Low-Valent Titanium–Pentafulvene Complexes – Formation of Dinuclear Titanium–Nitrogen Complexes

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Dedicated to Prof. Dr. Jan H. Teuben

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Sodium amalgam reduction of [(η^5-C_5Me_5)$TiCl_3$] (**1**) in the presence of the pentafulvenes {C_5H_4=CR_2, R: *p*-tol (**2**), *p*-FPh (**3**), CR_2: adamantyl (**4**)} under nitrogen smoothly produces dark green or dark blue dinuclear low-valent titanium complexes [{(η^5-C_5Me_5)Ti(η^6-C_5H_4=CR_2)}$_2$(μ$_2$,η^1,η^1-N_2)] {R: *p*-tol (**6**), *p*-FPh (**7**), CR_2: adamantyl (**8**)}, characterized by a bridging end-on coordinated dinitrogen ligand, in high yield. In the same way, the nitrogen-free, low-coordinated complex [(η^5-C_5Me_5)Ti(η^6-C_9H_6=C(*p*-tol)$_2$)] (**10**) is obtained by using the more sterically demanding benzofulvene C_9H_6=C(*p*-tol)$_2$ (**5**) instead of **2**–**4**. The solid-state structures of the dinitrogen compounds reveal weakly activated end-on bound N_2 ligands with identical N–N distances of 1.160(3) Å (**6**) and 1.160(5) Å (**8**). The dinitrogen complexes **6**, **7** and **8** show diamagnetic behaviour, which allowed a complete NMR spectroscopic characterization. So a correlation between the situation in solution, measured by NMR, and in the solid state (X-ray diffraction) becomes possible and shows a congruent picture. A broad range of reactions can be imagined concerning the easily replaceable dinitrogen ligand as well as the known reactivity of fulvene ligands in complexes of early transition metals.

Introduction

Low-valent titanium complexes are of great importance in the complexation and activation of molecular nitrogen. Different bonding modes are found in early transition metals, depending on the nature of the other ligands.[1–5] Titanocene- as well as zirconocene-based systems have been and are still being extensively investigated. It was found that the cyclopentadienyl substituent patterns have a strong influence on the N_2 coordination and activation modes.[6–11] In such a way, for example, the permethylated [(η^5-C_5Me_5)$_2$Zr] fragment coordinates the N_2 molecules by end-on bridging as well as in a terminal mode.[12–14] On the other hand, using the tetramethylcyclopentadiene ligand instead of the pentamethyl derivative, a side-on bridging coordination mode, characterized by an efficient N_2 activation, is found.[15,16] Results like this initiated further studies in order to obtain a detailed understanding of the field of N_2 activation reactions. In addition to the metallocene-based systems, Cp alternatives based on multidentate anionic ligands bearing N, O and P donor atoms were successfully used in order to obtain nitrogen complexes.[17–25] It was also shown that the introduction of nitrogen into organic substrates becomes possible under reductive conditions.[26–29]

Recently we were able to demonstrate that pentafulvene complexes of early transition metals are easily available from the reaction of titanium halides, reducing agents (Mg, Na/Hg), and free pentafulvenes.[30] Using fulvenes exhibiting asymmetric exocyclic carbon centres, a diastereoselective complexation of the fulvene ligand at different cyclopentadienyltitanium fragments is possible.[31]

Here we wish to report the one-step formation of dinitrogen-containing titanium complexes by reactions of [(η^5-C_5Me_5)$TiCl_3$] (**1**) with the pentafulvenes **2**, **3**, **4** and Na/Hg as reducing agent in the presence of dinitrogen. Using the bulky benzofulvene **5**, a low-coordinated mononuclear titanium compound is formed.

Results and Discussion

Treatment of a THF solution of equimolar amounts of [(η^5-C_5Me_5)$TiCl_3$] (**1**) [Equation (1)] and **2**, **3**, or **4** with three equivalents of Na (20% Na/Hg) under nitrogen leads to intensely coloured solutions. After removal of

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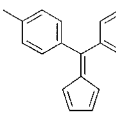

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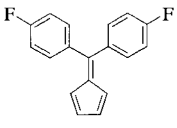

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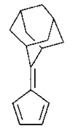

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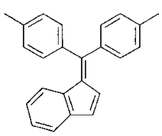

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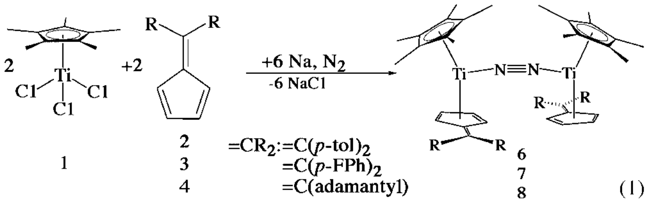


(1)

the solvent, addition of *n*-hexane to the residue and separation from the insoluble NaCl and mercury by filtration, **6**, **7**, and **8** can be isolated as dark green (**6**, **7**) or dark blue (**8**) crystals showing a fascinating cupric lustre. All complexes were isolated in high yields (**6**, **8** 90%; **7** 80%). It is also possible to use magnesium as the reducing agent, but the products could only be isolated in lower yields (40%), because the formation of $MgCl_2$ containing adducts with the dinitrogen complexes made it difficult to separate $MgCl_2$ quantitatively. All three dinitrogen complexes are thermally stable; melting points are found at 125 °C (**6**), 138–140 °C (**7**), and 175 °C (**8**). They are easily soluble in inert solvents like ethers and saturated or aromatic hydrocarbons.

Suitable crystals for X-ray diffraction were obtained from *n*-hexane/toluene (1:1) (**6**) or *n*-hexane (**8**) solutions at ambient temperature. In the case of **6** the asymmetric unit contains a disordered *n*-hexane molecule, which was refined on 3 positions (1/3, 1/3, 1/3) in idealised geometry; **8** shows two independent molecules in the asymmetric unit. Figure 1 and Figure 2 show ORTEP plots of the molecules with 50% probability ellipsoids, the hydrogen atoms, solvent molecules and the second molecule in the asymmetric unit (**8**) are omitted for clarity. Due to similarities of the structural values, we will limit our discussion mainly on the data of molecule one (Ti1, Ti2). Selected structural data are given in Table 1 and Table 2. The dinuclear structures consist of two $[(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5H_4{=}CR_2)Ti]$ moieties bridged by N_2 in an almost linear Ti–N≡N–Ti arrangement. However, a deviation from linearity of about 9–10° was found (**6** Ti1–Ti2–N2 9.4°, Ti2–Ti1–N1 9.0°; **8** Ti1–Ti2–N2 9.9°, Ti2–Ti1–N1 10°). In accordance with this observation, the Ti–N–N angles were found to be slightly smaller than 180° [**6** 171.0(2)°, 169.1(2)°; **8** 170.0(4)°, 169.6(4)°]. These values correspond well to the lower range of values found in comparable $\mu_2,\eta^1,\eta^1\text{-}N_2$ titanium complexes (168–180°, Table 1). The N–N bond lengths of 1.160(3) Å (**6**) and 1.160(5) Å (**8**) are also consistent with a just slightly activated N_2 molecule, since the N–N distance is not significantly different from that of free N_2 (1.0976 Å[32]). Thus, these values are in good agreement with metallocene type dinitrogen–titanium complexes (Table 1). Also, the Ti–N bond lengths are in the range of end-on coordinated dinitrogen–titanocene complexes [**6** 1.997(3), 2.001(3) Å; **8** 2.012(4), 2.003(4) Å]. Only in non-titanocene–nitrogen complexes derived from titanium amides are shorter Ti–N and longer N–N bonds found (Ti–N av. 1.72–1.76 Å, N–N 1.26–1.29 Å[17,24,25]).

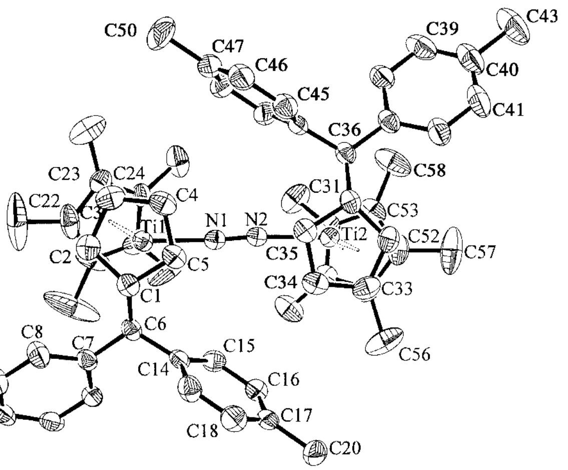


Figure 1. Solid state structure of **6** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Ti(1)–C(1) 2.195(3), Ti(1)–C(2) 2.253(3), Ti(1)–C(5) 2.303(3), Ti(1)–C(3) 2.375(3), Ti(1)–C(4) 2.409(3), Ti(1)–C(6) 2.601(3), C(1)–C(6) 1.436(4), C(1)–C(2) 1.439(4), C(1)–C(5) 1.434(4), C(2)–C(3) 1.416(5), C(4)–C(5) 1.412(4), C(3)–C(4) 1.393(5), Ti(1)–N(1) 1.997(3), N(1)–N(2) 1.160(3), Ti(1)–Ct(1) 2.056(3), Ti(1)–Ct(2) 1.968(3), Θ 28.4, Ct(1)–Ti(1)–Ct(2) 139.0 [Ct(1) = Centroid of Cp*, Ct(2) = centroid of the fulvene ring, Θ = tilt of C(6) out of the plane of C(11)–C(15)].

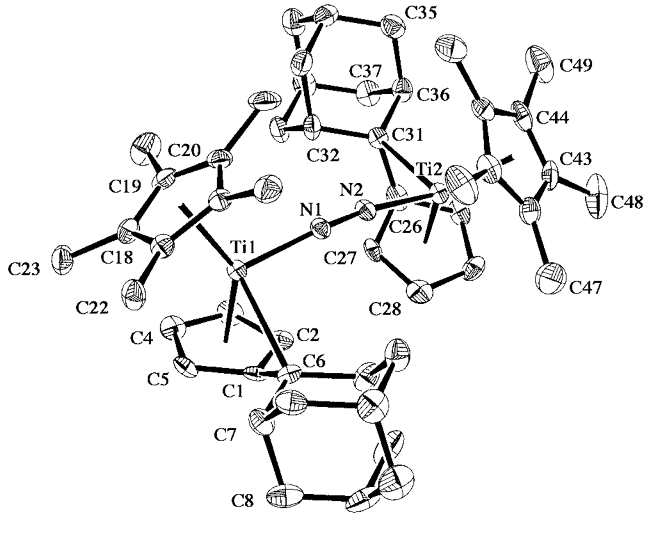


Figure 2. Solid state structure of **8** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Ti(1)–C(1) 2.179(5), Ti(1)–C(2) 2.301(5), Ti(1)–C(5) 2.291(5), Ti(1)–C(3) 2.424(5), Ti(1)–C(4) 2.426(5), Ti(1)–C(6) 2.511(5), C(1)–C(6) 1.441(6), C(1)–C(2) 1.437(6), C(1)–C(5) 1.448(7), C(2)–C(3) 1.413(8), C(4)–C(5) 1.419(7), C(3)–C(4) 1.397(7), Ti(1)–N(1) 2.012(4), N(1)–N(2) 1.160(5), Ti(1)–Ct(1) 2.061(4), Ti(1)–Ct(2) 1.986(4), Θ 30.4, Ct(1)–Ti(1)–Ct(2) 138.8 [Ct(1) = Centroid of Cp*, Ct(2) = centroid of the fulvene ring, Θ = tilt of C(6) out of the plane of C(1)–C(5)].

6 as well as **8** show similarities but also some marked differences compared with titanocene complexes. Probably the most striking point is the well-defined arrangement of the pentafulvene ligands which are located on the same side of the molecule. In general, a selective *trans* orientation of

Table 1. Selected bond lengths [Å] and angles [°] of **6** and **8**, compared with related dinitrogen complexes.

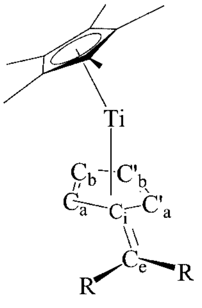
Compound	N–N	Ti–N	Ti–N–N	Ref.
6	1.160(3)	1.997(3), 2.001(3)	171.0(2), 169.1(2)	
8	1.160(5)	2.012(4), 2.003(4)	170.0(4), 169.6(4)	
$[\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$	1.165(14)	2.005(10), 2.016(10)	176.8(4), 178.1(4)	[33]
$[\{(\eta^5\text{-}C_5Me_4H)_2Ti\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$	1.170(4)	1.987(3)	178.5(3)	[8]
$[\{(\eta^5\text{-}C_5H_5)_2Ti(PMe_3)\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$	1.191(8)	1.920(6), 1.921(5)	169.0(5), 172.6(5)	[9]
$[\{(\eta^5\text{-}C_5H_5)_2Ti(p\text{-Tol})\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$	1.162(12)	1.962(6)	176.5(5)	[11]
$[\{(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2Ti\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$	1.164(5)	1.991(4)	176.0(3)	[7]
$[\{((Me_3Si)_2N)TiCl(TMEDA)\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$	1.289(9)	1.762(5)	168.5(2)	[25]
$[\{((Me_3Si)_2N)TiCl(Py)_2\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$	1.263(7)	1.759(3)	175.5(3)	[24]
$[\{((Me_2N)C(N\mathit{i}Pr)_2)_2Ti\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$	1.280(8)	1.723(8), 1.744(8)	180.0	[17]

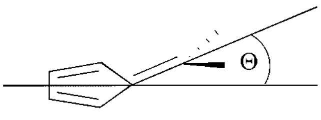
Table 2. Selected bond lengths [Å] and angles [°] of **6**, **8**, **10** compared with **2**,[30] **4**[35] and **5**.

	6	**2**	**8**	**4**	**10**	**5**
Ti–Ci	2.195(3) 2.195(2)		2.179(5) 2.188(4)		2.116(2)	
Ti–Ce	2.601(3) 2.612(3)		2.511(5) 2.471(5)		2.351(2)	
Ti–C_a	2.253(3) 2.258(3)		2.291(5) 2.282(5)		2.220(2)	
Ti–C'_a	2.303(3) 2.296(3)		2.301(5) 2.310(4)		2.350(3)	
Ti–C_b	2.375(3) 2.362(3)		2.426(5) 2.428(6)		2.360(2)	
Ti–C'_b	2.409(3) 2.399(3)		2.424(5) 2.424(5)		2.461(2)	
Ti–Ct* [a]	2.056(3) 2.056(3)		2.061(4) 2.068(4)		2.006(2)	
Ti–Ct^{Fv} [a]	1.968(3) 1.963(3)		1.986(4) 1.986(4)		1.956(2)	
Ci–C_e	1.436(4) 1.435(4)	1.359(2)	1.441(6) 1.427(8)	1.342(2)	1.465(3)	1.359(2)
Ci–C_a	1.439(4) 1.441(4)	1.465(2)	1.448(7) 1.459(8)	1.459(2)	1.449(4)	1.467(2)
Ci–C’$_a$	1.434(4) 1.430(4)	1.458(3)	1.437(6) 1.454(7)	1.459(2)	1.465(3)	1.488(2)
C_a–C_b	1.416(5) 1.406(5)	1.340(3)	1.419(7) 1.411(8)	1.327(3)	1.401(3)	1.340(3)
C'_a–C'_b	1.412(4) 1.412(4)	1.344(3)	1.413(8) 1.404(8)	1.337(3)	1.437(4)	1.416(2)
C_b–C'_b	1.393(5) 1.396(5)	1.445(3)	1.397(7) 1.416(8)	1.451(3)	1.414(4)	1.454(2)
Θ[b]	28.4 28.2	0	30.4 32.8	0	34.9	0
Ct*–Ti–Ct^{Fv} [a]	139.0 138.7		138.8 138.8		150.9	

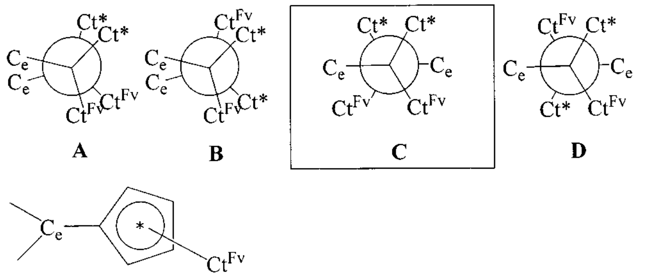
[a] Ct*: ring centroid of C_5Me_5 ligand; Ct^{Fv}: ring centroid of C_i, C_a, C'_a, C_b, C'_b.

[b] Deviation angle.





the non-Cp-type ligands is found in dinuclear, μ_2,η^1,η^1-dinitrogen-bridged titanocene complexes with tetrahedral coordinated titanium centres like $[\{(\eta^5\text{-}C_5H_5)_2Ti(p\text{-tol})\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$[11] and $[\{(\eta^5\text{-}C_5H_5)_2Ti(PMe_3)\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$.[9] In the case of **6** and **8**, in principle, four different stereoisomers are possible with respect to the position of the exocyclic fulvene carbon atoms (C_e) to each other (Scheme 1). Again, the formation of the "*cis* isomers" **A** and **B** was not observed, whereas of the two possible "*trans* isomers" **C** was found to be formed exclusively. This was confirmed not only in the solid state but also in solution (vide infra).

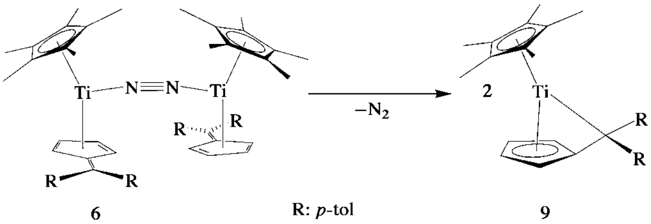


Scheme 1. Possible isomers of $[\{(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5H_4{=}CR_2)Ti\}_2(\mu^2,\eta^1,\eta^1\text{-}N_2)]$ complexes (Ct*: ring centroid of C_5Me_5; Ct^{Fv}: ring centroid of Ci, C_a, C'_a, C_b, C'_b; C_e *exo*-cyclic carbon of the fulvene ligand, see also Table 2).

The formal titanocene moieties $[(\eta^5\text{-}C_5Me_5)Ti(\eta^6\text{-}C_5H_4{=}CR_2)]$ are canted towards each other, forming a dihedral angle of 3.2° in **6** and 19.1° in **8** between the planes defined by the metallocene wedges, respectively (a value of 20.0° was found for the second molecule of **8** in the asymmetric unit). This is again in the same range as it was observed for similar complexes as, for example, in the case of $[\{(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2Ti\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$ where a dihedral angle of 9.6° was found.[7]

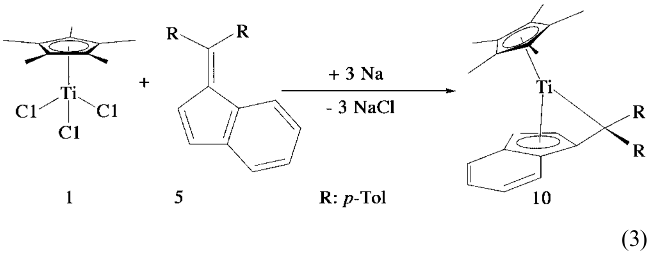
However, this behaviour is different from that of the Ti(II) dinitrogen complexes showing twisted metallocene units $[\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$ (av. 90°)[33] and $[\{(\eta^5\text{-}C_5H_5)_2Ti(PMe_3)\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$ (P–Ti–Ti–P 109°).[9] A nearly perpendicular twist was found also for tantalum–dinitrogen complexes $[\{(\eta^5\text{-}C_5Me_5)_2TaCl\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$ (90.8°).[34] Nevertheless, structural parameters that are comparable to those of **6** and **8** were found in the case of the diamagnetic Ti^{III} derivative $[\{(\eta^5\text{-}C_5H_5)_2Ti(p\text{-Tol})\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$[11] exhibiting a coplanar arrangement of both aryl groups and the centrosymmetric titanocene complex $[\{(\eta^5\text{-}C_5Me_4H)_2Ti\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$.[8]

Indeed, the N_2 coordination in our complexes is comparatively weak, and nitrogen is thus released quantitatively under reduced pressure or vacuum (0.49 moles per mole of Ti), forming the paramagnetic fulvene complex **9** [Equation (2)], characterized by elementary analysis ($C_{30}H_{33}Ti$ (M_τ = 441.47 $g\,mol^{-1}$): calcd. C 81.62, H 7.53; found: C 81.46, H 7.42). This observation is confirmed by MS analysis (EI, 70 eV) of **6**, **7**, and **8**, where only the monomeric $[(\eta^5\text{-}C_5Me_5)Ti(\eta^6\text{-}C_5H_4{=}CR_2)]$ units are detectable.



(2)

Unfortunately, crystals of **9** suitable for X-ray diffraction were not available up to now. However, using **5** instead of **2** under the reaction conditions described in Equation (1), the nitrogen-free fulvene complex **10** became available in a one-step synthesis. The low-coordinated complex **10** [Equation (3)] was isolated in the form of black, needle-shaped crystals (85%). In the mass spectrum, the peak of the molecular ion (*m*/*z* 491) was observed as the base peak. Suitable crystals for X-ray structure determination were obtained from *n*-hexane solutions at –20 °C. Due to the paramagnetic behaviour of the complex caused by the odd number of electrons at the titanium, it was not possible to record NMR spectra with distinct signals.



(3)

The molecular structure of **10** is given in Figure 3. The structure of the free ligand **5** was determined for comparison by X-ray diffraction (Figure 4). Selected structural parameters are summarized in Table 2.

Due to the two quite different π-ligands, ($\eta^5\text{-}C_5Me_5$) and ($\eta^6\text{-}C_5H_4{=}CR_2$), in **6** and **8** the bonding situation is remarkably different compared to bent-titanocene-derived dinitrogen complexes. The complexation of pentafulvenes to low-valent titanium fragments is generally assumed to be accompanied by electron transfer to the π-acceptor ligand. This leads to a situation that can probably be best described

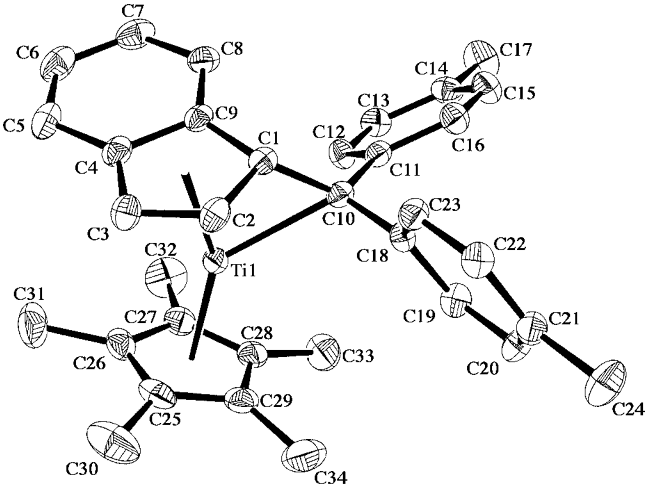


Figure 3. Solid-state structure of **10** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Ti(1)–C(1) 2.116(2), Ti(1)–C(2) 2.220(2), Ti(1)–C(9) 2.350(3), Ti(1)–C(3) 2.360(3), Ti(1)–C(4) 2.461(2), Ti(1)–C(10) 2.351(2), C(1)–C(10) 1.465(3), C(1)–C(2) 1.449(4), C(1)–C(9) 1.465(3), C(2)–C(3) 1.401(3), C(4)–C(9) 1.437(4), C(3)–C(4) 1.414(4), C(5)–C(6) 1.355(4), C(6)–C(7) 1.415(4), C(7)–C(8) 1.367(4), C(8)–C(9) 1.408(4), Ti(1)–Ct(1) 2.006(3), Ti(1)–Ct(2) 1.956(3), Θ 34.9, Ct(1)–Ti(1)–Ct(2) 150.9 [Ct(1) = Centroid of Cp*, Ct(2) = centroid of the fulvene ring, Θ = tilt of C(10) out of the plane of C(1)–C(9)].

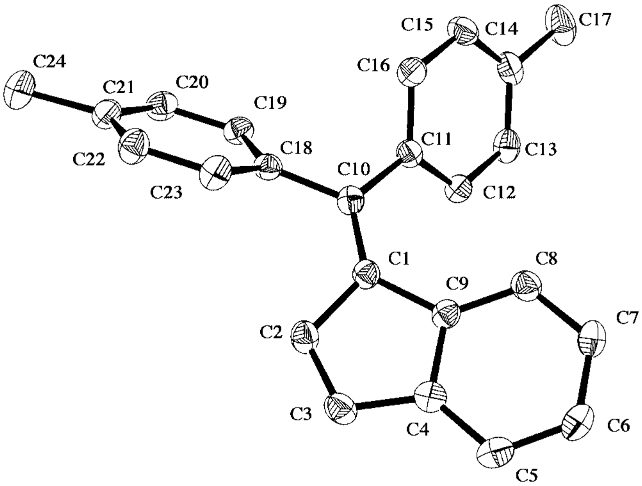


Figure 4. Solid-state structure of **5** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: C(1)–C(10) 1.359(2), C(1)–C(2) 1.467(2), C(1)–C(9) 1.488(2), C(2)–C(3) 1.340(3), C(3)–C(4) 1.454(2), C(4)–C(5) 1.390(3), C(4)–C(9) 1.416(2), C(5)–C(6) 1.382(3), C(6)–C(7) 1.387(3), C(7)–C(8) 1.390(3), C(8)–C(9) 1.387(2).

by the formation of a dianionic fulvene ligand coordinated in a π-η^5:σ-η^1 manner.[31,30] Thus, the five-membered ring of the pentafulvene becomes aromatic, the C_i–C_e bond is elongated, and the C_e atom is bent out of the ring plane (Θ, see footnote Table 2). A comparison of the structural data of the free ligands **2**,[30] **4**[35] and **5** with the titanium complexes **6**, **8** and **10** is given in Table 2. The exocyclicC_i–C_e distances in **2** [1.359(2) Å], **4** [1.342(2) Å][35] and **5** [1.359(2) Å] are elongated to av. 1.436 Å (**6**), av. 1.434 Å (**8**) and 1.465(3) Å (**10**) after complexation. The strongest elongation and, simultaneously, the shortest Ti–C_e bond lengths [2.351(2) Å] were observed in the mononuclear titanium complex **10**. On the other hand, the Ti–C_e distances in **6** and **8** were found to be av. 2.606 Å and av. 2.491 Å. A comparable value was found for [(η^5-C_5Me_5)Ti(η^6-C_5H_4=C(*p*-tol)$_2$)Cl] [2.535(5) Å].[30] In fulvene complexes substituted with one or two protons at the C_e-atom of the fulvene ligand, Ti–C_e distances close to typical bond lengths between titanium and sp^3-hybridized C-atoms were found as in [(η^5-C_5Me_5)Ti(η^6-C_5Me_4=CH_2)] [2.281(14) Å][36] and [(η^5-C_5Me_5)Ti(η^6-C_5H_4=CH(*t*Bu))Cl] [2.355(2) Å].[31] The fulvene ligands in **6**, **8** and **10** show characteristic deviations (Θ) of the C_e-atom from the plane of the five-membered ring (**6** av. 28.3°, **8** av. 31.6°, **10** 34.9°). The Ct*–Ti–Ct^{Fv} angles of **6** (av. 138.8°) and **8** (138.8°) were found in a typical range of bent-titanocene derivatives[37] {Ti^{IV}: [(η^5-C_5Me_5)(η^5-C_5H_5)$TiCl_2$] 132.0°,[38] Ti^{III}: [(η^5-C_5Me_4H)$_2$-TiCl] 139.1°,[39] [(η^5-C_5Me_5)$_2$TiCl] 143.6°[40]}. In contrast, the Ct*–Ti–Ct* angles in permethylated titanium(II) complexes are usually significantly larger {[{(η^5-C_5Me_5)$_2$-Ti}$_2$(μ_2,η^1,η^1-N_2)] 145.7(3)°,[33] [(η^5-C_5Me_5)$_2$Ti(CO)$_2$] 147.9°[41]}. Also, in the case of the bulky fulvene complex **10** a larger value of 150.9° was found. Compared to free fulvene **5**, the two double bonds of the six-membered ring are significantly shortened from av. 1.39 Å to av. 1.36 Å in **10** and therefore seem to be more localised, indicating a loss of aromaticity. This is in agreement with an η^5 complexation mode of the five-membered ring, thus no hints for a typical indenyl effect are found.[42,43]

The isolated dinitrogen complexes **6**, **7**, and **8** showed diamagnetic behaviour, which allowed a complete NMR spectroscopic characterization (Table 3). The magnetic behaviour is comparable to the titanium(III)–dinitrogen complex [{(η^5-C_5H_5)$_2$Ti(*p*-tol)}$_2$(μ_2,η^1,η^1-N_2)].[44] On the other hand the titanium(II)–dinitrogen complexes like [{(η^5-C_5Me_5)$_2$Ti}$_2$(μ_2,η^1,η^1-N_2)] are often paramagnetic compounds (μ_{eff} = 2.18 BM per titanium atom[33]), showing broad downfield-shifted signals at room temperature[45] and dynamic properties in solutions. In such a way, detailed ^{1}H NMR measurements of [{(η^5-C_5Me_5)$_2$Ti(N_2)}$_2$(μ_2,η^1,η^1-N_2)] in [D$_8$]toluene at low temperatures (–78 to –42 °C) are in full accord with an η^5-C_5Me_5 ring site exchange.[13]

However, strong upfield shifts of proton and carbon signals, e.g. of up to 3 ppm for H_a of **8**, clearly show the presence of low-valent titanium complexes. This is especially pronounced for the exocyclic fulvene carbon atoms of all titanium complexes compared to the free ligands. Interestingly, the signals for these carbons were found at almost the same chemical shifts in all complexes although the free fulvenes do show significant differences. Furthermore, a complete loss of symmetry indicated by separated signals for all protons and carbons of the fulvenes in the dinuclear titanium complexes compared to the highly symmetrical fulvenes themselves and the absence of saturation transfer phenomena clearly show the formation of conformationally rigid dinitrogen complexes in benzene solution at room temperature. This is in sharp contrast to the conformational behaviour found for the mononuclear fulvene complexes [(η^5-C_5Me_5)Ti(η^6-C_5H_4=C(*p*-tol)$_2$)Cl][30] and [(η^5-C_5Me_5)-Ti(η^6-C_5H_4=C(*p*-C_6H_4F)$_2$)Cl][46], where a fast rotation of the fulvene ligand was observed under similar conditions. Obviously, a free rotation of the fulvene ligand is hindered by the dimeric structure, although the Ti–C_e distances are in a similar range. NOE measurements at room temperature indicate that the favoured isomer C (Scheme 1) in the solid state is also found in benzene solution because strong NOE contacts were observed between fulvene ring protons H'_b–H'_a of **8** which do not only result from the interaction of these protons attached to one fulvene ring but also from the interaction of protons attached to different fulvenes.

Table 3. Selected ^{1}H- (C_6D_6, 500 MHz, 300 K) and ^{13}C NMR spectroscopic data (C_6D_6, 125 MHz, 300 K) of **6**, **7** and **8**, compared with **2**,[30] **3** and **4**[47] (assignment of the proton and carbon signals in accordance with footnote[b] in Table 2).

	6	**2**	**7**	**3**	**8**	**4**
^{1}H NMR data						
H_a	4.38 (m, 2 H)	6.57 (m, 1 H)	4.17 (m, 2 H)	6.29 (m, 1 H)	3.64 (m, 2 H)	6.66 (m, 1 H)
H'_a	3.98 (m, 2 H)	6.57 (m, 1 H)	3.87 (m, 2 H)	6.29 (m, 1 H)	4.20 (m, 2 H)	6.66 (m, 1 H)
H_b	4.79 (m, 2 H)	6.65 (m, 1 H)	4.86 (m, 2 H)	6.58 (m, 1 H)	5.10 (m, 2 H)	6.61 (m, 1 H)
H'_b	4.07 (m, 2 H)	6.65 (m, 1 H)	4.17 (m, 2 H)	6.58 (m, 1 H)	5.69 (m, 2 H)	6.61 (m, 1 H)
^{13}C NMR data						
C_e	108.5	152.2	105.7	149.0	107.9	164.8
C_a	104.0	124.8	104.1	124.4	103.2	119.8
C'_a	106.5	124.8	105.9	124.4	104.5	119.8
C_b	111.9	132.4	112.3	133.2	113.3	131.0
C'_b	108.4	132.4	108.0	133.2	103.7	131.0

Conclusion

An efficient type of one-step synthesis of end-on bridged dinuclear cyclopentadienyltitaniumfulvene complexes was presented. These complexes are formed in high yields from [(η^5-C_5Me_5)$TiCl_3$], bulky substituted pentafulvenes, and sodium amalgam as reducing agent under nitrogen. Along the Ti–N≡N–Ti axis the C_5Me_5 as well as the fulvene ligands are arranged in a stereoregular manner. The weak activation of the dinitrogen ligand suggests that the dinuclear [(η^5-C_5Me_5)Ti(η^6-C_5H_4=CR_2)] dinitrogen complexes serve as synthons for interesting titanocenes, derived from the displacement of the nitrogen molecule in combination with the known possibilities to functionalize the strongly nucleophilic exocyclic carbon atom of the fulvene ligand by electrophilic attack.

Experimental Section

General Remarks: All operations were performed under nitrogen with rigorous exclusion of oxygen and moisture by using glove box or Schlenk techniques. Solvents were thoroughly dried and saturated with nitrogen. ^{1}H- and ^{13}C NMR spectra were recorded with a Bruker AVANCE 500 spectrometer (^{1}H, 500.1 MHz; ^{13}C

125.8 MHz) or a Bruker AVANCE 300 spectrometer for ^{19}F- (282.4 MHz) and ^{1}H- or ^{13}C nuclei. The ^{1}H NMR chemical shifts were referenced to residual protons of the solvent. The ^{13}C NMR spectra were referenced to the signals of the solvent. The ^{19}F NMR spectra were referenced externally to $CFCl_3$. Assignment of the signals was done on the basis of ^{1}H, ^{13}C, H,H-COSY, HMQC, HMBC, and sel-1D NOESY NMR experiments.[48] Electron impact (EI) mass spectra were taken with a Finnigan-MAT 95 Spectrometer. IR spectra were recorded with a BIO-RAD FTS-7 Spectrometer by using KBr pellets. Elemental analyses were carried out by the Analytischen Laboratorien in Lindlar (Germany). $[(\eta^5\text{-}C_5Me_5)TiCl_3]$ (**1**) was prepared according to the literature.[49] Sodium amalgam was purchased as 20% pellets from Aldrich. The fulvenes **2** and **3** were prepared according to general literature procedures.[48,50] **5**[48,51] was obtained in a similar way under only slightly modified conditions. Compound **4** was prepared according to the literature.[47,48]

[Bis{[η^6-6,6-bis(*p*-tolyl)pentafulvene](η^5-pentamethylcyclopentadienyl)titanium}-μ^2,η^1,η^1-dinitrogen] (6): Sodium amalgam (2.38 g, 20% Na, 20.73 mmol Na), di-*para*-tolylfulvene (**2**) (1.78 g, 6.91 mmol) and $[(\eta^5\text{-}C_5Me_5)TiCl_3]$ (**1**) (2.00 g, 6.91 mmol) were placed in a Schlenk tube. At a temperature of 0 °C (ice bath) of THF (100 mL) was added under an excess nitrogen pressure of 200 mbar. The reaction mixture was stirred for 16 h. A colour change from red to dark green occurred. The reaction mixture was filtered twice (first P4/Celite, then P5). Removing the solvent under vacuum led to a brown residue, which became dark green again after adding N_2. After recrystallisation from of *n*-hexane (50 mL) at –20 °C, complex **6** could be isolated as dark green crystals showing a cupric lustre. Yield: 2.83 g (90%). M.p. 125 °C. ^{1}H NMR (500.1 MHz, C_6D_6, 300 K):[48] δ = 1.69 [s, 30 H, $C_5(CH_3)_5$], 2.14 (s, 6 H, outer CH_3), 2.16 (s, 6 H, inner CH_3), 3.98 (m, 2 H, H'_a), 4.07 (m, 2 H, H'_b), 4.38 (m, 2 H, H_a), 4.79 (m, 2 H, H_b), 6.83 (m, 4 H, inner C_6H_4), 6.92 (m, 4 H, outer C_6H_4), 6.98 (m, 4 H, inner C_6H_4), 7.28 (m, 4 H, outer C_6H_4) ppm. ^{13}C NMR (125.8 MHz, C_6D_6, 300 K):[48] δ = 12.5 [$C_5(CH_3)_5$], 21.0 (each C_6H_4-CH_3), 104.0 (C_a), 106.5 (C'_a), 108.4 (C'_b), 108.5 (C_e), 111.9 (C_b), 113.5 [$C_5(CH_3)_5$], 125.6 (Ci), 126.3 (outer C_6H_4), 128.5 (outer C_6H_4), 128.8 (inner C_6H_4), 132.0 (outer *i*-C_6H_4-C6), 132.2 (inner C_6H_4), 133.9 (inner *i*-C_6H_4-CH_3), 141.7 (outer *i*-C_6H_4-C6), 144.1 (inner *i*-C_6H_4-C6) ppm. IR (KBr): $\tilde{\nu}$ = 2915 (m), 2859 (m), 2745 (m), 1894 (w), 1746, 1605, 1505 (s), 1460 (s), 1375 (s), 1296, 1260 (w), 1159, 1103, 1067, 1020 (m), 905, 804, 731 cm^{-1}. MS (70 eV): *m/z* (%) = 441 (100) [M^+ – N_2 – Cp*Ti(*p*-Tolfv)], 307 (28). $C_{60}H_{66}N_2Ti_2$ (910.56): calcd. C 79.11, H 7.30, N 3.08; found C 78.93, H 7.42, N 3.05.

[Bis{[η^6-6,6-bis(*p*-fluorophenyl)pentafulvene](η^5-pentamethylcyclopentadienyl)titanium}-μ^2-η^1,η^1-dinitrogen] (7): Sodium amalgam (2.38 g, 20% Na, 20.73 mmol Na), di-*para*-fluorofulvene **3** (1.84 g, 6.91 mmol) and $[(\eta^5\text{-}C_5Me_5)TiCl_3]$ (**1**) (2.00 g, 6.91 mmol) were placed in a Schlenk tube. At a temperature of 0 °C (ice bath) THF (100 mL) was added under an excess nitrogen pressure of 200 mbar. The reaction mixture was stirred for 16 h. A colour change from red to dark green occurred. The reaction mixture was filtered twice (first P4/Celite, then P5). Removing the solvent under vacuum led to a brown residue, which became dark green again after adding N_2. After recrystallisation from *n*-hexane (20 mL) at –20 °C, **7** could be isolated as dark green crystals with a cupric lustre. Yield: 2.56 g (80%). M.p. 138–140 °C. ^{1}H NMR (500.1 MHz, C_6D_6, 300 K):[48] δ = 1.56 [s, 30 H, $C_5(CH_3)_5$], 3.87 (m, 2 H, H'_a), 4.17 (m, 4 H, H_a and H'_b), 4.86 (m, 2 H, H_b), 6.68 [m, *J* = 8.1 Hz, 4 H, ^3J(H,F) = 8.5 Hz, inner C_4H_6F], 6.75 (m, *J* = 8.4 Hz, 4 H, $^3J_{H,F}$ = 8.5 Hz, outer C_4H_6F), 6.81 (m, 4 H, inner C_4H_6F), 7.05 (m, 4 H, outer C_4H_6F) ppm. ^{13}C NMR (125.8 MHz, C_6D_6, 300 K):[48] δ = 12.4 [$C_5(CH_3)_5$], 104.1 (C_a), 105.7 (C_{exo}), 105.9 (C'_a), 108.0 (C'_b), 112.3 (C_b), 114.0 [$C_5(CH_3)_5$], 114.6 (outer C_4H_6F, d, $^2J_{C,F}$ = 21 Hz), 114.7 (inner C_4H_6F, d, $^2J_{C,F}$ = 21 Hz), 125.4 (Ci), 133.5 (outer C_4H_6F, d, $^3J_{C,F}$ = 8 Hz), 133.5 (inner C_4H_6F, d, $^3J_{C,F}$ = 8 Hz), 140.4 (outer *i*-C_6H_4-C6, d, $^4J_{C,F}$ = 3 Hz), 142.8 (inner *i*-C_6H_4-C6, d, $^4J_{C,F}$ = 3 Hz), 159.9 (outer *i*-C_6H_4-F, d, $^1J_{C,F}$ = 244 Hz), 162.2 (inner *i*-C_6H_4-F, d, $^1J_{C,F}$ = 244 Hz) ppm. ^{19}F NMR (282.4 MHz, C_6D_6, 303 K): δ = –115.8 (2F) ppm.- MS (CI, isobutane): *m/z* (%) = 938 (65) [469 × 2], 469 (100) [M^+ – N_2 – Cp*Ti(*p*-Ffv) + HF], 450 (20) [M+ – N_2 – Cp*Ti(*p*-Ffv) + H]. $C_{56}H_{54}F_4N_2Ti_2$ (926.81): calcd. C 72.57, H 5.87, N 3.02; found C 72.16, H 6.11, N 2.37.

[Bis{(η^6-adamantylidenepentafulvene)(η^5-pentamethylcyclopentadienyl)titanium}-μ^2-η^1,η^1-dinitrogen] (8): Sodium amalgam (2.38 g, 20% Na, 20.73 mmol Na), adamantylidenepentafulvene **4** (1.37 g, 6.91 mmol) and $[(\eta^5\text{-}C_5Me_5)TiCl_3]$ (**1**) (2.00 g, 6.91 mmol) were placed in a Schlenk tube. At a temperature of 0 °C (ice bath) THF (100 mL) was added under an excess nitrogen pressure of 200 mbar. The reaction mixture was stirred for 16 h. A colour change from red to dark blue occurred. The reaction mixture was filtered twice (first P4/Celite, then P5). Removing the solvent under vacuum led to a turquoise residue, which became dark blue again after adding N_2. After recrystallisation from *n*-hexane (20 mL) at –20 °C, **8** could be isolated as dark blue crystals with a cupric lustre. Yield: 2.46 g (90%). M.p. 175 °C. ^{1}H NMR (500.1 MHz, C_6D_6, 300 K):[48] δ = 1.75 (s, 30 H, $C_5(CH_3)_5$), 1.48–2.53 (m, 28 H, $H_{Adamantyl}$), 3.64 (m, 2 H, H_a), 4.20, (m, 2 H, H'_a), 5.10 (m, 2 H, H_b), 5.69 (m, 2 H, H'_b) ppm. ^{13}C NMR (125.8 MHz, C_6D_6, 300 K):[48] δ = 12.3 [$C_5(CH_3)_5$], 29.2, 30.2, 34.1, 34.9, 38.2, 38.8, 39.0, 43.4, 45.4 ($C_{Adamantyl}$), 103.2 (C_a), 103.7 (C'_b), 104.5 (C'_a), 113.3 (C_b), 107.9 (C_e), 112.8 [$C_5(CH_3)_5$], 125.2 (Ci) ppm. MS (70 eV): *m/z* (%) = 381 (100) [M^+ – N_2 – Cp*Ti{$C_5H_4(C_{10}H_{14})$}]. $C_{50}H_{66}N_2Ti_2$ (790.85): calcd. C 75.94, H 8.41, N 3.54; found C 75.76, H 8.45, N 3.47.

[{η^6-10,10-Bis(*p*-tolyl)benzofulvene}(η^5-pentamethylcyclopentadienyl)titanium] (10): Sodium amalgam (2.38 g, 20% Na, 20.73 mmol Na), di-*p*-tolylbenzofulvene (**5**) (2.13g, 6.91 mmol) and $[(\eta^5\text{-}C_5Me_5)TiCl_3]$ (**1**) (2.00 g, 6.91 mmol) were placed in a Schlenk tube. At a temperature of 0 °C (ice bath) THF (100 mL) was added under an excess nitrogen pressure of 200 mbar. The reaction mixture was stirred for 16 h. A colour change from red to brownish green occurred. The reaction mixture was filtered twice (first P4/Celite, then P5). Removing the solvent under vacuum led to a brown residue, which was recrystallised from *n*-hexane (20 mL) at –20 °C. Compound **10** could be isolated as black needle-shaped crystals. Yield: 2.8 g (85%). M.p. 115 °C. MS (70 eV): *m/z* (%) = 491 (100) [M^+], 308 (80) [di-*para*-tolylbenzofulvene$^+$]. $C_{34}H_{35}Ti$ (491.51): calcd. C 83.08, H 7.18; found C 83.04, H 7.21.

Di-*p*-tolylbenzofulvene (5): During 30 minutes, *n*BuLi (40.5 mL, 1.6 M) was added dropwise to a cooled solution (0 °C) of freshly distilled indene (9.8 mL, 0.082 mol) in THF (170 mL). The mixture was cooled to –60 °C, and 4,4′-dimethylbenzophenone (17.24 g, 0.082 mol) dissolved in THF (120 mL) was added. The reaction mixture was stirred overnight at room temperature. Then, water and diethyl ether were added, and the ether phase was extracted with water until pH 7 was reached. The ether phase was dried with $MgSO_4$, and the solvent was evaporated. After that the residue was dissolved in *n*-hexane (200 mL) and cooled rapidly. The precipitated crystalline solid was filtered and dried. Finally, the product could be isolated as orange crystals after recrystallisation from *n*-hexane/dichloromethane (2:1). Yield: 19.0 g (75%). M.p. 130–131 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K):[48] δ = 2.46 (s, 3 H, H-20), 2.52 (s, 3 H, H-15), 6.75 (m, 1 H, H-2), 6.79 (m, 1 H, H-8),

Table 4. Crystal structure data for compounds **6**, **8**, **10** and **5**.

	6	**8**	**10**	**5**
Empirical formula	$C_{66}H_{80}N_2Ti_2$	$C_{50}H_{66}N_2Ti_2$	$C_{34}H_{35}Ti$	$C_{24}H_{20}$
Formula mass	997.12	790.85	491.52	308.40
Diffractometer	STOE IPDS	STOE IPDS	STOE IPDS	STOE IPDS
Crystal dimensions [mm]	0.45 × 0.38 × 0.36	0.52 × 0.04 × 0.04	0.30 × 0.16 × 0.13	0.21 × 0.19 × 0.18
Colour, habit	dark green, red	dark blue, red	black	orange
Crystal system	triclinic	monoclinic	triclinic	triclinic
a [Å]	11.0985(6)	29.2685(18)	8.1648(5)	9.2556(10)
b [Å]	12.9268(5)	10.0234(4)	12.5378(9)	9.3584(12)
c [Å]	19.5985(10)	29.713(2)	13.9286(10)	11.0345(14)
α [°]	86.095(5)	90	74.338(8)	71.141(14)
β [°]	87.996(6)	104.619(8)	74.302(8)	67.960(13)
γ [°]	81.364(5)	90	77.604(8)	85.793(14)
V [Å]^3	2772.6(2)	8434.7(9)	1306.19(15)	837.12(18)
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	2	8	2	2
D_{calcd} [Mg·m^{-3}]	1.194	1.246	1.250	1.224
μ [mm^{-1}]	0.330	0.415	0.348	0.069
F(000)	1068	3392	522	328
λ (Mo-K_α, graphite) [Å]	0.71073	0.71073	0.71073	0.71073
Temperature [K]	193(2)	193(2)	193(2)	193(2)
θ range for data collection [°]	2.11 to 25.90	2.09 to 26.06	2.62 to 25.97	2.30 to 26.02
Number of reflections collected	33979	69268	16076	10252
Number of observed reflections [$I > 2\sigma(I)$]	6285	5786	3308	1760
Number of independent reflections	10040	15703	4750	3057
Absorption correction method	none	none	none	None
Max. and min. transmission	0.8906 and 0.8659	0.9836 and 0.8131	0.9562 and 0.9028	0.9877 and 0.9857
Number of data/restraints/parameters	10040/27/634	15703/0/973	4750/0/316	3057/0/297
R indices (all data)	$R1 = 0.0868$, $wR2 = 0.1370$	$R1 = 0.1626$, $wR2 = 0.1392$	$R1 = 0.0693$, $wR2 = 0.1131$	$R1 = 0.0824$, $wR2 = 0.0770$
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0510$, $wR2 = 0.1245$	$R1 = 0.0494$, $wR2 = 0.0946$	$R1 = 0.0427$, $wR2 = 0.1047$	$R1 = 0.0374$, $wR2 = 0.0680$
GoF on F^2	0.908	0.601	0.958	0.816
Largest difference peak and hole [e·Å^{-3}]	0.556 and –0.383	0.307 and –0.280	0.414 and –0.424	0.160 and –0.161

6.94 (m, 1 H, H-3), 6.94 (m, 1 H, H-7), 7.20 (m, 1 H, H-6) 7.24 (m, 2 H, H-18), 7.27 (m, 2 H, H-17), 7.30 (m, 2 H, H-13), 7.34 (m, 2 H, H-12), 7.35 (m, 1 H, H-5) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K):[48] δ = 21.3 (C-20), 21.4 (C-15), 120.7 (C-5), 123.4 (C-8), 124.3 (C-7), 126.8 (C-6), 128.5 (C-18), 129.2 (C-13), 130.4 (C-12), 130.7 (C-2, C-3), 131.7 (C-17), 136.0 (C-4), 138.1 (C-19*), 138.2 (C-9*), 138.4 (C-14), 138.7 (C-11), 139.7 (C-16), 144.3 (Ci), 147.4 (C_e) ppm (*assignment might be interchanged).

X-ray Crystallographic Study: Data for the structures **6**, **8**, **10** and **5** were collected on a STOE-IPDS diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). A summary of crystal data and intensity collection and refinement parameters is reported in Table 4. Intensity measurements were performed at 193(2) K. The structure of all complexes was solved by direct phase determination (SHELXL 97) and refined on F^2 (SHELXL 97)[52] with anisotropic thermal parameters for all non-hydrogen atoms.

Additionally crystallographic data for the structures **6**, **8**, **10**, and **5** have been deposited. CCDC-161093 (**6**), -252794 (**8**), -252795 (**10**), and -252796 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information Available (see also footnote on the first page of this article).

Acknowledgments

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