Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



ansa-Chromocenes: An alternative route to Me₂Si(C₅Me₄)₂Cr

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ARTICLE INFO

Article history: Received 23 January 2010 Received in revised form 25 February 2010 Accepted 26 February 2010 Available online 4 March 2010

Keywords: X-ray crystal structures Chromium complexes ansa-Chromocenes

1. Introduction

Metallocenes with bridged cyclopentadienyl rings (ansa-metallocenes) and their derivatives have found widespread application, since the introduction of the ansa-bridge prevents the rotation around the metal-cyclopentadienyl bond, ensures a rigid ligand framework and activates the metal centre by bending of the cyclopentadienyl rings out of a linear coordination [1]. In ansa-chromocenes this pre-formed bending allowed coordination of carbon monoxide at ambient conditions [2–4], whilst unbridged Cp₂Cr loses CO to revert to the coplanar orientation of the cyclopentadienyl rings [5]. Despite a large number of reported first-row metallocenes of the general formula $(C_5R_5)_2M$ and an equally large number of ansa-metallocenes $X(C_5R_4)ML_n$ (L = neutral or anionic ligand, X = ansa-bridge), first-row ansa-metallocenes of the general formula $X(C_5R_4)_2M$ have been reported only for iron and cobalt [6,7]. The reasons for the absence of these species might be found in the formation of the empty or half-occupied 2a₁ orbital in the mean ligand plane, which is obtained upon bending of the cyclopentadienyl rings out of the linear coordination geometry of typical sandwich compounds [8]. Stable $X(C_5R_4)_2M$ complexes were obtained, when the 2a₁ orbital is filled, i.e. for Fe and Co [6]. In the case of chromium complexes, attempted synthesis of $X(C_5R_4)_2Cr$ led to insoluble, coloured and probably polymeric material [2,4,9,10]. Isolable, monomeric complexes could only obtained if an ancillary ligand, such as CO, isocyanide, pyridine, or $B(C_6F_5)_3$, was coordinated to the metal [2,3,9-15]. Two exceptions from this rule have been published: Me₂Si(C₅Me₄)₂Cr, 1, [13] and $[Me_4C_2(C_5H_4)_2Cr][HB(C_6F_5)_3]$ [15]. Formation of **1** was somewhat

ABSTRACT

The mechanism for the preparation of Me₂Si(C₅Me₄)₂Cr, **1**, from CrCl₂(THF)_x and Me₂Si(C₅Me₄)₂Li₂ was investigated and – in contrast to earlier claims – no evidence was found for the participation of an auxiliary ligand. The formation and stability of **1** is attributed to the combination of correct reaction conditions and a highly substituted ligand framework. Reactions with other ligands under identical conditions did not lead to the formation of ansa-chromocenes. Reaction with $H_4C_2Ind_2Li_2$ afforded the η^3 -Ind bridged dimer { $H_4C_2(\eta^5-Ind)(\mu-,\eta^3-Ind)Cr$ }₂, **9**. Complex **1** does not coordinate PPh₃ or carbenes, but from reaction with two equivalents of xylyl isocyanide the CH-activated complex Me₂Si(C₅Me₄)($\eta^3-C_5Me_3(H)(=CH_2)Cr(CNC_6MeH_3)_2$, **7**, was obtained. Complexes **7** and **9** were characterised by X-ray crystallography.

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peculiar and depended strongly on the point when xylyl isocyanide was introduced in the reaction [13]: (i) Without xylyl isocyanide, reaction of $Me_2Si(C_5Me_4)_2Li_2$ with $CrCl_2$ (THF)_x had been reported to yield only polymeric material [9]. (ii) Combining xylyl isocyanide with $CrCl_2$ (THF)_x before the addition of Me₂Si(C₅Me₄)₂Li₂ led to the formation of Me₂Si(C₅Me₄)₂Cr(CNC₆Me₂H₃), **2**. (iii) Combining xylyl isocyanide with Me₂Si(C₅Me₄)₂Li₂ before the addition of $CrCl_2$ (THF)_x, on the other hand, led to the isolation of **1**. (iv) Addition of xylyl isocyanide to 1 formed 2 in less than 5 min. The mechanism in Scheme 1 was proposed to explain these apparently contradicting observations [13]. The reported alkyllithium-initiated trimerisation of xylyl isocyanide to a bidentate anionic ligand **3** [16] removes the isocyanide from the reaction mixture and thus prevents formation of 2. Intermediate coordination of 3 to chromium was proposed to protect the chromium centre from polymerisation during reaction with Me₂Si(C₅Me₄)₂Li₂. In the following, we will clarify the role of ancillary bidentate ligands in the formation of 1 in an attempt to prove or disprove the mechanism proposed earlier.

2. Results and discussion

2.1. Investigation of the proposed reaction mechanism

Preliminary attempts to confirm the proposed mechanism targeted the isolation of intermediate **4**, formed upon reaction of **3** with $CrCl_2$ (THF)_x. However, reactions of $CrCl_2$ (THF)_x with **3** (either obtained as blue THF solutions upon reaction of 0.3 equiv of BuLi with xylyl isocyanide or by isolation and subsequent deprotonation of the protonated form of **3**) did not afford any identified product. In the only occasion, in which single crystals suitable for



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^{0020-1693/\$ -} see front matter @ 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2010.02.034



analysis could be obtained, the product turned out to be the simple coordination complex CrCl₂(CNC₆Me₂H₃)₄ (see Supporting Information). We thus decided to investigate reactions of Me₂Si $(C_5Me_4)_2Li_2$ with simpler model compounds of **4**, in which **3** was replaced by structurally very similar β -diketiminate ("nacnac") ligands. Reaction of nacnac^{iPr}Li with CrCl₂ was reported to yield the THF-coordinated dimer. 5a. [17] which was obtained using a slight variation of the literature method. Following the same procedure, {nacnac^{Me}Cr(μ -Cl)(THF)}₂, **5b**, was prepared (Scheme 2).

The crystal structure of 5b (Fig. 1) is very similar to the one of 5a, with the chromium centre in a square-pyramidal coordination. Average Cr-Cl and Cr-N distances in 5b (2.405 ± 0.01 Å and 2.061±0.02 Å) are slightly shorter than those observed in 5a (2.4182(6) Å and 2.071(2) Å) [17] and the bite angle of the nacnac ligand is slightly smaller (N1-Cr-N2, 5b: 89.78(6)°, 5a [17]: 91.3(1)°), but the differences are barely significant. Whilst replacement of methyl by isopropyl is normally considered to increase the steric bulk of diketiminate ligands, the effects here are rather small and barely noticeable in the structure of the dimer.

Given the comparable solid state structures of **5a** and **5b**, both complexes were reacted with Me₂Si(C₅Me₄)₂Li₂ under conditions



Scheme 2.

equivalent to the formation of 1 (THF, 0 °C). As observed for the preparation of 1, red to brown THF solutions were obtained. Evaporation and extraction yielded red (in some cases, brown) hexane extracts and – after evaporation – a reddish-brown powder, again in accordance with observations made during the preparation of **1**. However, reaction of the unidentified crude product obtained, **6**, with xvlvl isocvanide did not vield diamagnetic 2 or any other diamagnetic species after reaction. Paramagnetic ¹H NMR spectra of **6** showed a clear difference to the paramagnetic spectra of **5a** or **5b**, 1 or decomposition products after exposure to air. Variation of the solvent (THF, toluene, hexane), reaction temperature (-20 °C to reflux), reaction time (2-24 h), or the order of reagent addition did not yield 1 in any noticeable amounts (<2% formation of 2 upon reaction with isocyanide). Despite numerous attempts, no single crystals of **6** have been obtained, nor could we isolate crystals after derivatisation attempts with xylyl isocyanide or Me₃SiCl.

Given the fact that the reported, crystallized yield of 1 (46%) exceeded the possible concentration of the trimer 3, the reaction mechanism in Scheme 1 was proposed to be catalytic [13]. Indeed, when 0.9 equiv of $CrCl_2$ (THF)_x and 0.05 equiv of dimer **5b** were added to $Me_2Si(C_5Me_4)_2Li_2$ in THF, the targeted compound 1 was now obtained from the hexane extracts. Coordination of the nacnac ligand thus seems to be preferred over coordination of the second cyclopentadienyl ring (Scheme 3) and nacnacLi is released from chromium only if additional CrCl₂ is present to reform the dimer 5. The products obtained above in the presence of equimolar amounts of nacnac ligand are thus most likely the mono-coordinated intermediates **6a** and **6b**, which did not seem to crystallize easily (Scheme 3). In accordance with this, Smith and coworkers observed that reaction of Cp₂Cr with nacnacLi salts yields the mixed compounds Cp(nacnac)Cr under probable elimination of CpLi [18,19].

The highest yields of the above mentioned reaction were obtained under conditions identical to the reported formation of 1, i. e. 0 °C in THF solution with slow addition of $CrCl_2$ (THF)_x to the reaction mixture. These conditions were thus chosen to investigate



Fig. 1. Crystal structure of 5b. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected geometrical data Cr1-N1: 2.0588(15) Å, Cr1-Cl12: 2.0629(14) Å, Cr1-Cl12: 2.3944(5) Å, Cr1-Cl1A: 2.4151(5) Å, Cr1-O1: 2.3944(14) Å, N1-Cr-N2: 89.78(6)°, Cl1-Cr1-Cl1A: 82.83(2)°.



Table 1

Yields of the hexane-soluble fraction^a in the presence of different sources of auxiliary ligand.

	Mol-% ^b	Yield (%)
5b	1	60
5b	5	70
5b	10	70
nacnac ^{Me} Li	1	60
nacnac ^{Me} Li	5	70
nacnac ^{Me} Li	10	50
nacnac ^{Me} H	10	60
nacnac ^{iPr} Li	5	60
None		65 ^c

^a corrected for the formation of hexane-soluble **6a/6b**.

^b Mol-% of nacnac ligand added, i.e. $2 \times \text{mol-}\%$ of dimer **5b**.

^c Isolated yield after recrystallisation: 44%.

the influence of different sources of the nacnac ligand and its concentration on the formation of **1** (Table 1, yields are reported for the amount of unpurified hexane-soluble product to exclude the influence of crystallisation.) Obtained yields of **1** were in the range of 60–70% and seem to be rather independent from the amount, source or type of nacnac ligand used. Most surprisingly, identical yields were obtained even in the absence of any auxiliary ligand, which is in contrast to literature reports that direct reaction of lithium salts with CrCl₂ yields insoluble products [2,4,9,10] and that the reported yields for the reaction of Me₂Si(C₅Me₄)₂Li₂ with CrCl₂ (THF)_x ligand in the presence of carbon monoxide never exceeded 39% [9]. Since neither the presence of nacnac ligands, nor the original protocol of pre-reacting xylyl isocyanide with the ligand lithium salt significantly improves the reaction yield, we conclude that the formation of **1** in the original synthesis was not due to the presence of an additional coordinating ligand, but to the serendipitous choice of reaction conditions.

2.2. Further reactions of 1

Complex **1**, despite being a 16 e⁻-metallocene with pre-bent cyclopentadienyl rings, does not readily coordinate ligands other

than isocyanide or carbonyl, most likely due to steric interactions of the incoming ligand with the cyclopentadienyl methyl substituents [13]. Addition of up to 5 equiv of PPh₃ to C_6D_6 solutions of **1** did not yield any diamagnetic, NMR-observable species. Reactions of **1** with ethyl diazoacetate, at 0 °C or reflux, likewise did not yield any isolable, diamagnetic species.

If C_6D_6 solutions of **1** are reacted with excess xylyl isocyanide for prolonged reaction times, signals of **2** begin to diminish and a new asymmetric species **7** is formed. Synthesis and isolation of **7** identified it as a CH-activated bis(isocyanide) complex (Scheme 1, Fig. 2). CH-activation of an α -methyl group and exocyclic allyl coordination, instead of a simple $\eta^5 - \eta^3$ haptotropic shift, has also been observed for the coordination of a second carbonyl ligand to Me₂Si(C₅Me₄)₂Cr(CO) and was ascribed to the release of the steric strain introduced by the single-atom bridge in **1** [9]. Not surprisingly, the geometrical data of **7** (Fig. 2) resembles very closely that of its dicarbonyl analogue, **8** [9]. The only remarkable difference are a slightly increased Cr-centroid distance in **7** (1.86 Å, 1.84 Å in **8**), increased Cr–C15 (2.209(4) Å, 2.19 Å in **8**) and Cr–C_{isocyanide} distances (1.87(1) Å, Cr–C_{CO} = 1.81 Å) and an increased C1–Si1–



Fig. 2. Crystal structure of **7**. Hydrogen atoms (with exception of H12a) were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected geometrical data (Z1 = centroid C1–C5): Cr1–Z1: 1.86 Å, Cr1–C10: 2.404(4) Å, Cr1–C11: 2.227(4) Å, Cr1–C15: 2.209(4) Å, Cr1–C27: 1.885(4) Å, Cr1–C36: 1.864(5) Å, C27–N1: 1.195(5) Å, C36–N2: 1.197(5) Å, Cr1–C27–N1: 177.7(4)°, Cr1–C36–N2: 178.6(4)°, Z1–C1–S11: 152°, C1–S11–C10: 99.2(2)°.



Fig. 3. Crystal structure of **9**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected geometrical data (Z1 = centroid C1-C4, C9; Z2 = centroid C21-C24, C29): Cr1-Cr2: 2.2601(4) Å, Cr1-Z1: 1.95 Å, Cr2-Z2: 1.98 Å, Cr1-C11: 2.195(2) Å, Cr1-C33: 2.153(2) Å, Cr2-C13: 2.180(2) Å, Cr2-C31: 2.193(2) Å, Cr1-C12: 2.269(2), Cr2-C32: 2.308(2) Å, Cr1-C32: 2.240(2), Cr2-C12: 2.281(2).

C10 angle (99.2(2)° versus 98°), which all indicate a stronger steric repulsion between the isocyanide ligand and the permethylated five-membered rings in **7** than in the dicarbonyl complex. The average C–N bond length of the coordinated isocyanide ligands (1.196(5) Å) and the Cr–C_{isocyanide} distance (1.875(15) Å) are within the margin of error identical to the values found for **2** (1.191(4) and 1.876(4) Å). The C–N bond is 0.02–0.04 Å longer, the Cr–C bond 0.04–0.14 Å shorter than in Cr(CNC₆Me₂H₃)₄Cl₂ (1.156(3) and 2.017(2) Å, see Supporting Information) or Cr(CNC₆Me₂H₃)₆(1.174(7) and 1.919(7) Å),[13] indicating an increased back-donation from the chromium centre in **7** in the presence of cyclopentadienyl ligand(s).

2.3. Extension to other ligands

Given the lack of reactivity of **1**, it was of interest to explore to which extent the reaction conditions employed for the synthesis of **1** could be applied to other ligand frameworks. Our initial attempts focussed on the Me₂Si(C₅H₄)₂-ligand framework to explore the effects of unsubstituted cyclopentadienyl rings. Reaction of Me₂Si-(C₅H₄)₂Li₂ with CrCl₂ (THF)_x, initially under conditions identical to those employed in the formation of **1**, but later at different temperatures ($-78 \degree C$ to $50 \degree C$), reaction times (4-72 h), or in the presence of 0.1 equiv nacnac^{Me}Li, did not yield any characterised product. Varying amounts of hexane-soluble powders were isolated, which could neither be crystallized, nor did they show the formation of diamagnetic complexes by reactions with xylyl isocyanide.

Reaction of $CrCl_2$ (THF)_x with $H_4C_2(Ind)_2Li_2$ as well did not yield an ansa-chromocene. From isolated crystals, obtained in insufficient amounts for further analysis, the reaction product was $Ind)Cr_{2}$, 9. The structure of 9 resembles that of the unbridged compound {Ind₂Cr₂, which also crystallizes as a dimer with two η^{3} -coordinated, bridging indenyl ligands [20]. The main difference upon introduction of the ansa-bridge is the orientation of the bridging indenyl ligand which is syn (both annulated rings oriented in the same direction) in 9 and anti in {Ind₂Cr}₂. The geometric data varies slightly between 9 and $\{Ind_2Cr\}_2$, with a longer Cr-Cr distance (0.08 Å), shorter Cr-C12/C32 distances (0.03-0.05 Å) and shorter Cr-centroid distances (0.02–0.05 Å) in 9, but does not indicate noticeable steric strain introduced by the C₂ bridge. The chromium-chromium distance of 2.2601(4) Å is above the 2.0 Å threshold for Cr-Cr quadruple bonds [21], but close enough that a quadruple bond might still be considered reasonable (Fig. 3).

3. Conclusions

Formation of **1** does not rely, as was postulated before, on the presence of an ancillary ligand to prevent the formation of polymeric product. Instead, the correct choice of reaction conditions allowed the isolation from a simple reaction between the ligand lithium salt and chromium dichloride. Problems encountered by us and others in isolating ligand-free ansa-chromocenes with other ligand frameworks indicate that the stability of **1** is closely related to the permethylation of its ligand framework, which also prevents the coordination of nucleophiles other than CO and isocyanide.

4. Experimental section

All reactions, except ligand synthesis, were carried out under nitrogen atmosphere using Schlenk or glove box techniques. Solvents were dried by passage through activated aluminum oxide (MBraun SPS) and de-oxygenated by repeated extraction with nitrogen. C_6D_6 was distilled from Na and de-oxygenated by three freeze-pump-thaw cycles. $CrCl_2$ (THF)_x [22], Me₂Si(C_5Me_4)₂Li₂ [9], nacnac^{Me}H [23], nacnac^{iPr}H [24], H₄C₂(C_9H_8)₂ [25], and Me₂Si-(C_5H_5)₂ [26] were prepared as described in the literature. All other chemicals were obtained from commercial suppliers and used as received. NMR spectra were recorded on a Bruker AV 400 MHz spectrometer and referenced to residual solvent (C_6D_5H : δ 7.15). Elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montréal).

4.1. {(Nacnac^{Me})Cr(THF)(μ-Cl)}₂, 5b

Nacnac^{Me}H (7.00 g, 22.8 mmol) in THF (50 mL) is deprotonated by addition of ^{*n*}BuLi in hexane (2.7 M, 8.4 mL, 22.8 mmol) at -78 °C and warmed to room temperature under stirring. CrCl₂ (THF)_x (1 < x < 2, 6.09 g, 22.8–31.2 mmol), suspended in a minimum of THF, is added and the reaction is stirred for 24 h at room temperature to yield a green solution. The solvent is evaporated and the residue extracted with dichloromethane (100 mL). The solvent is again evaporated, the residue dissolved in a minimum of THF and kept at -30 °C to yield 6.20 g (6.67 mmol, 59%) of green crystals. ¹H RMN (400 MHz, 298 K, C₆D₆) δ 118 (bs). *Anal.* Calc. for C₅₀H₆₆Cl₂Cr₂N₄O₂: C, 64.57; H, 7.15; N, 6.04. Found: C, 63.86; N, 6.85; H, 6.09%.

4.2. {(Nacnac^{iPr})Cr(THF)(μ-Cl)}₂, **5a** [17]

Prepared using the same protocol as for **5b** in 72% yield. ¹H RMN (400 MHz, 298 K, C_6D_6) δ 127 (bs). *Anal.* Calc. for $C_{66}H_{98}Cl_2Cr_2N_4O_2$: C, 68.67; H, 8.56; N, 4.85. Found: C, 67.65; H, 8.27; N, 5.47%.

4.3. Me₂Si(C₅Me₄)₂Cr, **1** [13]

To a solution of $Me_2Si(C_5Me_4Li)_2$ (0.20 g, 0.64 mmol) in THF (20 mL) at 0 °C, a suspension of $CrCl_2$ (THF)_x (1 < x < 2, 0.17 g, 0.64–0.87 mmol) in THF (70 mL) is added dropwise over 30 min and afterwards stirred for 24 h at room temperature. The resulting red solution is evaporated to dryness and extracted with hexane (50 mL, 10 mL & 10 mL). The solution is concentrated and stored at -30 °C to yield **1** in the form of red crystals (0.10 g, 0.28 mmol, 44 %). ¹H RMN (400 MHz, 298 K, C₆D₆) δ -4 (bs). (X-ray diffraction yielded a unit cell identical to the one obtained for **1** [13].

4.4. Formation of 1 in the presence of different nacnac ligands

To a solution of Me₂Si(C₅Me₄)₂Li₂ (300 mg, 0.96 mmol) in THF (320 mL) at 0 °C, the required amount of nacnac ligand is added (see Table 1). A suspension of CrCl₂ (THF)_x (1 < x < 2, 260 mg, 0.97–1.3 mmol) in THF (80 mL) is added dropwise over 30–60 min. After stirring at room temperature for 24 h, the resulting solution is evaporated to dryness and extracted with hexane until the extract remains colourless. The hexane extracts were evaporated and yields were determined under the assumption that only 1 and **6a/6b** were obtained. (Reaction of the obtained powders with xylyl isocyanide resulted in complete disappearance of paramagnetic peaks in ¹H NMR spectra and in no other diamagnetic products than **2** and **7**.)

4.5. $Me_2Si(\eta^5-C_5Me_4)(\eta^3-C_5Me_3(H)(=CH_2))Cr(CNC_6Me_2H_3)_2$, 7

To a solution of **1** (0.10 g, 0.28 mmol) in THF (25 mL), 2,6-xylyl isocyanide (75 mg, 0.57 mmol) in THF (15 mL) were added. The solution was stirred for 48 h, concentrated and kept at $-30 \degree$ C to yield deep-orange crystals (74 mg, 71%). ¹H NMR (400 MHz, 298 K, C₆D₆): δ 6.72–6.85 (m, 6H), 2.75 (s, 3H), 2.32 (s, 6H), 2.08

Tab	le 2

Details of X-ray Diffraction Studies.

	5b	7	9
Formula M _w (g/mol); F(000) T (K); wavelength Crystal system Space group	$C_{50}H_{66}Cl_2Cr_2N_4O_2$ 929.97; 984 220; 1.54178 monoclinic $P2_1/c$	C ₃₈ H ₄ CrN ₂ Si 612.87; 656 150; 1.54178 triclinic <i>P</i> 1	C ₄₀ H ₃₂ Cr ₂ 616.66; 2560 150; 1.54178 monoclinic P2 ₁ /c
Unit cell dimensions	.,		
$a (\mathring{A})$ $b (\mathring{A})$ $c (\mathring{A})$	12.9618(3) 12.7209(3) 15.1066(4)	8.8863(7) 12.4106(9) 15.4473(12)	39.9472(8) 9.9804(2) 15.0248(3)
α (°) β (°) γ (°)	97.6750(10)	89.255(4) 89.255(4) 79.292(4)	110.4370(10)
V (Å ³); Z	2468.5(1); 2	1673.8(2); 2	5613.2(2); 8
D _{calc} (g/cm ³) θ Range (°); completeness	1.251 4.2–72.0; 1.00	1.216 2.9–71.4; 0.95	1.459 2.4–67.8; 0.99
Collected reflections;	14877; 0.022	20260; 0.095	44756; 0.015
unique reflections; R_{int}	4848; 0.022	6184; 0.041	5011; 0.036
μ (mm ⁻¹); Abs. Corr.	4.936; multiscan	3.353; multiscan	6.587; multiscan
$R_1(F); wR(F^2)$ $(I > 2\sigma(I))$	0.038; 0.112	0.065; 0.160	0.032; 0.091
$R_1(F)$; $wR(F^2)$ (all data) GoF (F^2)	0.042; 0.115 1.09	0.111; 0.185 1.04	0.033; 0.092 1.04
Residual electron	0.52, -0.30	0.67, -0.87	0.42, -0.43

(s, 6H), 2.02 (s, 6H), 1.87 (s, 3H), 1.58 (s, 3H), 1.33 (d, 3H), 1.32 (s, 3H), 0.72 (s, 3H), 0.02 (s, 3H).

4.6. $H_4C_2(C_9H_7)_2Cr$, 9

To a solution of $C_2H_4(C_9H_6Li)_2$ (0.40 g, 1.48 mmol) in THF (70 mL) at 0 °C, a suspension of CrCl₂ (THF)_x (1 < x < 2, 0.39 g, 1.5–2.0 mmol) in THF (125 mL) is added dropwise over 2 h and afterwards stirred for 24 h at room temperature. The orange solution obtained is evaporated to dryness and extracted with toluene (2 × 50 mL). The brown-orange extract is reduced to 10 mL and kept at -30 °C to yield **9** as orange crystals in amounts insufficient for further characterisation.

5. X-ray diffraction studies

Diffraction data were collected on a Bruker SMART 6000 with Montel 200 monochromator (**5b**) and a Bruker Microstar-Proteum with Helios optics (**7**, **9**), both equipped with a rotating anode source for Cu K α radiation. Cell refinement and data reduction were done using APEX2 [27]. Absorption corrections were applied using SADABS [27]. Structures were solved by direct methods using SHELXS97 and refined on F² by full-matrix least squares using SHEL XL97 [28]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropic on calculated positions using a riding model. Further experimental details are listed in Table 2 and given in the supporting information.

Acknowledgements

We thank Francine Bélanger-Gariépy for the crystal structure determination of complex **5b**. Funding was provided by the Fonds québécois de la recherche sur la nature et les technologies, and the University of Montreal.

Appendix A. Supplementary material

CCDC 723529, 723531 and 723532 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.02.034.

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