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Mono- and bi-dentate Group 6-coordinated and titanium-containing isocyanide ligands prepared from benzoxazole†

Jin An, Lizette van Niekerk, Catharine Esterhuysen and Helgard G. Raubenheimer*

Department of Chemistry, University of Stellenbosch, Private Bag X1, 7602 Matieland, South Africa. E-mail: hgr@sun.ac.za

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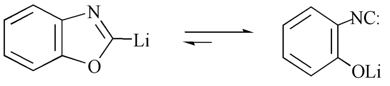
Reaction of lithiated benzoxazole with Group 6 carbonyl complexes and subsequently with Cp_2TiCl_2 affords bimetallic systems in which the titanium is O-bonded and the Group 6 metal isocyanide-coordinated. Depending on starting material and reaction conditions the cyclopentadienyl titanium complex may act as either a mono- or bi-dentate ligand. Crystal and molecular structures of $[(CO)_5Cr\{CN(C_6H_4\text{-}o)O\}Ti(Cl)Cp_2]$ (**1**) and $[(CO)_4Cr\{CN(C_6H_4\text{-}o)O\}_2TiCp_2]$ (**2**), are reported. The heterometallacyclic ring in **2** contains 12 atoms.

Introduction

Anionic Fischer-type carbene ligands, prepared by the standard addition of organolithium compounds to metal carbonyls, act as monodentate ligands towards transition metals like titanium and zirconium.[1] We were recently able to show that such compounds, with certain heteroatom-containing organo-groups, also coordinate in a bidentate fashion.[2] In a preliminary attempt to utilise an anionic carbene complex, $[(CO)_5Cr{=}C(O)\overline{C{=}NC_6H_4O}\text{-}o]^-$, as a bidentate ligand towards Cp_2TiCl_2, $Cr(CO)_6$ was treated with lithiated benzoxazole and the product mixture reacted with titanocene dichloride. The penta- and tetra-carbonyl chromium isocyanide complexes **1** and **2** (*vide infra*) formed in low yields, indicating that the tautomeric equilibrium in Scheme 1[3] cannot be reversed to afford nucleophilic CO attack. Di- and even tri-dentate isocyanide containing ligands have been prepared and studied in the groups of Angelici,[4] Hahn[5] and others.[6] Chelate formation is only possible if twelve or larger membered rings are formed. Usually, complex formation involves the substitution of labile ligands such as of COD (COD = cyclooctadiene), NOR (NOR = norbornadiene) or η^6-C_7H_8 respectively, in $[Rh(COD)Cl]_2$,[4] $[M(CO)_4(NOR)]$ (M=Cr, Mo),[5] $[M(CO)_3(\eta^6\text{-}C_7H_8)]$ (M = Cr, Mo, W)[5] or by occupying the free coordination position after reaction of $[M(CO)_5I][Et_4N]$ (M = Cr, W) and Ag^+ ions.[4] All ligands are similar in that they consist of isocyanide units connected by nonmetallic atoms or groups, thus forming nonmetallic di- and tri-dentate isocyanide ligands. The chemistry of multidentate isocyanide ligands has attracted special attention, due to their potential use in nuclear medicine for the complexation of ^{99m}Tc.[7]



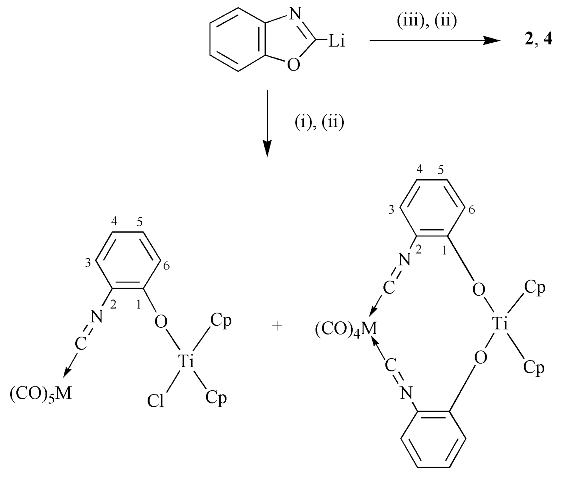
Scheme 1

We describe here labile ligand substitution in $M(CO)_5(THF)$ and $M(CO)_4(NOR)$ (M = Cr, Mo or W) with lithiated benzoxazole in isocyanide isomeric form and subsequent O-coordination of Cp_2TiCl_2 to furnish mono- and bi-dentate titanium-containing isocyanide ligands coordinated to Group 6 carbonyl complexes.

Results and discussion

Synthesis

Deprotonation of benzoxazole with butyllithium at −78 °C, substitutive addition to $Cr(CO)_5(THF)$ at 0 °C, and transmetallation with Cp_2TiCl_2 afforded the bimetallic compounds **1** and **2** (Scheme 2). The yield of the disubstituted carbonyl (and thus disubstituted metallocene derivative as the only product) was increased from 30 to 49% by replacing $Cr(CO)_5(THF)$ with $Cr(CO)_4(NOR)$. Molybdenum (**3** and **4**) and tungsten (**5** and **6**) analogues were prepared similarly. We have previously also observed disubstitution despite the presence of only one labile ligand in Group 6 metal complexes, with ligands containing exocyclic S- and endocyclic N- and S-donor atoms.[8]



1 M = Cr
3 M = Mo
5 M = W

2 M = Cr
4 M = Mo
6 M = W

(i) $M(CO)_5(THF)$, (ii) Cp_2TiCl_2, (iii) $M(CO)_4(NOR)$

Scheme 2

It is significant that the lithiated oxazole prefers C-isocyanide coordination to $M(CO)_5$ (M = Cr, Mo, W) whereas $CN{-}C_6H_4{-}$

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† Electronic supplementary information (ESI) available: rotatable 3-D molecular structure and packing diagrams for **1** and **2** in CHIME format. See http://www.rsc.org/suppdata/dt/b2/b200859a/

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OH-*o* readily and quantitatively converts into the aminocarbene complexes $[(CO)_5M\overline{CNHC_6H_4O}\text{-}o]$.[9] The oxophilic titanium complex, however, would drive the equilibrium completely away from a carbene form towards the isocyanide containing isomer. The ring-opened isomers in Scheme 1 have not previously been successfully trapped by O-coordination to metal compounds. Both Me_3SnCl[10] and $ZnCl_2$[11] afford C-coordinated azolyls. Even addition of only Cp_2TiCl_2 has not yet provided an exception since, in our efforts, no single products could be separated (probably due to isocyanide coordination).

Spectroscopic characterisation of complexes 1 to 6

The infrared spectra (CH_2Cl_2 solutions) of the two classes of compounds were normal in the *ν*(CO) region (see Experimental section). The CN frequencies of the monodentate isocyanide complexes **1**, **3** and **5** appear as one peak between 2142 and 2145 cm^{-1} for the pentacarbonyl complexes and increase from chromium to tungsten. The corresponding vibrations in the tetracarbonyls are more constant at 2146–2150 cm^{-1} and at 2110 cm^{-1}.

Molecular ions for all the new compounds were observed in the 70 eV mass spectra. This was followed by consecutive loss of carbonyl ligands as indicated in the Experimental section.

The NMR resonances are in general normal and the chemical shifts for carbonyl ligands agree with previous studies. It is significant that the doublet of doublets for H^6 (Scheme 2) appearing at *ca.* δ 7.0 for compounds **1**, **3** and **5** is shifted significantly upfield — anisotropic effects of the Cp-rings — in the disubstituted carbonyl complexes **2** (δ 6.37) and **4** (δ 6.39) but less so in complex **6** (δ 6.80) that contains the large W central atom.

Crystal and molecular structures of 1 and 2

The molecular structures of complexes **1** (Fig. 1) and **2** (Fig. 2) confirm that complex **1** contains only one isocyanide group linking the Cr and Ti moieties, whereas there are two such groups in complex **2** (the second group replacing a Cl ligand in complex **1**), resulting in the formation of a 12-membered chelate ring. In both instances the ligands are planar (maximum deviations from planarity: in complex **1**: 0.037(2) Å for C(9); in complex **2**: 0.130(1) Å for C(5) and 0.104(2) Å for C(6) in the respective isocyanide groups). In complex **2** the two isocyanide ligands are nearly co-planar, with the angle between the two planes being 5.61(9)°.

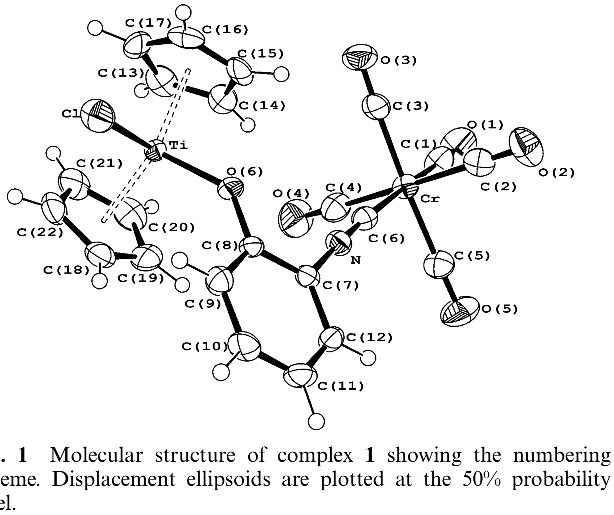

Fig. 1 Molecular structure of complex **1** showing the numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

Surprisingly the formation of the chelate ring has no significant effect on the bond lengths and angles involving Ti and Cr. All Ti–O, Ti–C and Cr–C bond lengths are comparable for complexes **1** and **2**. C–Cr–C angles vary between 86.8(1) and 92.7(1)° for complex **1**, while for complex **2** they vary between 86.5(1) and 93.3(1)°, with a chelate "bite angle" of 86.90(9)°. The bond angles around the Ti are also very similar for complexes **1** and **2**, with Cl–Ti–O(6) (**1**) and O(5)–Ti–O(6) (**2**) angles of 95.71(5) and 95.33(7)° respectively (see Table 1). The Cp rings are similarly oriented at angles of 23.71(10) and 28.42° with respect to the O(6)–Ti–Cl plane in complex **1** and 26.6(7) and 26.7(2)° with respect to the O(5)–Ti–O(6) plane in complex **2**. This is a common characteristic: a search of the Cambridge Structural Database[12] shows that in 95% of comparable complexes (2389 structures containing any atom coordinated to two η^5-Cp rings and any two other atoms were found), the Cp rings are orientated at angles of between 16 and 37°. However, the orientation of the $TiCp_2$ moiety as a whole is the most affected by the addition of the second isocyanide donor group in complex **2**, as the severe twisting of the $TiCp_2$ unit toward the ligand plane observed in complex **1** is reduced in complex **2**. In addition, the Ti lies significantly above the isocyanide ligand plane (1.067(2) Å) in complex **1**, whereas it only elevates 0.073(1) Å above the best plane through the bidentate ligand (maximum deviation of 0.200(2) Å for C(5) in complex **2**). The opposite is observed for Cr, where in complex **1** it lies only 0.088(2) Å above the ligand plane, while in complex **2** the distance is 0.419(2) Å.

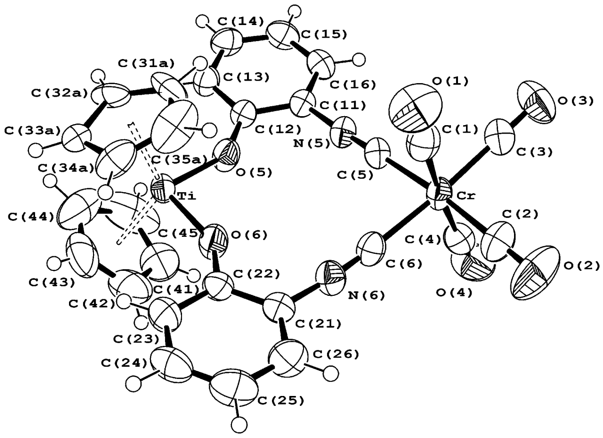

Fig. 2 Molecular structure of complex **2** showing the numbering scheme; for clarity one disordered Cp ring has been omitted. Displacement ellipsoids are plotted at the 50% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

	1	**2**
Ti–O(5)		1.9015(15)
Ti–O(6)	1.9046(14)	1.8883(17)
Ti–Cl(1)	2.3766(7)	
Cr–C(5)		1.981(2)
Cr–C(6)	1.995(3)	1.993(3)
Cl–Ti–O(6)	95.71(5)	
O(5)–Ti–O(6)		95.33(7)
C(5)–Cr–C(6)	86.76(10)	86.90(9)

The packing in complex **1** is directed by weak C–H ··· O[13] interactions between carbonyl oxygens and Cp or phenyl hydrogens (H atoms are placed in calculated positions, so H-bonds are given in terms of C ··· O and C ··· Cl distances — C(21) ··· O(3) = 3.362(3) Å, C(21)–H(21) ··· O(3) = 159.5°; C(19) ··· O(5) = 3.463(4) Å, C(19)–H(19) ··· O(5) = 153.5°) and C–H ··· Cl interactions (C(17) ··· Cl = 3.585(3) Å, C(17)–H(17) ··· Cl = 143.1°), resulting in an interlinking network of molecules with the $TiCp_2$ moieties directed towards each other in layers. These H-bonding distances compare well with literature values, with separations up to 3.59 Å ascribed to C–H ··· O bonding[14] and distances up to 3.74 Å to C–H ··· Cl bonding.[15] Similar weak C–H ··· O interactions are also observed in complex **2** between carbonyl oxygens and phenyl hydrogens (C(15) ··· O(3) = 3.417(3) Å, C(15)–H(15) ··· O(3) = 138.3°; C(24) ··· O(4) = 3.449(3) Å, C(24)–H(24) ··· O(4) = 138.9°). There is also a relatively short C–H ··· O distance on one of the disordered Cp ligands (C(32A) ··· O(2) = 3.26(2) Å, C(32A)–H(32A) ··· O(2) = 146.0°), although the accuracy of this value could be suspect.

Experimental

General procedures

All reactions and manipulations were carried out under a dry argon atmosphere using standard Schlenk and vacuum-line techniques. All solvents were dried and purified by conventional methods and were freshly distilled under argon shortly before use. Other reagents were used without further purification. Elemental analyses (C, H, N) were done on a Carlo Erba 1106 instrument. Melting points were measured in sealed capillaries with a Büchi 535 melting point apparatus and are uncorrected and NMR spectra on a Varian VXR 300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75.48 MHz) at 25 °C. Chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C in the deuterated solvents. The IR spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer. Mass spectra (EI, 70 eV) were obtained using a Finnigan Mat 8200 instrument. Only characteristic fragments containing the isotopes of the highest abundance are listed. Relative intensities, in %, are given in parentheses.

Materials

Benzoxazole, [$Cr(CO)_6$], [$Mo(CO)_6$], [$W(CO)_6$], silica gel 60 and n-butyllithium (Merck) were used without further purification. $M(CO)_5(THF)$ (M = Cr, Mo, W), bicyclo[2,2,1]heptadiene (tetracarbonyl)chromium and bicyclo[2,2,1]heptadiene (tetracarbonyl)molybdenum were prepared according to literature methods.[16] Tetrahydrofuran and diethyl ether were distilled under N_2 from sodium diphenylketyl, pentane and hexane from sodium wire and CH_2Cl_2 from CaH_2.

Synthesis of compounds

[$(CO)_5Cr\{CN(C_6H_4\text{-}o)O\}Ti(Cl)Cp_2$] (1) and [$(CO)_4Cr\{CN(C_6H_4\text{-}o)O\}_2TiCp_2$] (2). Benzoxazole (0.60 g, 5 mmol) was dissolved in THF (50 ml) and cooled to −78 °C. Standardised n-butyllithium in hexane (3.3 ml, 1.6 M, 5.3 mmol) was slowly added. The yellow solution was stirred at −78 °C for 30 min, then slowly warmed to 0 °C. After stirring for an additional 15 min, the solution was added slowly to a solution of $Cr(CO)_5(THF)$, prepared from [$Cr(CO)_6$] (3 mmol, 0.66 g) in THF (100 ml) under UV light for 3 hours. The mixture changed colour to a deep red–brown. The mixture was stirred overnight between 0 and 10 °C, to yield a red–brown solution. It was slowly added to a solution of Cp_2TiCl_2 (0.75 g, 3.0 mmol) in THF (50 ml) at −78 °C. The mixture was allowed to warm to room temperature overnight, during which time the colour changed from red–brown to deep red–brown. Solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2) at −15 °C and eluted with CH_2Cl_2–pentane (1 : 1). The red fraction containing complex **1** was collected and dried. Red–orange crystals were obtained by layering a solution of CH_2Cl_2 with pentane and cooling to −20 °C (0.053 g, 10%). mp 154–156 °C (Found: C, 50.7; H, 2.5; N, 2.4%. $C_{22}H_{14}ClCrNO_6Ti$ requires C, 50.5; H, 2.7; N, 2.7%); ν_{max}/cm^{-1} (CH_2Cl_2) 2142m (CN); 2056m, 1996sh, 1951s br (CO); δ_H (CD_2Cl_2) 7.31–7.28 (2H, m, H^3, H^5), 7.05 (1H, dd, H^6), 6.83 (1H, td, H^4), 6.44 (10H, s, 2Cp); δ_C (CD_2Cl_2) 217.3 (*trans* CO), 215.4 (*cis* CO), 178.0 (CN), 165.5, 130.4, 127.2, 119.7, 119.3 (aromatic carbons), 118.5 (2Cp); *m*/*z* 523 (M$^+$, 68), 495 (M − CO, 45), 439 (M − 3CO, 14), 411 (M − 4CO, 18), 383 (M − 5CO, 100).

The orange fraction containing complex **2** was collected, and dried. Red prismatic crystals were obtained by layering a solution of CH_2Cl_2 with hexane and cooling to −20 °C (0.17 g, 30%). mp 229–231 °C (Found: C, 57.9; H, 3.2; N, 4.9%. $C_{28}H_{18}CrN_2O_6Ti$ requires C, 58.2; H, 3.1; N, 4.8%); ν_{max}/cm^{-1} (CH_2Cl_2) 2150m, 2110m (CN); 2010m, 1924s br (CO); δ_H ($CDCl_3$) 7.31–7.21 (4H, m, H^3, H^5), 6.78 (2H, td, H^4), 6.46 (10H, s, 2Cp), 6.37 (2H, dd, H^6); δ_C ($CDCl_3$) 222.5 (*trans* CO), 219.2 (*cis* CO), 176.0 (CN), 165.3, 130.5, 128.0, 119.2, 119.1 (aromatic carbons), 117.7 (2Cp); *m*/*z* 578 (M$^+$, 8), 494 (M − 3CO, 2), 466 (M − 4CO, 28).

Repeating the above procedure with $Cr(CO)_4(NOR)$ instead of $(CO)_5Cr(THF)$ afforded only complex **2** in 49% yield.

[$(CO)_5Mo\{CN(C_6H_4\text{-}o)O\}Ti(Cl)Cp_2$] (3) and [$(CO)_4Mo\{CN(C_6H_4\text{-}o)O\}_2TiCp_2$] (4). Complexes **3** and **4** can be synthesised using a similar method to the one above, with $Mo(CO)_6$ replacing $Cr(CO)_6$.

Red crystals of complex **3** were obtained (0.067 g, 12%). mp 168–170 °C (Found: C, 46.6; H, 2.5; N, 2.3%. $C_{22}H_{14}ClMoNO_6Ti$ requires C, 46.6; H, 2.5; N, 2.5%); ν_{max}/cm^{-1} (CH_2Cl_2) 2143m (CN); 2063m, 2009sh, 1953s br (CO); δ_H (CD_2Cl_2) 7.30–7.20 (2H, m, H^3, H^5), 7.00 (1H, dd, H^6), 6.80 (1H, td, H^4), 6.41 (10H, s, 2Cp); δ_C (CD_2Cl_2) 208.0 (*trans* CO), 206.9 (*cis* CO), 166.9, 131.7, 128.2, 120.7, 120.2 (aromatic carbons), 119.6 (2Cp); *m*/*z* 567 (M$^+$, 0.2), 538 (M − CO, 4), 511 (M − 2CO, 3), 455 (M − 4CO, 3), 427 (M − 5CO, 24).

Yellow crystals of complex **4** were obtained (0.13 g, 21%). mp 182 °C (dec.) (Found: C, 54.3; H, 2.9; N, 4.3%. $C_{28}H_{18}MoN_2O_6Ti$ requires C, 54.0; H, 2.9; N, 4.5%); ν_{max}/cm^{-1} (CH_2Cl_2) 2146m, 2110m (CN); 2014m, 1935s br (CO); δ_H ($CDCl_3$) 7.25–7.18 (4H, m, H^3, H^5), 6.72 (2H, td, H^4), 6.40 (10H, s, 2Cp), 6.30 (2H, dd, H^6); δ_C (CD_2Cl_2) 211.4 (*trans* CO), 206.9 (*cis* CO), 164.5, 130.3, 127.7, 118.7, 118.6 (aromatic carbons), 117.4 (2Cp); *m*/*z* 622 (M$^+$, 12), 537 (M − 3CO, 22), 510 (M − 4CO, 10).

Replacing $(CO)_5Mo(THF)$ by $Mo(CO)_4(NOR)$ yielded only complex **4**.

[$(CO)_5W\{CN(C_6H_4\text{-}o)O\}Ti(Cl)Cp_2$] (5) and [$(CO)_4W\{CN(C_6H_4\text{-}o)O\}_2TiCp_2$] (6). Using a similar method to that for preparing complexes **1** and **2**, complexes **5** and **6** were synthesized from $W(CO)_6$ instead of the $Cr(CO)_6$.

Red crystals of complex **5** were obtained (0.19 g, 29%). mp 158–160 °C (Found: C, 40.4; H, 2.2; N, 2.3%. $C_{22}H_{14}ClWNO_6Ti$ requires C, 40.3; H, 2.2; N, 2.1%); ν_{max}/cm^{-1} (CH_2Cl_2) 2145m (CN); 2060m, 1998sh, 1947s br (CO); δ_H (CD_2Cl_2) 7.30–7.22 (2H, m, H^3, H^5), 7.01 (1H, dd, H^6), 6.80 (1H, td, H^4), 6.41 (10H, s, 2Cp); δ_C (CD_2Cl_2) 196.3 (*trans* CO), 194.4 (*cis* CO), 178.0 (CN), 165.7, 130.5, 126.9, 119.3, 118.9 (aromatic carbons), 118.2 (2Cp); *m*/*z* 655 (M$^+$, 8), 627 (M − CO, 35), 599 (M − 2CO, 2), 571 (M − 3CO, 28), 543 (M − 4CO, 23), 515 (M − 5CO, 100).

Yellow crystals of complex **6** were obtained (0.062 g, 8.7%). mp 174–176 °C (Found: C, 47.6; H, 2.4; N, 3.9%. $C_{28}H_{18}WN_2O_6Ti$ requires C, 47.4; H, 2.6; N, 3.9%); ν_{max}/cm^{-1} (CH_2Cl_2) 2146m, 2110w (CN); 2014m, 1930s br (CO); δ_H (CD_2Cl_2) 7.29 (2H, dd, H^3), 7.19 (2H, td, H^5), 6.80 (2H, dd, H^6), 6.78 (2H, td, H^4), 6.36 (10H, s, 2Cp); δ_C (CD_2Cl_2) 196.5 (*trans* CO), 194.5 (*cis* CO), 165.9, 130.8, 127.4, 120.3, 119.2 (aromatic carbons), 117.6 (2Cp); *m*/*z* 710 (M$^+$, 6), 625 (M − 3CO, 8), 599 (M − 4CO, 20).

X-Ray structure determination of complexes 1 and 2

Complex 1. Recrystallisation from CH_2Cl_2–pentane (1 : 1) at −20 °C gave crystals suitable for X-ray structure analysis. Diffraction data for an red–orange crystal of complex **1** were collected at 173(2) K on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) using ϕ and ω scans to fill the Ewald sphere (Nonius COLLECT).[17]

Table 2 Crystal data and structure refinement for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{22}H_{14}ClCrNO_6Ti$	$C_{28}H_{18}CrN_2O_6Ti$
Formula weight	523.69	578.34
T/K	173(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a/Å	25.700(1)	11.9512(1)
b/Å	10.426(1)	14.8432(2)
c/Å	16.804(2)	15.7525(2)
β/°	99.044(2)	111.644(1)
V/Å^3	4446.6(7)	2597.2(9)
Z	8	4
Calculated density/Mg m^{-3}	1.565	1.479
μ/mm^{-1}	1.006	0.771
F(000)	2112	1176
Crystal size/mm	0.35 × 0.25 × 0.15	0.28 × 0.25 × 0.23
Reflections collected	10123	17312
Unique reflections	4163 [R_{int} = 0.023]	5900 [R_{int} = 0.025]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4163/0/289	5900/10/389
R ($I > 2\sigma(I)$)	0.035	0.038
R (all data)	0.048	0.056
WR' ($I > 2\sigma(I)$)	0.094	0.095
WR' (all data)	0.102	0.104

Details of the data collection and structural refinement are summarised in Table 2. Data reduction was performed using DENZO.[18] The positions of the Ti and Cr atoms were identified from a Patterson synthesis, while the rest of the atomic positions were found from difference Fourier maps. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. All calculations were performed using SHELX-97[19] within the WINGX package.[20] Figures were generated using Ortep3 for Windows;[21] displacement ellipsoids are at the 50% probability level. Selected bond lengths and angles are given in Table 1.

Complex 2. Diffraction data for a red crystal of complex **2** were collected as for complex **1**. Details of the data collection and structural refinement are summarised in Table 2. Data reduction was performed using DENZO.[18] The positions of the Ti and Cr atoms were identified from a Patterson synthesis. After identifying the remainder of the structure from difference Fourier maps the presence of further peaks of electron density indicated that one of the Cp rings was disordered. The bond lengths in the disordered Cp ring were restrained to be identical and the sum of the site occupancies was constrained to 1. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. All calculations were performed using SHELX-97[19] within the WINGX package.[20] Figures were generated using Ortep3 for Windows.[21] Selected bond distances and angles are given in Table 1.

CCDC reference numbers 178238 and 178239.

See http://www.rsc.org/suppdata/dt/b2/b200859a/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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