www.rsc.org/chemcomm

munication

New binucleating ligands to support dizirconium organometallics

John R. Hagadorn

Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, USA. E-mail: hagadorn@stripe.colorado.edu

Received (in West Lafayette, IN, USA) 2nd August 2001, Accepted 1st September 2001 First published as an Advance Article on the web 2nd October 2001

A new class of bis(amidinato) ligands, which feature dibenzofuran or 9,9-dimethylxanthene spacers, are used to prepare structurally characterized dizirconium complexes.

The development of single-site catalysts for selective bond forming and cleaving processes is a major topic in organometallic chemistry. Toward this goal, much effort has gone into controlling chemical reactivity through the modification of supporting ligands.¹ This approach has been highly successful for the preparation of new mononuclear catalysts; however, equivalent advances have not been made for bimetallic complexes. The use of well-defined bimetallics as catalysts, however, is highly desirable because multiple metals acting cooperatively can activate substrates and perform reactions that fail to occur in mononuclear systems.^{2,3} Thus, we have begun to develop new binucleating ligands which will allow us to explore the reactivity of binuclear organometallic complexes. Here we report two new bis(amidinato)⁴ ligands and their structurally characterized Zr derivatives.



The bis(amidine) ligands (Pri_4DBF) H_2 [†] and (Pri_4Xan) H_2 were prepared by the reaction of diisopropylcarbodiimide with doubly deprotonated dibenzofuran or 9,9-dimethylxanthene.⁵ The ligands are highly soluble in hydrocarbon solvents, but they can be readily isolated as colorless crystals from warm acetonitrile solutions in moderate yield. Combustion analysis and ¹H NMR spectroscopy confirmed their formulations. IR absorption spectroscopy of (Pri_4Xan) H_2 (Nujol) revealed characteristic absorptions at v_{NH} 3440 and v_{CN} 1639 cm⁻¹. Related parameters for (Pri_4DBF) H_2 were observed at 3434, 3427, 3402 and 1633 cm⁻¹.

Entry into transition metal derivatives was accomplished by reaction of $(Pri_4DBF)H_2$ with 2 equivalents of $Zr(CH_2Ph)_4$ in toluene solution [eqn. (1)]. Removal of the volatiles under

$$(Pri_4DBF)H_2 + 2Zr(CH_2Ph)_4 \rightarrow (Pri_4DBF)Zr_2(CH_2Ph)_6 + 2PhCH_3 \quad (1)$$

reduced pressure afforded yellow $(Pri_4DBF)Zr_2(CH_2Ph)_6$ in quantitative yield. ¹H and ¹³C NMR spectroscopy (C_6D_6) reveal a symmetrical ligand environment and equivalent benzyl ligands, consistent with fast fluxional behavior in solution. Crystallization of the product, however, was slow, and crystals suitable for X-ray diffraction‡ studies were obtained only after storing Et₂O solutions at -40 °C for two weeks. The solid-state structure (Fig. 1) confirmed the formulation of the dizirconium complex. Geometry at each Zr center resembles that of the guanidinate derivative {CyNC[N(SiMe_3)_2]NCy}Zr(CH_2Ph)_3, which was recently reported by Richeson and coworkers.⁶ The η^2 -benzyl ligands feature Zr-CH₂-C_{ipso} angles of 90.9(2) and 88.1(2)° with Zr-C_{ipso} distances of 2.721(3) and 2.682(3) Å, values which are similar to other reported Zr(η^2 -benzyl) compounds.⁷ The intermetal distance of 8.574(1) Å is sig-



Fig. 1 Molecular structure of $(Pr_{4}DBF)Zr_{2}(CH_{2}Ph)_{6}$ ·1.5Et₂O drawn with 50% thermal ellipsoids. Half occupancy ether is omitted. Selected distances (Å) and angles (°): Zr1–N_{av} 2.25, Zr1–C_{av} (excl. C28) 2.27, Zr1–C28 2.721(3), Zr1–C69 4.467(4), Zr2–N_{av} 2.25, Zr2–C_{av} (excl. C49) 2.28, Zr2–C49 2.682(3), Zr2–C69 4.273(4), C48–C69, 3.756(6), Zr1–Zr2 8.574(1); Zr1–C27–C28 90.9(2), Zr2–C48–C49 88.1(2).

nificantly longer than the value predicted from simple MM2 calculations (7.3 Å). Interestingly, this is due to the presence of a cocrystallized Et₂O that is located between the two Zr atoms yet is not coordinated to either metal. The Zr–ether distances are short (Zr1–C69, 4.46 Å; Zr2–C69, 4.27 Å), with the H atoms bound to C69 approaching to within 3.5 Å of Zr2. This presents the intriguing possibility of using the intermetal gap as a docking site for incoming substrates that could subsequently react with metal-bound ligands.

The related xanthene-bridged dizirconium complex (Pri_4 -Xan) $Zr_2(CH_2Ph)_6$ was prepared following the methodology similar to that used for (Pri_4DBF) $Zr_2(CH_2Ph)_6$ (Scheme 1). The product was isolated as yellow microcrystals from toluenehexamethyldisiloxane mixtures in high yield. ¹H NMR spectra (C_6D_6) reveal a fluxional ligand environment. Crystals suitable for X-ray diffraction studies were grown from Et₂O at -40 °C. Metrical parameters (Fig. 2) are very similar to those of (Pri_4 -DBF) $Zr_2(CH_2Ph)_6$; however, the xanthene-bridge closes the gap between the two $Zr(CH_2Ph)_3$ moieties. Consequently, there is not a solvent molecule present between them, and the intermetal distance is reduced by over 2 Å [Zr1-Zr2 6.489(1)Å].

Reaction of a single equivalent $Zr(CH_2Ph)_4$ with $(Pri_4Xan)H_2$ (Scheme 1) yielded an orange solution. After stirring overnight and removal of the volatiles, the residue was extracted into warm Et₂O. Cooling to -40 °C gave orange crystals in good yield. Combustion analysis of the product indicated the





Fig. 2 Molecular structure of $(Pri_4Xan)Zr_2(CH_2Ph)_6$ ·Et₂O drawn with 50% thermal ellipsoids. Cocrystallized ether is omitted. Selected distances (Å) and angles (°): Zr1–N_{av} 2.24, Zr1–C_{av} (excl. C31) 2.28, Zr1–C31 2.627(3), Zr2–N_{av} 2.24, Zr2–C_{av} (excl. C52) 2.28, Zr2–C52 2.678(4), Zr1–Zr2 6.489(1); Zr1–C30–C31 86.2(2), Zr2–C51–C52 89.8(2).



Fig. 3 Views of the molecular structure of $(Pr_4Xan)Zr(CH_2Ph)_2$ drawn with 50% thermal ellipsoids. Prⁱ groups omitted in (b) for clarity. Selected distances (Å) and angles (°): Zr1–N1 2.269(2), Zr1–N2 2.247(2), Zr1–N3 2.288(2), Zr1–N4 2.308(2), Zr1–C30 2.280(2), Zr1–C37 2.284(2); C30–Zr1–C37 88.87(8).

empirical formula [(Pri4Xan)Zr(CH2Ph)2]n. 1H NMR spectra $(C_6 D_6)$ were also consistent with this formulation and featured a single set of resonances for the benzyl ligands. Single crystal X-ray diffraction studies revealed the product to be mononuclear, with a single Zr atom bridging the two amidinates of the (Pri₄Xan) ligand (Fig. 3). Geometry at the Zr center closely resembles that observed for Group 4 dialkyl derivatives of N₄macrocycles.8 Interestingly, there appears to be significant ring strain as a result of this binding mode. As shown in Fig. 3(b), the amidinates are bent towards Zr giving angles of 114.1(2) and 115.2(2)° for C7-C8-C13 and C23-C21-C17, respectively. Additionally, the Zr atom is coordinated ca. 1.2 Å out of each NCN amidinate plane, and the Zr-N bond lengths suggest stronger coordination to one of the amidinates. Asymmetric binding, however, is not observed by 1H NMR spectroscopy (in C_6D_6), and it is unclear whether this is due to fluxionality or a lack of asymmetry.

We thank Professor Clark R. Landis for helpful discussions and the University of Colorado for funding.

Notes and references

† All compounds analyzed satisfactorily. *Selected data* for (Pri_4DBF)H₂: ¹H NMR (d₆-acetone): δ 8.12 (d, *J* 7.7 Hz, 2H), 7.42 (t, *J* 7.5 Hz, 2H), 7.33 (d, *J* 7.3 Hz, 2H), 4.20 (br, 2H), 3.10 (br, 2H), 2.86 (br, 2H), 1.22 (br, 12H), 0.98 (br, 12H). For (Pri_4Xan)H₂: ¹H NMR (d₆-acetone): δ 7.53 (d, *J* 7.7 Hz, 2H), 7.11 (t, *J* 7.5 Hz, 2H), 6.94 (d, *J* 7.1 Hz, 2H), 4.13 (br, 2H), 2.85 (m, br, 4H), 1.63 (s, 6H), 1.36–0.80 (br, 24H). For (Pri_4DBF)Zr₂Bn₆: ¹H NMR

(C₆D₆): δ7.52 (dd, J 1.2, 7.5 Hz, 2H), 7.25 (t, J 7.6 Hz, 12H), 7.11 (t, J 7.5 Hz, 2H), 7.06-7.00 (m, 20H), 3.27 (sept, J 6.5 Hz, 4H), 2.53 (s, 12H), 1.08 (d, J 6.5 Hz, 12H), 0.93 (d, J 6.5 Hz, 12H). ¹³C{¹H} NMR (C₆D₆): δ175.9, 152.1, 143.8, 129.9, 128.5, 128.3, 126.8, 124.7, 123.7, 123.2, 121.8, 116.6, 77.2, 50.9, 25.3, 24.2. For (Pri₄Xan)Zr₂Bn₆: ¹H NMR (C₆D₆): δ7.18 (t, J7.7 Hz, 12H), 7.04 (dd, J 1.6, 7.8 Hz, 2H), 7.00 (d, J 7.3 Hz, 12H), 6.97 (t, J 7.4 Hz, 6H), 6.92 (t, 7.5 Hz, 2H), 6.71 (dd, J 1.6, 7.3 Hz, 2H), 3.36 (sept, J 6.6 Hz, 4H), 2.65 (s, 12H), 1.35 (s, 6H), 1.31 (d, J 6.5 Hz, 12H), 0.91 (d, J 6.7 Hz, 12H); ¹³C{¹H} NMR (C₆D₆): δ 177.1, 146.2, 144.3, 130.2, 129.7, 128.6, 128.3, 128.1, 127.9, 127.5, 123.7, 123.0, 120.5, 78.2, 51.0, 34.2, 33.4, 26.4, 24.2. For (Prⁱ₄Xan)ZrBn₂: ¹H NMR (C₆D₆): δ7.61 (d, J 7.6 Hz, 4H), 7.42 (t, J 7.6 Hz, 4H), 7.08 (t, J 7.3 Hz, 2H), 7.05 (dd, J 1.4 Hz, 7.3 Hz, 2H), 6.93 (dd, J 1.4, 7.9 Hz, 2H), 6.74 (t, J 7.6 Hz, 2H), 3.54 (sept, J 6.5 Hz, 4H), 2.92 (s, 4H), 1.27 (s, 6H), 1.12 (d, J 6.5 Hz, 12H), 0.84 (d, J 6.3 Hz, 12H); ¹³C{¹H} NMR (C₆D₆): δ 165.2, 148.5, 144.5, 129.1, 128.5, 128.3, 127.9, 126.7, 126.5, 125.1, 123.0, 121.6, 75.2, 50.8, 34.2, 32.5, 25.6, 25.1.

 $\ddagger Crystal data$ for (Prⁱ₄DBF)Zr₂(CH₂Ph)₆·1.5Et₂O: C₇₄H₉₁N₄O_{2.5}Zr₂, M =1258.95, triclinic, space group $P\overline{1}$ (no. 2), a = 11.392(2), b = 18.274(4), c= 18.717(4) Å, α = 109.66(3), β = 102.65(3), γ = 105.50(3)°, V = 3324.7(12) Å³, $Z = 2, \mu = 0.34 \text{ mm}^{-1}, T = -138 \text{ °C}, 20243$ independent reflections, $R_{\text{int}} = 0.0482$, 11705 observations, 783 parameters, $R_1 =$ 0.0603, $wR_2 = 0.1571$, GOF = 0.973. For $(Pr_4Xan)Zr_2(CH_2Ph)_6 \cdot Et_2O$: $C_{75}H_{92}N_4O_2Zr_2$, M = 1263.97, monoclinic, space group $P2_1/n$ (no. 14), a= 17.940(4), b = 18.075(4), c = 21.577(4) Å, $\beta = 105.70(3)^{\circ}$, V =6736(2) Å³, Z = 4, μ = 0.36 mm⁻¹, T = -138 °C, 21557 independent reflections, $R_{\text{int}} = 0.1058$, 10074 observations, 752 parameters, $R_1 =$ 0.0637, $wR_2 = 0.1561$, GOF = 0.929. For $(Pr_4Xan)Zr(CH_2Ph)_2$: $C_{43}H_{54}N_4OZr, M = 734.12$, monoclinic, space group P_{21}/c (no. 14), a =10.887(2), b = 16.325(3), c = 21.427(4) Å, $\beta = 96.47(3)^{\circ}$, V = 3784.1(13)Å³, Z = 2, $\mu = 0.33$ mm⁻¹, T = -138 °C, 12039 independent reflections, $R_{\text{int}} = 0.0554, 8425$ observations, 452 parameters, $R_1 = 0.0455, wR_2 =$ 0.1176, GOF = 1.008. Refinements were performed (SHELXTL-Plus V5.0) on F2.

CCDC reference numbers 170218–170220. See http://www.rsc.org/ suppdata/cc/b1/b106972a/ for crystallographic data in CIF or other electronic format.

- For selected reviews, see: F. Fache, E. Schulz, M. L. Tommasino and M. Lemaire, *Chem. Rev.*, 2000, **100**, 2159; A. Togni and L. M. Vananzi, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 497; M. J. Bartos, S. W. Gordon-Wylie, B. G. Fox, L. J. Wright, S. T. Weintraub, K. E. Kauffmann, E. Münck, K. L. Kostka, E. S. Uffelman, C. E. F. Rickard, K. R. Noon and T. J. Collins, *Coord. Chem. Rev.*, 1998, **174**, 361; G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.
- 2 For metalloenzymes, see: F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley Interscience, New York, 1988, 5th edn., ch. 30.
- 3 For selected synthetic examples and reviews, see: G. J. Rowlands, *Tetrahedron*, 2001, **57**, 1865; N. Wheatley and P. Kalck, *Chem. Rev.*, 1999, **99**, 3379; *Catalysis by Di- and Polynuclear Metal Cluster Complexes*, ed. R. D. Adams and F. A. Cotton, Wiley-VCH, Inc., New York, 1998; R. G. Konsler, J. Karl and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1998, **120**, 10780; T. Ooi, M. Takahashi and K. Maruoka, *Angew. Chem., Int. Ed.*, 1998, **37**, 835; J. D. Wuest, *Acc. Chem. Res.*, 1999, **32**, 81; A. Cottone III and M. J. Scott, *Organometallics*, 2000, **19**, 5254; M. E. Broussard, B. Juma, S. G. Train, W.-J. Peng, S. A. Laneman and G. G. Stanley, *Science*, 1993, **260**, 1784.
- 4 For other binucleating amidinates, see: J. R. Babcock, C. Incarvito, A. L. Rheingold, J. C. Fettinger and L. R. Sita, *Organometallics*, 1999, **18**, 5729; S. Appel, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1990, **583**, 7; C. Chen, L. H. Rees, A. R. Cowley and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 2001, 1761; M. Ruben, D. Walther, R. Knake, H. Görls and R. Beckert, *Eur. J. Inorg. Chem.*, 2000, **5**, 1055.
- 5 For related bis(phosphine) and bis(porphyrin) ligands, see: C. J. Chang, Y. Q. Deng, A. F. Heyduk, C. K. Chang and D. G. Nocera, *Inorg. Chem.*, 2000, **39**, 959; M. W. Haenel, D. Jakubik, E. Rothenberger and G. Schroth, *Chem. Ber.*, 1991, **124**, 1705.
- 6 D. Wood, G. P. A. Yap and D. S. Richeson, *Inorg. Chem.*, 1999, **38**, 5788.
- 7 B. Qian, W. J. Scanlon, M. R. Smith and D. H. Morty, *Organometallics*, 1999, **18**, 1693; R. F. Jordan, R. E. Lapointe, C. S. Bajgur, S. F. Echols and R. Willett, *J. Am. Chem. Soc.*, 1987, **109**, 4111; S. L. Latesky, A. K. McMullen, G. P. Niccolai, I. P. Rothwell and J. C. Huffman, *Organometallics*, 1985, **4**, 902.
- 8 D. G. Black, D. C. Swenson, R. F. Jordan and R. D. Rogers, *Organometallics*, 1995, **14**, 3539; M. J. Scott and S. J. Lippard, *Inorg. Chim. Acta*, 1997, **263**, 287; H. Brand and J. Arnold, *Coord. Chem. Rev.*, 1995, **140**, 137; L. Giannini, E. Solari, S. De Angelis, T. R. Ward, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1995, **117**, 5801.