waals radii (2.75 Å), consequently the interaction can be described as a C–H···N hydrogen bond [9]. Similar interactions were observed in the solid state structures of **1a** and **2a** [6]. However, the orientation of the dimethylamino group is not ideal for such an interaction and the lone pair seems to point beside the H7 atom (the plane defined by N1, C2 and H7 is not bisecting the angle C16–N1–C17) (Scheme 2).



Scheme 2. Formation of the iron complexes **5** and **6** with the ligand **1**. The quinolyl substituted derivative **2** leads directly to the binuclear complex **7** (analogue to **6**).

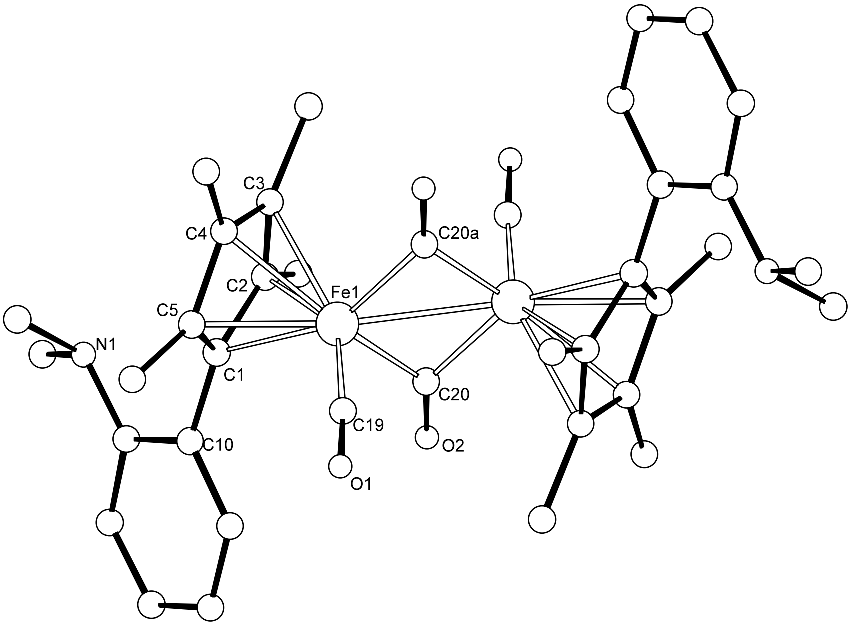


Fig. 3. Solid state structure of **6**. Selected bond lengths (Å) and angles (°): Fe–C_{Cp} 2.108(1)–2.162(1); Fe–C19 1.758(2), Fe–C20 1.928(1), C19–O1 1.143(2), C20–O2 1.180(2), Fe–Fe 2.562(1), C_{Cp}–C_{Cp} 1.426(2)–1.438(2), C19–Fe–C20 95.69(6), Fe–C20–Fe 83.28(6), C20–Fe–C20a 96.72(6), C19–Fe–C20a 93.31(6).

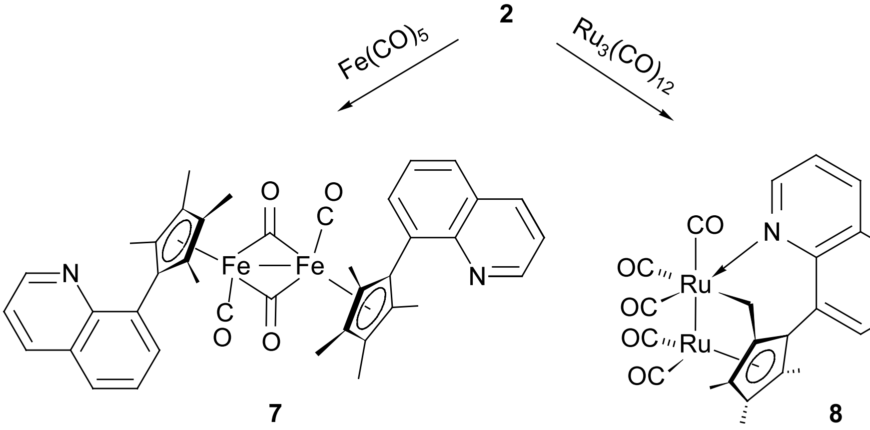
Compound **5** is thermally stable and does not convert to the binuclear complex **6**. The derivative (η^4-C_5H_6)$Fe(CO)_3$, is very reactive and converts thermally or upon exposure to air to the dimer [(η^5-C_5H_5)$Fe(CO)_2$$]_2$ [1]. In order to eliminate CO-ligands, a *n*-hexane solution of **5** was irradiated with UV-light. After 24 h small red–brown plates precipitated. The IR-spectrum indicates the formation of the new compound **6** with terminal and bridging CO ligands. The mass spectrum reveals the molecular ion of **6** at $m/z = 704$. Therefore **6** is a binuclear compound analogous to [η^5-$C_5H_5Fe(CO)_2$$]_2$. The solid state structure of **6** is shown in Fig. 3.

The arrangement of the ligands and the distances in **6** compared to [η^5-$C_5Me_5Fe(CO)_2$$]_2$ are very similar [10]. The dimethylaniline substituents are located in *trans* positions, the molecule displays a centre of symmetry in the middle of the iron–iron bond.

In order to compare the coordination behaviour of the *N*,*N*-dimethylaniline substituted cyclopentadiene **1** with the quinoline functionalised cyclopentadiene **2**, a solution of $Fe(CO)_5$ and **2** in *n*-heptane was heated to reflux for 40 h. However, no η^4-complex comparable to **5** could be identified. The IR-spectrum shows that the binuclear compound **7** with bridging CO ligands was formed directly.

Treatment of **2** with $Ru_3(CO)_{12}$ takes a different course. A mixture of products formed and analysis by FD-mass spectrometry revealed the presence of several bi and trinuclear ruthenium compounds. Purification by chromatography led to the isolation of the binuclear complex **8** in 34% yield (Scheme 3).

Brown crystals of the ruthenium compound **8**, suitable for X-ray diffraction, have been obtained from toluene at room temperature. The result is shown in Fig. 4. The former ligand **2** has lost two hydrogen atoms, one from the cyclopentadiene ring, another from a CH_3 group. The resulting fulvene derivative is coordinated to a diruthenium unit via six carbon atoms and the nitrogen atom of the quinoline moiety. The bond



Scheme 3. Formation of the binuclear compounds **7** and **8**.

lengths in the fulvene framework are nearly equalised (1.47–1.43 Å) and the six carbon atoms lie in a plane (max. deviation C12 0.05 Å). The geometry of the ligand allows the coordination of the quinoline nitrogen atom to the second ruthenium atom, which is octahedrally surrounded by three CO ligands, one ruthenium atom, the CH_2-group of the fulvene and the nitrogen atom. The deviations from an ideal octahedral arrangement are small and all angles at Ru2 are within a range of 82.1°–104.6°. A few cases of fulvene coordination to a diruthenium unit have been reported [11]. However, the formation of a fulvene complex from a cyclopentadiene derivative is unexpected. This reactivity is caused by the predefined, rigid geometry of **2**. When the quinoline nitrogen atom is bound to the metal centre, the cyclopentadiene must be close to the metal complex fragment and is therefore easily coordinated.

The reactions described so far show, that the functionalised cyclopentadiene **1** may serve as a neutral ligand (compound **5**). However, **1** as well as **2** readily lose hydrogen, leading to η^5-complexes. In order to favour η^2-coordination it is suitable to embed the second C–C double bond of the cyclopentadiene moiety into an aromatic system. Consequently the novel, functionalised indenes **3** and **4** were used as ligands and were treated with metal carbonyl complexes. Reaction of $Mo(CO)_6$ with **3** leads to the formation of the new complex **9** (Fig. 5) where a molybdenum atom is octahedrally surrounded by four CO-ligands, one nitrogen atom and a C–C double bond. The maximum deformation of the bonding angles around the central atom is only 7° with respect to the ideal 90°. The ring systems are almost planar with maximum deviations of 0.028 Å in the indene and 0.072 Å in the quinoline system. The interplanar angle is 50.0°. The C–C double bond C11–C12 is slightly lengthened (1.396(5) Å) because of the interaction with the molybdenum metal. Experiments to transform the η^2-indene complex **9** into a η^5-indenyl derivative by prolonged heating, by irradiation or by deprotonation proved unsuccessful.

Treatment of $[Rh(CO)_2Cl]_2$ with the indene ligand **4** as well as with the cyclopentadiene **2** in diethylether at room temperature lead to the precipitation of the new complexes **10** and **11**, respectively, as yellow powders. After crystallisation from dichloromethane–hexane solutions, the structures have been revealed by X-ray diffraction (see Figs. 6 and 7). In both cases one C–C double bond and the nitrogen atom of the quinoline are bound to the rhodium atom which is itself in a square planar environment. The geometry of both compounds is very similar. The coordination of the nitrogen atom with a distance Rh–N of 2.105(1) and 2.103(4) Å brings the C–C double bond of the ligand **2** or **4** in an ideal position for an interaction with the rhodium metal. Because of strong interactions of the olefin-π-systems with the rhodium atoms, the C–C double bond lengths

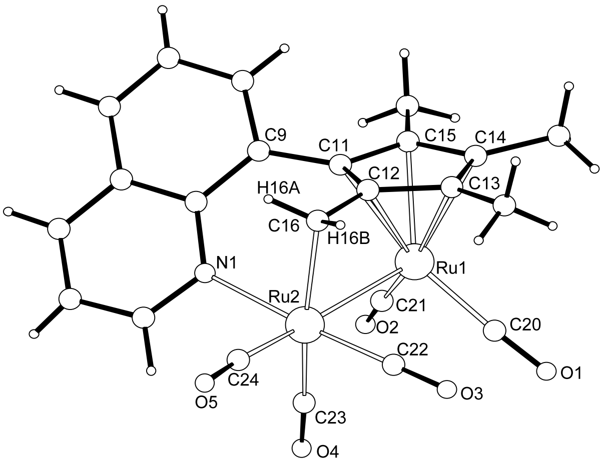


Fig. 4. Solid state structure of **8**. Selected bond lengths (Å) and angles (°): C9–C11 1.470(6), C11–C12 1.471(6), C12–C13 1.439(7), C13–C14 1.428(6), C14–C15 1.434(7), C15–C11 1.452(6), C12–C16 1.453(6), Ru1–C_{Cp} 2.226(4)–2.312(4), Ru1–C_{CO} 1.859(5), 1.866(5), Ru1–Ru2 2.875(1), Ru2–N1 2.252(4), Ru2–C16 2.193(5), Ru2–C22 1.875(5), Ru2–C23 1.950(5), Ru2–C24 1.929(5), C21–Ru1–C20 89.0(2), N1–Ru2–C16 86.6(2), C16–Ru2–C22 93.0(2), Ru1–Ru2–C16 82.1(1), Ru1–Ru2–C22 82.9(1).

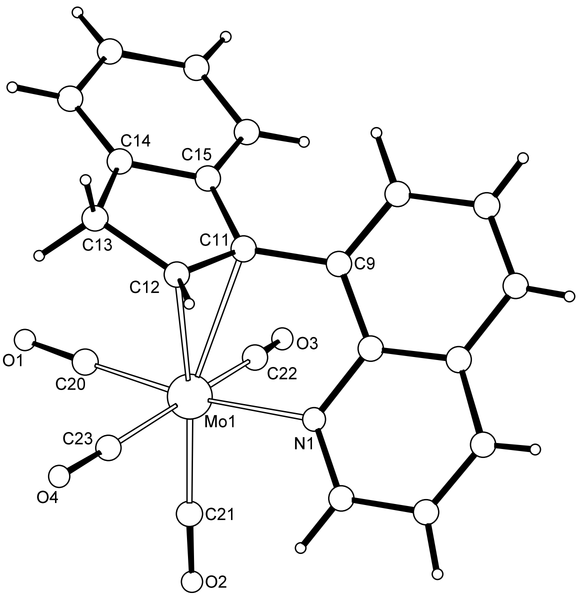


Fig. 5. Solid state structure of **9**. Selected bond lengths (Å) and angles (°): C11–C12 1.396(5), C12–C13 1.523(5), C13–C14 1.504(5), C14–C15 1.402(5), C15–C11 1.483(5), C9–C11 1.490(5), Mo1–C12 2.460(4), Mo1–C11 2.489(4), Mo1–C20 1.967(4), Mo1–C21 1.972(4), Mo1–C22 2.034(4), C20–O1 1.161(4), C21–O2 1.155(5), C22–O3 1.149(4), C23–O4 1.138(5), N1–Mo1–C21 95.9(2), N1–Mo1–C22 95.0(1), N1–Mo1–C23 93.8(2), N1–Mo1–C20 173.1(1).

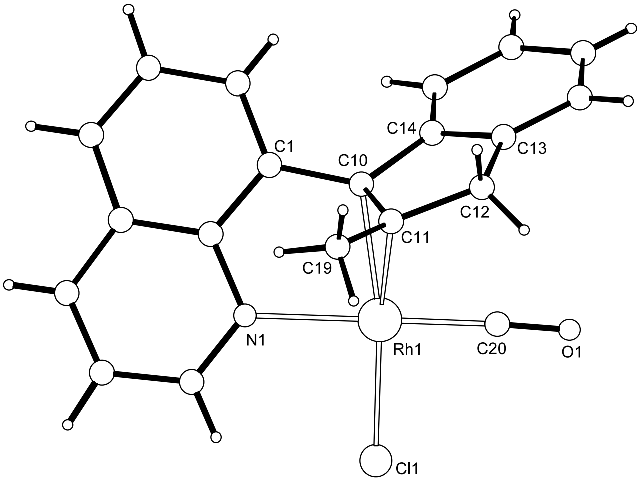


Fig. 6. Solid state structure of **10**. Selected bond lengths (Å) and angles (°): C1–C10 1.485(2), C10–C11 1.431(2), C11–C12 1.530(2), C12–C13 1.505(2), C13–C14 1.404(2), C14–C10 1.486(2), Rh1–N1 2.105(1), Rh1–Cl1 2.349(1), Rh1–C10 2.157(2), Rh1–C11 2.157(2), Rh1–C20 1.841(2), C20–O1 1.141(2), N1–Rh1–Cl1 90.9(1), Cl1–Rh1–C20 87.2(1), Rh1–C20–O1 177.6(2).

are raised to 1.431(2) Å (**10**) and 1.428(6) Å (**11**), respectively. The CO acceptor ligands lie in *trans* positions relative to the quinoline nitrogen atoms. The quinoline rings as well as the indene and the cyclopentadiene are almost planar (max. deviation from the best plane 0.06 Å). The interplanar angles are 58.0° (**10**) and 55.0° (**11**). In compound **11** the atom C15 (CH_3 group) lies in endo position relative to Rh1. A possible second isomer (H11 *endo*, C15 *exo* related to rhodium) was never observed in solution or in the solid state, although it should have a similar or somewhat higher thermodynamic stability compared to **11**. Therefore the formation of isomer **11** by reaction of the ligand **2a** with $[Rh(CO)_2Cl]_2$ must be controlled kinetically and is a consequence of the preferred conformation of **2a** with a C–H···N hydrogen bridge [6].

To our knowledge the compounds **10** and **11** are the first examples of η^2-indene or η^2-cyclopentadiene complexes of rhodium which have been characterised by X-ray diffraction.

3. Conclusions

The donor functionalised cyclopentadiene and indene derivatives **2**–**4** are able to act as neutral two electron π-ligands with additional coordination of the nitrogen donor. With ligand **1** no η^2-coordination was observed, but the η^4-iron complex **5** has been isolated, in which the nitrogen group is not interacting with the metal atom. The cyclopentadiene derivatives **1** and **2** may lose the ring hydrogen atom during complexation reaction leading to the usual η^5-coordinated C_5R_5-metal complexes. Hydrogen loss is of course more difficult in the indene derivatives **3** and **4**. As a result, we always obtained η^2-coordinated metal complexes with indene derivatives. However, η^5-coordination with functionalised indenyl derivatives is possible when the ligands are deprotonated prior to the reaction with metal complex fragments [12,13]. In the rhodium complex **11** the cyclopentadiene derivative **2** acts as a two π-electron ligand via a C–C double bond. This coordination mode is very unusual in cyclopentadiene chemistry and only a few examples are known in the literature, mainly in binuclear complexes [4,5].

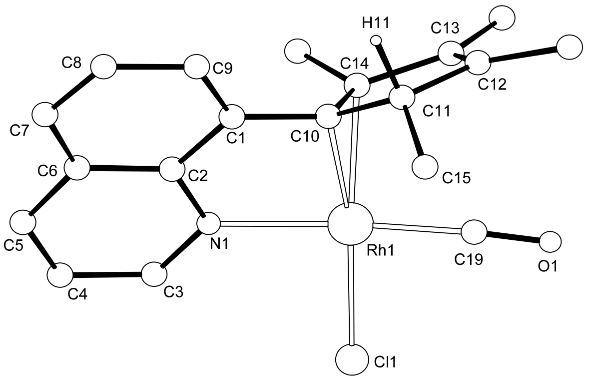


Fig. 7. Solid state structure of **11**. Selected bond lengths (Å) and angles (°): C1–C10 1.487(6), C10–C11 1.517(6), C11–C12 1.520(6), C12–C13 1.337(6), C13–C14 1.490(7), C14–C10 1.428(6), Rh1–N1 2.103(4), Rh1–Cl1 2.353(1), Rh1–C10 2.164(4), Rh1–C14 2.191(4), Rh1–C19 1.841(5), C19–O1 1.139(6), N1–Rh1–Cl1 91.3(1), Cl1–Rh1–C19 86.4(2), Rh1–C19–O1 175.9(5).

4. Experimental

4.1. General remarks

All experiments were carried out under an atmosphere of dry nitrogen. Solvents were dried by using standard procedures and distilled prior to use. The following compounds were prepared according to literature procedures: 1-(2-*N*,*N*-dimethylaminophenyl)-2,3,4,5,-tetramethyl-cyclopentadiene (**1**) [6], 2,3,4,5-tetramethyl-1-(8-quinolyl)-cyclopentadiene (**2**) [7], 8-bromoquinoline [14], tetracarbonyldi-μ-chlorodirhodium(I) [15]. All other reagents were used as purchased. NMR: Bruker AC 200 and Bruker DRX 200 (200.13 and 50.32 MHz for ^{1}H and ^{13}C, 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 of the deuterated solvent ($CDCl_3$: 77.0 ppm, C_6D_6: 128.0 ppm). IR: Bruker IFS 28. MS: VG Micromass 7070 H, Finnigan MAT 8230 and JEOL JMS-700.

*4.2. 1-(8-Quinolyl)-indene (**3**)*

A solution of 10.4 g (50 mmol) of 8-bromoquinoline in 100 ml of THF was cooled to -100 °C and 20 ml of a 2.5 M solution of *n*-butyllithium in hexane (50 mmol) was added with stirring within 15 min. After stirring for another 15 min at -80 °C, a solution of 6.6 g (50 mmol) of 1-indanone in 30 ml of THF was added dropwise. The mixture was allowed to warm to room temperature (r.t.) and was then heated at reflux for 3 h. After cooling down, some ice and HCl were added up to pH 1, and the mixture was stirred for 30 min. After separation of the phases the aqueous one was subsequently alkalised with aqueous NH_3 up to pH 9 and extracted with diethylether. The combined organic layers were evaporated to dryness in vacuum. The crude product was treated with concentrated HCl up to pH 0 and was then heated at reflux for 2 h. After neutralisation with aqueous NH_3, extraction of the aqueous layer with diethylether and evaporation of the solvent, **3** was obtained as a white solid, yield 6.6 g (27 mmol, 55%), m.p. 108 °C. ^{1}H-NMR ($CDCl_3$): $\delta = 3.69$ (d, $^{3}J(H,H) = 2.0$ Hz, 2H, CH_2); 6.80 (t, $^{3}J(H,H) = 2.0$ Hz, 1H, CH); 7.12–7.26 (m, 3H); 7.41 (dd, $^{3}J(H^2,H^3) = 4.2$ Hz, $^{3}J(H^3,H^4) = 8.3$ Hz, 1H, H^3); 7.55–7.64 (m, 2H); 7.81–7.88 (m, 2H); 8.21 (dd, $^{3}J(H^3,H^4) = 8.3$ Hz, $^{4}J(H^2,H^4) = 1.8$ Hz, 1H, H^4); 8.92 (dd, $^{3}J(H^2,H^3) = 4.2$ Hz, $^{4}J(H^2,H^4) = 1.8$ Hz, 1H, H^2). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): $\delta = 38.8$ (CH_2); 121.0, 121.2, 123.8, 124.5, 125.8, 126.3, 127.8, 130.0, 133.5, 136.1, 150.0 (CH); 128.6, 135.9, 143.7, 144.0, 145.6, 146.7 (quart. C). EIMS; *m*/*z* (%): 243 (65) [M^+], 242 (100) [$M^+ - H$]. EIHRMS: Calc. for $C_{18}H_{13}N$: 243.1048; Found: 243.1038. Anal. Calc. $C_{18}H_{13}N$ (243.31): C 88.86, H 5.39, N 5.75. Found: C 87.55, H 5.52, N 5.92%.

*4.3. 1-(8-Quinolyl)-2-methyl-indene (**4**)*

The procedure was repeated in an analogous manner to **3**. Scale: 3.50 g (16.8 mmol) of 8-bromoquinoline, 6.70 ml (16.8 mmol) of a 2.5 M solution of *n*-BuLi in hexane, 2.45 g (16.8 mmol) of 2-methyl-1-indanone. The purification of the resulting crude oil is achieved by distillation. The ligand **4** was obtained as the third fraction of the distillation at 150–160 °C/10^{-2} mbar as a yellow viscous oil, yield 1.50 g (5.8 mmol, 35%). ^{1}H-NMR ($CDCl_3$): $\delta = 2.07$ (CH_3); 3.52 (d, $^{2}J(H,H) = 22.6$ Hz, 1H, CH_2) 3.73 (d, $^{2}J(H,H) = 22.6$ Hz, 1H, CH_2); 6.79–6.89 (m, 1H, $H_{aromat.}$); 7.10–7.18 (m, 2H, $H_{aromat.}$); 7.38–7.50 (m, 2H, $H_{aromat.}$); 7.58–7.75 (m, 2H, $H_{aromat.}$); 7.88 (dd, $^{3}J(H,H) = 7.6$ Hz, $^{4}J(H,H) = 2.2$ Hz, 1H, $H_{aromat.}$); 8.24 (dd, 1 H, $^{3}J(H,H) = 8.3$ Hz, $^{4}J(H,H) = 1.8$ Hz, $H_{aromat.}$); 8.93 (dd, $^{3}J(H^2,H^3) = 4.3$ Hz, $^{4}J(H^2,H^4) = 1.8$ Hz, 1H, H^2). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): $\delta = 15.3$ (Cp CH_3); 43.3 (CH_2); 119.8, 121.0, 123.2, 123.7, 125.8, 126.3, 127.6, 131.0, 136.4, 150.0 ($CH_{aromat.}$); 128.7, 135.2, 137.2, 142.2, 142.6, 146.7, 147.4 (quart. $C_{aromat.}$). EIMS; *m*/*z* (%): 257 (100) [M^+], 242 (44) [$M^+ - CH_3$], 130 (17) [$C_{10}H_{10}^{+}$].

*4.4. Tricarbonyl[η^4-1-(2-N,N-dimethylaminophenyl)-2,3,4,5-tetramethylcyclopentadiene]iron (**5**)*

A solution of 0.40 g (1.66 mmol) of **1** and 0.32 g (1.63 mmol) of $Fe(CO)_5$ was refluxed for 16 h. The resulting orange–red solution was cooled to r.t., concentrated and purified by column chromatography on Al_2O_3–5% H_2O using toluene as eluent. The resulting red brown main fraction was concentrated in vacuum and cooled to -30 °C. Orange red crystals of **5** (0.28 g, 0.73 mmol, 45%) were formed, which were suited for X-ray crystallographic studies, m.p. 73 °C. IR (hexane) $\tilde{\nu}(CO)$ (cm^{-1}) = 1952 (s), 1961 (s), 2032 (s). ^{1}H-NMR ($CDCl_3$): $\delta = 1.34$ (s, 6H, Cp CH_3); 1.83 (s, 6H, Cp CH_3); 2.41 (s, 6H, N CH_3); 4.79 (s, 1H, Cp H); 6.64 (d, $^{3}J = 7.5$ Hz, 1H, $H_{aromat.}$); 6.99–7.10 (m, 2H, $H_{aromat.}$); 7.27–7.38 (m, 1H, $H_{aromat.}$). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$): $\delta = 14.5$, 14.8 (Cp CH_3); 45.6 (N CH_3); 64.7, 74.0, 101.3 (quart. C_{Cp}); 117.6, 121.6, 125.0, 126.0, 139.0, 153.0 ($C_{aromat.}$); 214.0 (CO). EIMS; m/z (%): 353 (35) [$M^+ - CO$], 325 (8) [$M^+ - 2CO$], 295 (100) [$M^+ - 3CO - 2H$], 280 (11) [$M^+ - 3CO - 2H - CH_3$], 241 (7) [**1**$^+$], 28 (6) [CO^+].

*4.5 Bis{dicarbonyl-η^5-[1-(2-N,N-dimethylamino-phenyl)-2,3,4,5-tetramethylcyclopentadienyl]iron} (**6**)*

A solution of 130 mg (0.34 mmol) of **5** in 50 ml of hexane was irradiated (150 W high-pressure mercury lamp). After 24 h brown crystals precipitated. The solution was removed with a syringe and the crystals dried in vacuum; yield 70 mg (0.10 mmol, 59%) of **6**, m.p. 277 °C. IR (CH_2Cl_2) $\tilde{\nu}$(CO) (cm^{-1}): 1923.0 (s); 1762.1 (s). ^{1}H-NMR ($CDCl_3$): $\delta = 1.70$ (s, 12 Cp CH_3), 1.93 (s, 12 Cp CH_3); 2.57 (s, 12 H, N CH_3); 7.10 (t, ^3J(H, H) = 7.9 Hz, 4H, $H_{aromat.}$); 7.32–7.37 (m, 4H, $H_{aromat.}$); 7.66–7.71 (m, 2H, $H_{aromat.}$). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): $\delta = 8.0$, 9.2 (Cp CH_3); 41.9 (N CH_3); 92.9, 101.1, 116.9, 120.8, 128.1, 133.1 ($CH_{aromat.}$). EIMS; *m/z* (%): 704 (6) [M^+]; 592 (2) [$M^+ - 2CO - Fe$]; 536 (1) [(**1**–H)$_2$Fe$^+$]; 352 (20) [**1**Fe(CO)$_2^+$]; 324 (37) [**1**FeCO$^+$]; 294 [100, (**1**–H)Fe–H$^+$]. Anal. Calc. $C_{38}H_{44}N_2O_4Fe_2$ (704.47): C 64.72, H 6.30, N 3.98. Found: C 64.13, H 6.32, N 3.92%.

4.6. *Bis{dicarbonyl-η⁵-[1-(8-quinolyl)-2,3,4,5-tetramethylcyclopentadienyl]iron}* (**7**)

A solution of 0.272 mg (1.09 mmol) of **2** and 380 mg (1.94 mmol) of ironpentacarbonyl in 50 ml of *n*-heptane was heated at reflux for 40 h. After cooling to r.t. a violet precipitate of **7** formed and was collected by filtration. Isolated yield 259 mg (0.36 mmol, 66%). IR (toluene) $\tilde{\nu}$(CO) (cm^{-1}): 1760.7 (s), 1922.6 (s). ^{1}H-NMR (C_6D_6): $\delta = 1.69$ (s, 6H, CH_3), 1.72 (s, 6H, CH_3), 6.72 (m, 1H), 7.45 (m, 2H), 7.54 (m, 1H), 8.55 (m, 1H), 8.75 (m, 1H). EIMS; *m/z* (%): 720 (0.7) [M^+], 662 (0.9) [$M^+ - 2CO$], 552 (45) [Fe(**2**–H)$_2^+$], 304 (100) [Fe(**2**–H)$^+$].

4.7. *Binuclear rutheniumcomplex* **8**

A mixture of 900 mg (4.2 mmol) of $Ru_3(CO)_{12}$ and 631 mg (2.5 mmol) of **2** in 70 mg of toluene was heated at reflux for 16 h, the resulting solution was purified by column chromatography on Al_2O_3–5% H_2O using toluene as eluent. The solution was concentrated and **8** crystallised at r.t.: Yield: 423 mg (0.7 mmol, 34%). IR (toluene) $\tilde{\nu}$(CO) (cm^{-1}): 1903 (s), 1962 (s), 1977 (s), 2046 (s). ^{1}H-NMR (C_6D_6): δ 1.48 (s, 3H, CH_3); 1.89 (s, 3H, CH_3); 2.19 (s, 3H, CH_3); 5.98 (dd, $^3J(H^3,H^2) = 5.4$ Hz, $^3J(H^3,H^4) = 8.1$ Hz, 1H, H^3); 6.78 (dd, ^3J(H,H) = 7.1 Hz, ^3J(H,H) = 8.1 Hz, 1H, H^6); 6.91 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.8 Hz, 1H, $H_{aromat.}$); 7.01 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.7 Hz, 1H, $H_{aromat.}$); 7.10–7.16 (m, 1H, $H_{aromat.}$); 9.07 (dd, $^3J(H^2,H^3) = 5.2$ Hz, $^4J(H^2,H^4) = 1.7$ Hz, 1H, H^2). $^{13}C\{^1H\}$-NMR (C_6D_6): $\delta = -4.4$ (CH_2); 9.5, 11.7, 13.1 (CH_3); 82.4, 88.1, 95.5, 99.1, 101.6 (quart. C_{Cp}); 119.5, 125.9, 129.7, 134.0, 139.8, 158.2 ($CH_{quinoline}$); 189.1, 198.5, 209.5, 212.0 (CO). FDMS; *m/z* (%): 591 (100) [M^+].

4.8. *Tetracarbonyl[η²-1-(8-quinolyl)indene]molybdenum* (**9**)

A solution of 1.0 g (4.1 mmol) of **3** and 1.1 g (4.1 mmol) of $Mo(CO)_6$ in 50 ml of toluene was refluxed for 16 h. The resulting orange solution was cooled to r.t. and concentrated in vacuum. Cooling to −30 °C resulted 684 mg (1.52 mmol, 37%) of **9** as small yellow–orange crystals, m.p. 180 °C (decomposition). IR (toluene) $\tilde{\nu}$(CO) (hexane) (cm^{-1}): 1880.3 (m), 1931.6 (s), 2028.1 (m). ^{1}H-NMR (CD_2Cl_2): $\delta = 3.84$ (m, 2H, CH_2); 5.82 (dd, ^3J(H,H) = 1.6 Hz, ^3J(H,H) = 2.4 Hz, 1H, CH); 7.24–7.33 (m, 2H, $H_{aromat.}$); 7.38–7.46 (m, 2H, $H_{aromat.}$); 7.56 (dd, $^3J(H^5,H^6) = 7.2$ Hz, $^3J(H^6,H^7) = 8.2$ Hz, 1H, H^6); 7.69 (dd, $^3J(H^6,H^7) = 8.2$ Hz, $^4J(H^5,H^7) = 1.5$ Hz, 1H, H^7); 7.94–8.01 (m, 2H, $H_{aromat.}$); 8.20 (dd, $^3J(H^3,H^4) = 8.2$ Hz, $^4J(H^2,H^4) = 1.6$ Hz, 1H, H^4); 8.77 (dd, $^3J(H^2,H^3) = 4.8$ Hz, $^4J(H^2,H^4) = 1.6$ Hz, 1H, H^2). ^{13}C $\{^1H\}$-NMR (CD_2Cl_2): $\delta = 43.2$ (CH_2); 94.7, 121.1, 122.0, 125.3, 126.8, 126.9, 127.1, 127.5, 127.9, 138.2, 154.2 (CH); 110.3, 129.7, 138.8, 143.2, 145.4, 149.8 (quart. C); 209.5, 213.2, 218.1, 221.8 (CO). FDMS; *m/z* (%): 453 (100) [M^+]; 243 (15) [**3**$^+$]. FDHRMS: Calc. for $C_{22}H_{13}NO_4Mo$: 452.9899; Found: 452.9957. Anal. Calc. $C_{22}H_{13}NO_4Mo$ (451.29): C 58.56, H 2.90, N 3.10; Found: C 58.38, H 2.97, N 3.00%.

4.9. *Carbonylchloro-1,2-η²-[1-(8-quinolyl)-2-methylindene]rhodium(I)* (**10**)

A total of 220 mg (0.57 mmol) of tetracarbonyldi-μ-chlorodirhodium(I) was added to a solution of 300 mg (1.17 mmol) of **4** in 30 ml of diethylether. A yellow precipitate was formed immediately. The resulting suspension was stirred for 16 h at r.t. and then suction filtered through a frit. The collected yellow solid was washed two times with 5 ml of diethylether and dried in vacuum; yield 290 mg (0.68 mmol, 58%), m.p. 254 °C (decomposition). IR (THF) $\tilde{\nu}$(CO) (cm^{-1}): 2020 (vs, $\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$): $\delta = 1.70$ (s, 3H, CH_3); 3.35 (d, ^2J(H,H) = 21.4 Hz, 1H, CH_2), 3.74 (d, ^2J(H,H) = 21.4 Hz, 1H, CH_2); 7.30–7.38 (m, 3H, $H_{aromat.}$); 7.55 (dd, $^3J(H^3,H^2) = 5.0$ Hz, $^3J(H^3,H^4) = 8.3$ Hz, 1H, H^3); 7.67 (dd, ^3J(H,H) = 7.2, ^3J(H,H) = 8.2 Hz, 1H, H^6); 7.80–7.94 (m, 3H, $H_{aromat.}$); 8.37 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.5 Hz, 1H, $H_{aromat.}$); 9.29 (dd, $^3J(H^2,H^3) = 5.0$ Hz, $^4J(H^2,H^4) = 1.2$ Hz, 1H, H^2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 22.3$ (CH_3); 51.2 (CH_2); 87.7 (d, ^1J(Rh,C) = 14.0 Hz, quart. $C_{indenyl}$); 93.2 (d, ^1J(Rh,C) = 13.0 Hz, quart. $C_{indenyl}$); 121.6, 122.1 (d, $J = 1.0$ Hz), 125.1, 126.3, 126.9, 127.1, 128.0, 128.1, 138.6, 150.4 ($CH_{aromat.}$); 129.0, 137.7, 141.1, 148.3 (d, $J = 1.5$ Hz), 149.9 (d, $J = 1.0$ Hz) (quart. $C_{aromat.}$); 184.6 (d, ^1J(Rh,C) = 74.0 Hz, CO). EIMS; *m/z* (%): 423 (14) [M^+], 395 (4) [$M^+ - CO$], 359 (100) [$M^+ - CO - Cl$], 257 (36) [**4**$^+$], 242 (10) [**4**$^+$–CH_3], 127 (11) [$C_9H_5N^+$]. Anal. Calc. $C_{20}H_{15}ClNORh$ (423.70): C 56.70, H 3.57, N 3.31; Found C 56.74, H 3.83, N 3.39%.

4.10. Carbonylchloro-1,2-η^2-(1-(8-quinolyl)-2,3,4,5-tetramethylcyclopenta-1,3-diene)rhodium(I) (**11**)

A total of 170 mg (0.87 mmol) of **2** was added to a solution of 218 mg (0.44 mmol) of tetracarbonyldi-μ-chlorodirhodium(I) in 20 ml of diethylether. After 6 h of stirring a bright yellow precipitate formed and was separated from the solution by filtration, washed two times with 5 ml of diethylether and dried in vacuum; yield 190 mg (0.46 mmol, 53%) of **11**, m.p. 176 °C (decomposition). IR (toluene) $\tilde{\nu}$(CO) (cm^{-1}): 2016 (vs). ^{1}H-NMR (CDCl$_3$): $\delta = 1.40$ (d, ^3J(Rh,H) = 0.8 Hz, 3H, CH$_3$); 1.61 (d, ^3J(H,H) = 7.5 Hz, 3H, CH$_3$); 1.69 (m, ^5J(H,H) = 1.0 Hz, 3H, CH$_3$); 1.96 (m, ^5J(H,H) = 1.0 Hz, 3H, CH$_3$); 3.22 (q, ^3J(H,H) = 7.6 Hz, 1H, CH$_{\text{Cp}}$); 7.46 (dd, ^3J(H^3,H^2) = 5.0 Hz, ^3J(H^3,H^4) = 8.3 Hz, 1H, H^3); 7.57–7.65 (m, 1H, H^6); 7.69–7.75 (m, 2H, H^5, H^7); 8.27 (dd, ^3J(H^4,H^3) = 8.3 Hz, ^4J(H^4,H^2) = 1.6 Hz, 1H, H^4); 9.21 (ddd, ^3J(H^2,H^3) = 5.0 Hz, ^3J(H^2,H^4) = 1.5 Hz, ^3J(H^2,Rh) = 1.1 Hz, 1H, H^2). ^{13}C{^{1}H}-NMR (CDCl$_3$): $\delta = 10.9$, 11.5, 14.4 (CH$_3$); 18.6 (d, ^2J(Rh,C) = 2.3 Hz, CH$_3$); 49.8 (CH$_{\text{Cp}}$); 95.8 (d, ^1J(Rh,C) = 11.9 Hz, quart. C$_{\text{Cp}}$); 96.9 (d, ^1J(Rh,C) = 16.9 Hz, quart. C$_{\text{Cp}}$); 121.9, 125.5, 127.4, 128.2, 138.4, 150.0 (CH$_{\text{quinoline}}$); 128.8, 139.0, 140.3, 144.1, 149.4 (quart. C); 184.3 (d, ^1J(Rh,C) = 74.0 Hz, CO). EIMS; m/z (%): 387 (26) [M$^+$ − CO]; 372 (26) [M$^+$ − CO − CH$_3$], 351 (17) [M$^+$ − CO − HCl], 336 (19) [M$^+$ − CO − HCl − CH$_3$], 249 (11) [HCp^{Q+}], 175.5 (71), [M^{2+} − CO − HCl], 167 (23), 154 (15), 129 (18) [C$_9$H$_7$N$^+$], 36 (17) [HCl$^+$], 28 (100) [CO$^+$]. Anal. Calc. C$_{19}$H$_{19}$ClNORh (415,73): C 54.89, H 4.61, N 3.37. Found C 54.34, H 4.63, N 3.29%.

Table 1
Crystal data and structure refinement details for **5**, **6**, **8**, **9**, **10**, **11**

	5	**6**	**8**	**9**	**10**	**11**
Empirical formula	$C_{20}H_{23}FeNO_3$	$C_{38}H_{44}Fe_2N_2O_4$	$C_{23}H_{17}NO_5Ru_2$	$C_{22}H_{13}MoNO_4$	$C_{20}H_{15}ClNORh$	$C_{19}H_{19}ClNORh$
Formula weight	381.24	704.45	589.52	451.27	423.69	415.71
Temperature (K)	203	173	203	203	173	203
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/a$	$P2(1)/n$	$P\bar{1}$	$P2(1)/c$
Unit cell dimensions						
a (Å)	8.006(4)	8.7334(1)	9.731(5)	7.207(7)	8.2253(1)	8.562(4)
b (Å)	10.706(5)	9.0432(1)	14.572(7)	16.327(16)	8.5890(1)	13.613(7)
c (Å)	11.893(6)	12.5867(2)	14.913(8)	15.803(16)	13.0312(2)	14.721(7)
α (°)	77.11(3)	69.811(1)	90	90	101.873(1)	90
β (°)	85.07(3)	82.044(1)	92.66(3)	96.63(8)	99.484(1)	94.83(3)
γ (°)	80.02(3)	61.964(1)	90	90	108.593(1)	90
V (Å^3)	977.5(8)	823.17(2)	2112(2)	1847(3)	827.14(2)	1709(1)
Z	2	1	4	4	2	4
D_{calc} (g cm^{-3})	1.295	1.421	1.854	1.623	1.701	1.615
Absorption coefficient (mm^{-1})	0.788	0.925	1.465	0.739	1.199	1.158
F(000)	400	370	1160	904	424	840
Crystal size (mm)	0.60 × 0.55 × 0.25	0.53 × 0.28 × 0.10	0.40 × 0.40 × 0.40	0.6 × 0.25 × 0.20	0.38 × 0.22 × 0.18	0.50 × 0.50 × 0.08
Theta range for data collection (°)	1.76–33.00°	1.72–28.28°	1.95–30.00°	1.80–25.00°	1.65–28.30°	2.04–28.00°
Index ranges	$-12 \le h \le 9$, $-15 \le k \le 16$, $0 \le l \le 18$	$-11 \le h \le 11$, $-10 \le k \le 11$, $0 \le l \le 16$	$-13 \le h \le 13$, $0 \le k \le 20$, $0 \le l \le 20$	$-8 \le h \le 8$, $0 \le k \le 19$, $0 \le l \le 18$	$-10 \le h \le 10$, $-11 \le k \le 11$, $0 \le l \le 17$	$-11 \le h \le 11$, $0 \le k \le 17$, $0 \le l \le 19$
Reflections collected	6631	11 070	6136	3254	12 131	4128
Independent reflections	6631	4012 [$R_{\text{int}} = 0.025$]	6136	3254	4007 [$R_{\text{int}} = 0.0291$]	4128
Absorption correction	Psi-scan	Semi-empirical from equivalents	None	Psi-scan	Semi-empirical from equivalents	Psi-scan
Max./min. transmission	1.000, 0.914	0.862, 0.757		0.999, 0.845	0.8621, 0.7319	1.000, 0.597
Data/restraints/parameters	6631/0/318	4012/0/296	6136/0/317	3254/0/305	4007/0/277	4128/0/285
Goodness-of-fit on F^2	1.026	1.074	1.045	1.033	1.064	1.026
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0403$, $wR_2 = 0.1020$	$R_1 = 0.0288$, $wR_2 = 0.0769$	$R_1 = 0.0458$, $wR_2 = 0.1146$	$R_1 = 0.0336$, $wR_2 = 0.0805$	$R_1 = 0.0210$, $wR_2 = 0.0555$	$R_1 = 0.0432$, $wR_2 = 0.1050$
R indices (all data)	$R_1 = 0.0591$, $wR_2 = 0.1101$	$R_1 = 0.0329$, $wR_2 = 0.0785$	$R_1 = 0.0692$, $wR_2 = 0.1259$	$R_1 = 0.0449$, $wR_2 = 0.0858$	$R_1 = 0.0220$, $wR_2 = 0.0561$	$R_1 = 0.0747$, $wR_2 = 0.1167$
Largest differential peak and hole (e Å^{-3})	0.348 and −0.456	0.435 and −0.189	0.729 and −1.617	0.337 and −0.870	0.694 and −0.374	1.079 and −0.551

5. Crystal structure determinations of 5, 6, 8, 9, 10, 11

Crystal data are compiled in Table 1. Intensity data were collected for **5**, **8**, **9**, and **11** on a Siemens–Stoe AED2 diffractometer (Mo–K_α radiation, ω-scan, $T = -70$ °C) and for **6** and **10** on a Bruker AXS CCD area detector (Mo–K_α radiation, ω-scan, $T = -100$ °C). The structures were solved by direct methods [16] and refined by least-squares methods based on F^2 using all measured reflections with anisotropic temperature factors for all non-hydrogen atoms [16]. Hydrogen atoms were located in difference Fourier maps and refined isotropically, except those of the methyl groups in **8**, which were treated as part of a rigid group.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 164703–164708 for compounds **5**–**11**, respectively. Copies of this information 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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