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Synthesis, characterization and crystal structure of diamagnetic tetracoordinated chromium (II) complexes supported by α-diimine ligands

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Abstract

The α -diimine ligands Ar—N=C(R)—C(R)=N—Ar (**ai**, **bi**, **c**) react with CrCl₃(thf)₃ **1** in the presence of zinc to give new diamagnetic tetrahedral chromium (II) complexes supported by α -diimine ligands **2ai** (i = 1-2), **2bi** (i = 1-2) and **2c** in good yields. All compounds were characterized by NMR and IR spectroscopy. The solid-state structure of **2b2**, which crystallized in the Orthorhombic space group P2₁2₁2₁ with unit cell parameters a = 11.825(5) Å, b = 12.034(4) Å and c = 16.393(8) Å, was established by X-ray crystallography. © 2006 Elsevier B.V. All rights reserved.

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The coordination chemistry of 1,4-diazabutadiene (dab) ligands, bis (arylimino)acenaphtene (Ar-BIAN) ligands, bis (phenylimino)camphene (Ph-BIC) and their complexes [1–8] has attracted much interest due to their unusual electron donor and acceptor properties [9,10]. Their complexes have been reported essentially for late transition metals. Organometallic compounds with diazadiene (dad) ligands have been extensively studied in recent years. Group 10 compounds with specially designed ligands containing a bulky side group have found practical uses as olefin polymerisation catalysts [11–14]. Poli et al. have recently reported about the synthesis of $MoCl_2(iPr_2-dad)_2$ [15].

Ziegler et al. have recently shown a variety of $(dad)M(CO)_4$ [16,17] with M = Cr, Mo,W. Photolysis of $M(CO)_4(iProp-dab)$ [M = Mo, W; *iProp-dab* = 1,4-diiso-propyl-1,4-diazadbuta-1,3-diene] in the presence of (E)-

cyclooctene (eco) afforded high yields of the unprecedented olefin-substituted derivatives fac-M(CO)₃(*i*Prop-dab)(η^2 -eco) [18]. Recently, Poli et al. have reported the controlled radical polymerisation of styrene with new CpMoCl₂(dad) complexes (dad:RN=CH-CH=NR with R = Ph, p-Tol, 2,6-*i*Pr₂C₆H₃ and *i*Pr) [19] and have presented results demonstrating that CpMoCl₂(*i*Pr₂-diazadiene) is an efficient catalyst for the controlled free radical polymerisation of methylacrylate, butylacrylate and styrene in the presence or absence of a catalytic promoter [20].

Diazadiene complexes of the type $(dad)CrCl_2$ have not been known, only few analogues have been recently prepared in our laboratory [(dad)MCl₂, M = Mo, W] [21,22]. Similar complexes [CrX₂(L^L) with phosphorous ligands [L^L = dippe:1,2-bis(di-*i*-propylphosphino)ethane] have been reported [23].

In the present paper, we describe the preparation of divalent chromium (II) compounds (**2ai**, **2bi**, **2c**) [24] with bulky aryl-substituted α -diimine ligands and the structure of the Cr(II) species as determined in the solid state by X-ray crystallography. Despite their formal 12-electron

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counts, neither of the diazadiene complexes (2ai, 2bi, 2c) shows any sign of agostic interactions in either the solid state or solution.

Reaction of $CrCl_3(thf)_3$ [25] with α -dimine ligand (**ai**, **bi**, **c**) in the presence of zinc at ambient temperature resulted in the formation of the Cr(II) coordination compounds (**2ai**, **2bi**, **2c**) (Scheme 1).

Compounds **2ai**, **2bi** and **2c** crystallize as green or brown crystals for **2ai**, orange or orange brown for **2bi** and yellow for **2c** from CH_2Cl_2/n -hexane. All these complexes are soluble in methylene chloride, dimethylsulfoxide, acetone and acetonitrile; they are air-sensitive and non-soluble in unpolar solvents. These compounds have been characterized by ¹H, ¹³C NMR and IR spectroscopy. The new complexes (dad)CrCl₂ exhibit spectroscopic data in agreement with the proposed structures and they are low-spin, since they

show normal NMR spectra of diamagnetic compounds, which has not been expected for d₄ complexes shown in the literature [26]. The ¹H and ¹³C NMR chemical shifts of the Ar—N=CR—CR=N—Ar subunit in the complexes **2ai**, **bi**, **c** are slightly shielded in comparison to those of the free ligands dab, Ar-BIAN and Ph-BIC similar to other complexes [17]. The iminic carbon appears between 163 and 176 ppm. The IR spectra of complexes **2ai**, **2bi** and **2c** are also instructive since, the $v_{C=N}$ stretching frequencies are different from those of the free diazadiene ligands. It is observed at 1590–1650 cm⁻¹. The Cr—Cl stretching vibration in the IR spectroscopy is observed at 540 cm⁻¹ as a weak bond which is consistent with known literature value for other chromium complexes [27].

Single crystal of $(o-Me-C_6H_4-BIAN)CrCl_2$ (2b2)[28] suitable for X-ray structural study could be grown from



a1: Ar = 2,4,6-(CH₃)₃-C₆H₂; R = CH₃ a2: Ar = 2,6-iPr₂-C₆H₃; R = CH₃

b1 : Ar = 2,6-iPr₂-C₆H₃ b2 : Ar = 0-Me-C₆H₄





Fig. 1. ORTEP representation of the molecular structure of complex **2b2** with 30% probability ellipsoids (Hydrogen atoms are omitteds for clarity). Selected bond lengths (Å) and angles (°): Cr-N1 = 2.070(8), Cr-N2 = 2.074(8), Cr-C11 = 2.190(3), Cr-C12 = 2.197(4),N1-C12 = 1,283(12), N2-C1 = 1.287(11), C1-C12 = 1.502(12), N1-C19 = 1.449(13), N2-C13 = 1.482(13), N1-Cr-N2 = 81.2(3), C1-Cr-C12 = 120.65(18), N2-Cr-C12 = 118.4(3), N1-Cr-C11 = 111.9(2), Cr-N1-C12 = 110.9(6), Cr-N2-C1 = 112.4(6).

a mixture of methylene chloride and hexane solution at ambient temperature. The molecular structure of **2b2** and the associated atom-numbering scheme are depicted in Fig. 1. The geometry around the chromium center in **2b2** is that of a distorted tetrahedral, where the relatively small N1–Cr–N2 bond angle of $81.2(3)^\circ$ is a result of chelating ligand steric constraints. The bond lengths Cr–N1 and Cr–N2 are in the order of 2.07 Å, which are very close to other Cr-imino-nitrogen bonds (2.058 Å) [29] and Arylchromium complexes (2.137 Å) [30]. The N1–C12, N2–C1 and C1–C12 bond distances are equal to 1.28(12), 1.28(11) and 1.50(12) in complex **2b2**, confirming the conjugate diimine nature of this ligand [18].

The metal-chelate ring (Cr—N2—C1—C12—N1) in complex **2b2** is almost flat as indicated by the torsion angles of $-2.02 (1.20)^{\circ}$, $1.01 (0.95)^{\circ}$ and $1.85 (1.02)^{\circ}$ for N2—C1—C12—N1, Cr—N1—C12—C1 and Cr—N2—C1 —C12, respectively. This result is very similar to those of other reported palladium acenaphtene complexes [31]. The *o*-methylphenyl groups make an angle of approximately 90° to the plane of the C=N bonds, due to the presence of the *o*-methyl substituents as appears from the torsion angles of 99.66 (1.09)°, $-86.90 (1.22)^{\circ}$, 91.58 (1.10)° and $-94.64 (1.05)^{\circ}$ for C1—N2—C13—C14, C1—N2—C13—C18, C12—N1—C19—C24 and C12—N1—C19—C20, respectively. These torsion angles are comparable to those measured for nickel complexes [8].

In conclusion, a straightforward synthetic procedure for chromium (II) complexes with α -diimine ligands was described. The application of these complexes in catalytic reactions such as polymerisation and copolymerisation of functional alkenes (methyl acrylate, styrene) is in progress.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.03.011.

References

- [1] R.A. Klein, F. Hartl, C.J. Elsevier, Organometallics 16 (1997) 1284.
- [2] R. van Asselt, C.J. Elsevier, C. Amatore, A. Jutand, Organometallics 16 (1997) 317.
- [3] R. van Asselt, K. Vrieze, C.J. Elsevier, J. Organomet. Chem. 27 (1994) 480.
- [4] J.H. Groen, J.G.P. Delis, W.N.M. van Leeuwen, K. Vrieze, Organometallics 16 (1997) 68.
- [5] J.H. Groen, C.J. Elsevier, K. Vrieze, W.J.J. Smeets, A.L. Spek, Organometallics 15 (1996) 3445.
- [6] A. Mechria, M. Rzaigui, F. Bouachir, Tetrahedron Lett. 41 (2000) 7199.
- [7] A. Mechria, M. Rzaigui, F. Bouachir, Tetrahedron Lett. 44 (2003) 6773.
- [8] A. Mechria, C. Bavoux, F. Bouachir, J. Organomet. Chem. 53 (2003) 677.
- [9] G. Van Koten, K. Vrieze, Adv. Organomet. Chem. 21 (1982) 151.

- [10] K. Vrieze, G. Van Koten, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, 1987, p. 206.
- [11] M.D. Leatherman, S.A. Svejda, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 125 (2003) 3068.
- [12] P. Preishuber-Pflugl, M. Brookhart, Macromolecules 35 (2002) 6074.
- [13] L.H. Shultz, M. Brookhart, Organometallics 20 (2001) 3975.
- [14] D.J. Tempel, L.K. Johnson, R.L. Hoff, P.S. White, M. Brookhart, J. Am. Chem. Soc. 122 (2000) 6686.
- [15] F. Stoffelbach, B. Rebiere, R. Poli, Eur. J. Inorg. Chem. (2004) 726– 731.
- [16] R.S. Herrick, C.J. Zeigler, H.B. Bohan, M. Corey, M. Eskander, J. Gigere, N. McMicken, I.E. Wrona, J. Organomet. Chem. 687 (2003) 178–184.
- [17] B. Bildstein, M. Malaun, H. Kopacka, M. Fontani, P. Zanello, Inorganica. Chim. Acta. 16–22 (2000) 300–302.
- [18] F.W. Grevels, K. Kerpen, W.E. Klotzbucher, K. Schaffner, Organometallics 20 (2001) 4775–4792.
- [19] F. Stoffelbach, R. Poli, P. Richard, J. Organomet. Chem. 663 (2002) 269–276.
- [20] F. Stoffelbach, D.M. Haddleton, R. Poli, Eur. Poly. J. 39 (2003) 2099–2105.
- [21] T. Turki, T. Guerfel, F. Bouachir, Polyhedron, in press.
- [22] T. Turki, T. Guerfel, F. Bouachir, J. Organomet. Chem. in press.
- [23] A.R. Hermes, R.J. Morris, G.S. Girolami, Organometallics 7 (1988) 2372.
- [24] The diazadiene ligands: dab [32], Ar-BIAN, Ph-BIC [31], and CrCl₃(thf)₃ [25] were obtained according to the literature procedures. General method: In an inert atmosphere, CrCl₃(thf)₃ (1 equiv.) was added to diazadiene ligand (3 equiv.) in 20 ml of anhydrous CH₂Cl₂. Zinc powder was added (5 equiv.) as a reducing agent. The product was precipitated by addition of hexane. Pure compound was isolated as a solid by crystallization from methylene chloride/ hexane solution at ambient temperature. Yields ranged from 73 to 83%. Preparation of 2a2: Complex 2a2 was obtained in 74% yield by the same procedure as a green solid. Decomposition = 345 °C; IR $(v_{C=N} = 1643; 1599 \text{ cm}^{-1}; v_{Cr-Cl} = 537 \text{ cm}^{-1})$. Anal. Calc. for C₂₈H₄₀N₂CrCl₂ (527): C, 63.75; H, 7.59; N, 5.31. Found: C, 64.05; H, 7.62; N, 5.08. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C, δ[ppm]) : $\delta = 1.40 - 1.05$ (2d, 24H, $J_{\rm HH} = 6.9$ Hz, CHMe₂) ; 2.25 (s, 6H, Me on ligand); 2.82 (sept., 4H, CH-CH₃); 7.15-7.28 (m, 6H, H_{ar} on ligand). ¹³C NMR(75.5 MHz, CD₂Cl₂, 25 °C, δ [ppm]): $\delta = 19.45$ (Me on ligand); 22.17 (Me on *i*Pr group); 22.38 (Me on *i*Pr group); 27.98 (CH on iPr group); 123.93 (Cmeta); 127.36 (Cpara);138.34 (C_{ipso}); 169.25 (C=N).
- [25] W. Herwig, H.H. Zeiss, J. Org. Chem. 9 (1958) 1404.
- [26] M.A. Babar, L.F. Larkworthy, Inorg. Chim. Acta 148 (1988) 25.
- [27] M.E. Jacox, D.E. Milligian, J. Chem. Phys. 51 (1969) 4143.
- [28] Crystallographic data for **2b2**: C26H20Cl2N2Cr; f.w. = 483.34; orthorhombic; P2₁₂₁₂₁; Z = 4; a = 11.825(5) Å; b = 12.034(4) Å; c = 16.393(8) Å; $\alpha = \beta = \gamma = 90^{\circ}$; V = 2332.8(17) Å³; $D_{calc} = 1.376$ g cm⁻³; R = 0.0735; Rw = 0.1921; $-14 \le h \le 14$; $0 \le k \le 15$; $0 \le l \le 20$; Mo (Rw = 0.7107 Å); T = 293(2) K. Atomic coordinates and anisotropic temperature factors have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 261978. 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, or deposit@ccdc.cam.ac.uk.
- [29] L.A. Mac Adams, W. Kim, L.M. Liable-sands, I. Guzei, A.L. Rheingold, K.H. Theopold, Organometallics 21 (2002) 952–960.
- [30] J.J.H. Edema, S. Gambarotta, F. Van Bolhuis, W.J.J. Smeets, A.L. Spek, M.Y. Chiang, J. Organomet. Chem. 47 (1990) 389.
- [31] R. Van Asselt, C.J. Elsevier, A.L. Spek, R. Benedix, Recl. Trav. Chim. Pays-Bas 113 (1994) 88.
- [32] H.T. Dieck, I.W. Renk, Chem. Ber. 92 (1971) 104.