Thorium Naphthalene Complexes

The First Thorium Arene Complex: A Divalent Synthon**

Ilia Korobkov, Sandro Gambarotta, and Glenn P. A. Yap*

Very strong reducing power[1] and a marked inclination toward performing cooperative attack on the same substrate[2] are the basis of the distinctive reactivity of divalent f-block metals.[3] In spite of the great interest in this field, divalent actinides remain basically unknown, possibly as a result of an intrinsic instability of this oxidation state. Moreover, the significance of the low oxidation states remains questionable, since the f electrons are expected to be more likely engaged in backbonding with the ligand rather than being metal-centered, nonbonding electrons. As a consequence, even simple salts such as UI_2[4] and ThI_2[5] are regarded as divalent only from the point of view of formula, since the f electrons are believed to be located in a type of conduction band. Nevertheless, the electron-rich nature of these species raises expectations for high reactivity and strong reducing power. This idea is substantiated by the chemical behavior of the two known U^{II} synthons,[6] and by some recent findings that a trivalent calix-tetrapyrrolide uranium compound resulted, upon reduction, in a complex series of transformations including dinitrogen cleavage, solvent deoxygenation, and depolymerization of silicone grease.[7] For thorium such chemistry is limited to a handful of trivalent compounds or synthons.[8]

Given this scenario, we became interested in exploring the chemistry of divalent Th complexes, most likely synthons, with the dual purpose of: 1) probing the stability of an oxidation state unknown for thorium and 2) preparing potent two-electron reductants for further reactivity studies. For this purpose, we focused on pyrrole-based polyanions as ligands. These species have proved their ability both to stabilize low oxidation states in large cluster structures[9] and to increase the high reactivity of the low-valent compounds even further.[3f–n] Here we describe the reduction of a tetravalent polypyrrolide thorium complex, which resulted in both solvent fragmentation and formation of the first divalent synthon thorium arene complex.

The reactions of $[\{(Et_8\text{-calix[4]tetrapyrrole})Th(\mu\text{-Cl})\}_2][K(dme)]_2$[10] (dme = 1,2-dimethoxyethane) with two equivalents of M(naphthalene) (M = K, Li) in DME afforded dark

---

[*] Prof. S. Gambarotta, Dr. I. Korobkov, Dr. G. P. A. Yap
Department of Chemistry
University of Ottawa
Ottawa, Ontario, K1N 6N5 (Canada)
Fax: (+1) 613-5672-5170
E-mail: sgambaro@science.uottawa.ca

[**] This work was supported by the Natural Sciences and Engineering Council of Canada (NSERC).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

brown solutions from which very similar diamagnetic compounds **1a** and **1b** were obtained in good yield as dark brown, extremely air sensitive crystals (see Scheme 1).

[{(Et$_8$-calix[4]tetrapyrrole)Th}{K(dme)}(η^4-C$_{10}$H$_8$)][Li(dme)$_3$] **1a**

[{(Et$_8$-calix[4]tetrapyrrole)Th}{K(dme)}(μ-η^4 : η^6-C$_{10}$H$_8$)(μ-K)]$_n$ **1b**

The formulations were provided by X-ray crystal structures (Figures 1 and 2). In both structures the Th and K atoms are located on either side of the calix[4]tetrapyrrole tetraanion. While the K atom adopts the usual bonding mode with two π- and two σ-bonded pyrrolyl rings, the coordination of the Th atom is rather unusual in comparison with other U and lanthanide complexes of the same ligand system.[11] While two rings are σ-bonded as usual, only one of the other two rings is symmetrically π-bonded. The remaining ring, located on the opposite side of the ligand, displays considerable slippage due to η^4 coordination of thorium by one ring of a naphthalene molecule.

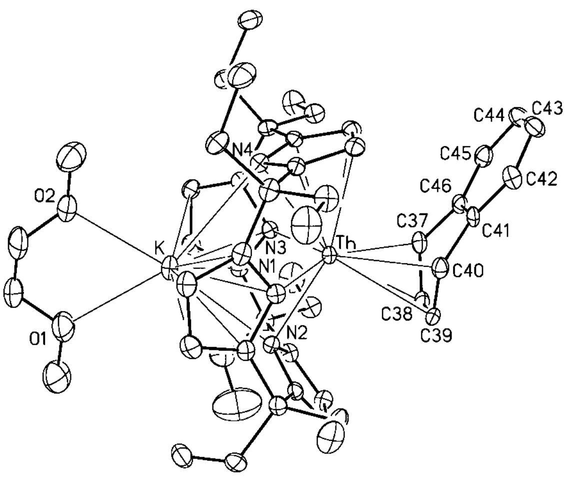


Figure 1. Thermal ellipsoid plot of the anionic moiety of **1a**. Selected bond lengths [Å]: Th-C37 2.704(6), Th-C38 2.761(6), Th-C39 2.754(6), Th-C40 2.675(6), C37-C38 1.445(9), C38-C39 1.378(9), C39-C40 1.457(9), Th-N1 2.544(5), Th-N2 2.569(5), Th-N3 2.533(5), Th-N4 2.729(5), K-N1 3.195(5), K-N2 3.024(5), K-N3 3.242(5), K-N4 3.214(5).

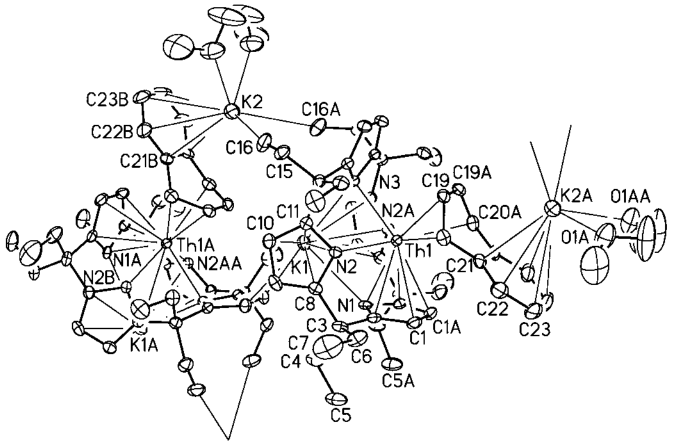


Figure 2. Thermal ellipsoid plot of **1b**. Selected bond lengths [Å]: Th-C19 2.775(4), Th-C20 2.684(5), C19-C20 1.446(6), C19-C19A 1.375(8), Th-N1 2.690(5), Th-N2 2.529(5), Th-N3 2.545(4), K1-N1 3.126(5), K1-N2 3.169(4), K1-N3 3.054(6), K2A-C21 2.982(5), K2A-C22 3.197(6), K2A-C23 3.428(6).

The major structural difference between **1a** and **1b** is determined by the second alkali-metal cation. In **1a**, an Li cation is solvated by three molecules of DME and is unconnected with the Th-containing anion. In **1b**, a second potassium atom is coordinated η^6 to the other naphthalene ring without perturbing its planarity. This second potassium atom is also engaged in substantial agostic interactions with two methyl groups of the ethyl substituents of a second molecule, and a polymeric framework is thus assembled. However, the fact that **1a** and **1b** display nearly identical NMR spectra (apart from the higher content of dme in **1a**) clearly indicates that both the agostic interactions and the polymeric structure are unlikely to be preserved in solution. Furthermore, only two signals of equal intensity are observed for the pyrrolyl rings, in agreement with two different bonding modes (σ and π), that is, slippage of one of the two π-bonded rings is rapidly averaged with the other. The naphthalene ligand shows four double doublets. The ethyl groups produced only one slightly broad triplet for the terminal methyl groups coupled to two different resonances in the ^{13}C NMR spectrum and four partly overlapping quadruplets for the methylene protons, each coupled to one ^{13}C resonance.

We observed that formation of **1b** is occasionally accompanied by tiny amount of colorless, air-sensitive, crystalline solid. The crystal quality was sufficient to allow a crystallographic structural determination. The complex is formulated as **2** (Figure 3).

[{(Et$_8$-calix[4]tetrapyrrole)Th}$_2$(μ-O)(μ-Me){K(dme)}(μ-K){K(dme)$_4$}]$_n$ **2**

In the dinuclear moiety two {(Et$_8$-calix[4]tetrapyrrole)Th} units are bridged by one oxo and one methyl ligand. In each unit, a potassium atom is both σ- and π-bonded to the ligand system. For one of them, the potassium coordination sphere is completed by one molecule of dme, and in the other the alkali metal atom interacts with one of the pyrrolyl rings of a second dinuclear unit and thus forms an infinite array. A third K atom, solvated by four molecules of DME, is unconnected to the Th-containing moiety. Regrettably, the presence of **2** in

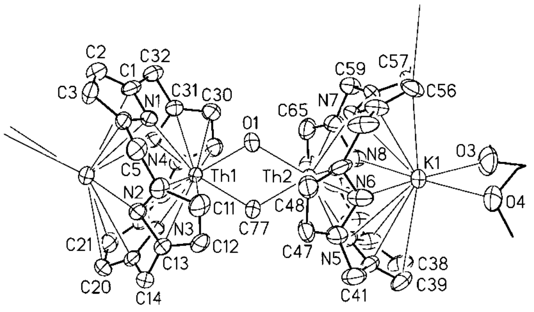


Figure 3. Thermal ellipsoid plot of the anionic moiety of **2**. Selected bond lengths [Å]: Th1-O1 2.24(2), Th2-O1 2.15(2), Th1-C77 2.50(3), Th2-C77 2.43(4), Th1-N1 2.583(9), Th1-N2 2.752(11), Th1-N3 2.610(9), Th1-N4 2.767(10), K2-N1 3.179(10), K2-N2 3.017(9), K2-N3 3.049(11), K2-N4 2.937(10), K2A-C56 3.280(14), K2A-C57 3.074(14).

the reaction mixture was not always reproducible, and the very low yield prevented satisfactory characterization. Nevertheless, the presence of the bridging methyl group was conclusively indicated by NMR spectroscopy: one sharp ^{1}H resonance at $\delta = -2.68$ ppm with the appropriate intensity ratio, coupled with a resonance at $\delta = 7.52$ ppm in the ^{13}C NMR spectrum. The formation of **2** is most likely the result of solvent fragmentation, which is a recurrent feature in the chemistry of low-valent f-block metals.[2a,b,3j,3k,7,11a] However, since **1a** and **1b** do not react with DME even on prolonged reflux, the occasional formation of **2** indicates that intermediate species, generated during reduction, are sufficiently reactive to attack the solvent.

Complexes **1** are the first thorium arene complexes to be added to the small family of actinide arene compounds.[1,6,12] Although the connectivity may imply a formal divalent oxidation state, the folding of the naphthalene ring, closely reminiscent of the bonding mode of butadiene to Cp_2Th moieties[13] or of that observed in Ln(η^4-$C_{10}H_8$) complexes,[14] clearly indicate that the f-electrons are primarily engaged in backbonding to the aromatic ring. These observations, in addition to the diamagnetism, indicate that it is unlikely this species contains the metal in the oxidation state +2. Nevertheless, **1** reacts as a Th^{II} synthon. An unusual reaction was observed on treatment of **1a** with Me_3SiN_3, which required two equivalents for the complete disappearance of **1a** (Scheme 1). After an induction period of about 15 s, vigorous gas evolution took place and a colorless suspension formed. A small amount of residual solid was identified as a DME-solvated form of KN_3 on the basis of its intense absorption at 2115 cm^{-1} in the IR spectrum, the presence of K, and the absence of the SiN band. The reaction mother liquor afforded, upon layering with heptane, the new diamagnetic and colorless complex **3** in high yield.

[(Et$_8$-calix[4]tetrapyrrole)Th{N(SiMe$_3$)$_2$}][Li(dme)$_3$] **3**

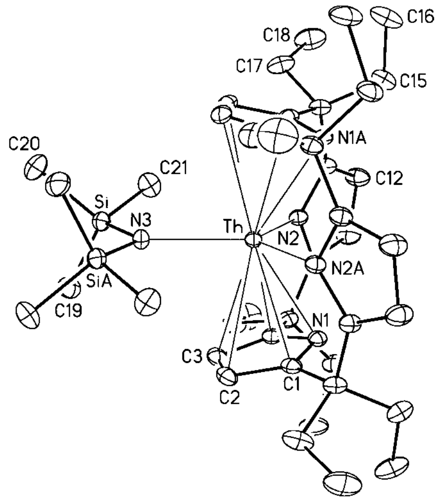
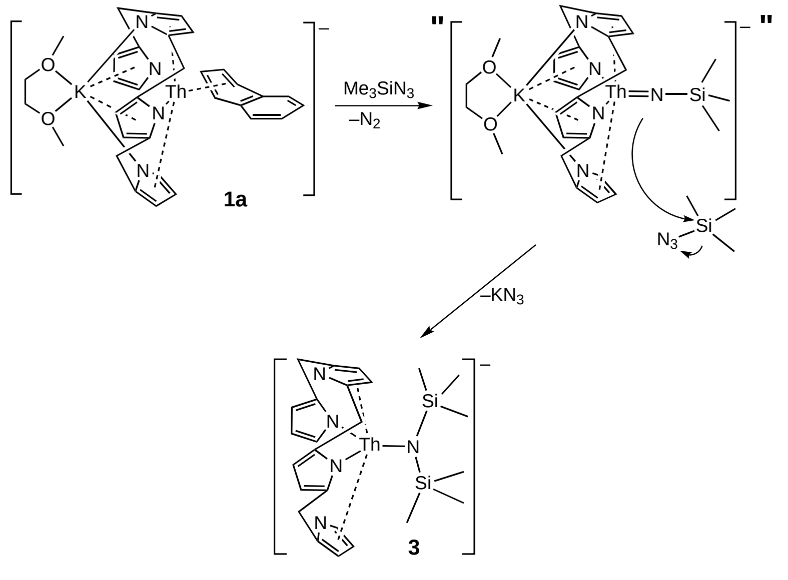


Figure 4. Thermal ellipsoid plot of the anionic moiety of **3**. Selected bond lengths [Å] and angles [°]: Th-N1 2.6640(19), Th-N2 2.4968(19), Th-N3 2.398(3), Th-C1 2.817(2), Th-C2 2.969(2), Th-C4 2.780(2); N2-Th-N2A 126.11(9), N2-Th-N3 116.94(4), Th-N3-Si 121.02(8).

The crystal structure (Figure 4) showed the ligand adopting the usual arrangement with two rings π- and two σ-bonded to the metal atom. A silazanate group is σ-bonded to the Th atom in a coplanar arrangement characteristic of metal amides. An Li atom solvated by three molecules of DME and unconnected with the Th anion completes the structure. The NMR data were in complete agreement with the crystal structure, showing two different pyrrolyl ring resonances and two sharp triplets for the eight methyl groups in accordance with their positions with respect to the silazanate group. The resonances of the methylene protons consist of four partly overlapping pseudoquadruplets coupled to only two ^{13}C NMR resonances, that is, geminal inequivalency.

The formation of **3** clearly indicates that **1a** acts as a two-electron reductant Th^{II} synthon. The first step (Scheme 1) is likely the decomposition of azide to form an imido derivative, most likely mononuclear. As usual, this process is accompanied by N_2 evolution. The final formation of **3** necessarily requires intervention of a second azide to transfer the Me_3Si group to the imide N atom and to form the silazanate group and KN_3. Further work to clarify the promising behavior of mononuclear imide derivatives is in progress.



Scheme 1. Reaction of **1a** with Me_3SiN_3.

Experimental Section

1a: In a glove box, a dark-green solution of Li(napthalene), prepared in situ by stirring Li foil (0.007 g, 1.023 mmol) and naphthalene (0.132 g, 1.030 mmol) in DME (5 mL) was rapidly added to a colorless solution of [{(Et$_8$-calix[4]tetrapyrrole)Th(μ-Cl)}$_2$][K(dme)]$_2$[10] (0.501 g, 0.512 mmol) in DME (7 mL). The color of the reaction mixture changed to dark brown-red, and stirring was continued at room temperature for 6 h. A small amount of insoluble material was separated by filtration. The resulting solution was concentrated to about 5 mL and layered with heptane (10 mL). After the mixture had been left to stand for two days at room temperature, the mother liquor was placed in a freezer at −37 °C. After 12 h, dark-brown prisms of **1a** separated (0.427 g, 0.328 mmol, 64 %). Elemental analysis (%) calcd for $C_{62}H_{96}N_4O_8ThLiK$: C 57.13, H 7.42, N 4.30, found: C 57.01, H 7.37, N 4.25. ^{1}H NMR (500 MHz, [D$_8$]THF): $\delta = 6.27$, 5.57 (s, each 4 H, CH pyrrolyl), 1.93–1.62 (4 q, overlapping, 16 H, CH_2 ethyl), 0.51 (t, 24 H, CH_3 ethyl), 5.96, 5.39, 4.56, 2.18 (dd, each 2 H, CH naphthalene), 3.27 (s, 24 H, CH_3 dme), 3.41 ppm (s, 16 H, CH_2 dme); ^{13}C NMR (125.72 MHz, [D$_8$]THF): $\delta = 115.79$, 101.94 (CH pyrrole), 34.73, 32.66, 31.93, 31.09 (CH_2 ethyl), 10.01, 9.65 (CH_3 ethyl), 125.75, 119.56, 114.95, 94.42 (CH naphthalene), 59.06 (CH_3 dme), 72.94 (CH_2 dme), 149.87, 128.75, 47.86, 47.27 ppm (quaternary C).

1b: Yield 79 % at room temperature. Elemental analysis (%) calcd for $C_{50}H_{66}N_4O_2ThK_2$: C 56.37, H 6.24, N 5.26; found: C 56.01, H 6.07, N 5.15. ^{1}H NMR (500 MHz, [D$_8$]THF): $\delta = 6.31$, 5.60 (s, each 4 H, CH pyrrolyl), 2.03–1.81 (4 q, overlapping, 16 H, CH_2 ethyl), 0.52 (2 t, overlapping, 24 H, CH_3 ethyl), 6.03, 5.43, 4.60, 2.20 (br s, each 2 H, CH naphthalene), 3.27 (s, 6 H, CH_3 dme), 3.43 ppm (s, 4 H, CH_2 dme); ^{13}C NMR (125.72 MHz, [D$_8$]THF): $\delta = 116.02$, 102.23 (CH pyrrole), 34.72, 31.86, 30.91, 29.61 (CH_2 ethyl), 9.95, 9.78, 9.67, 9.51 (CH_3 ethyl), 126.65, 120.40, 115.32, 92.80 (CH naphthalene), 59.07 (CH_3 dme), 72.94 (CH_2 DME), 149.78, 128.75, 47.89, 47.21 ppm (quaternary C).

3: A dark brown-red solution of **1a** (0.400 g, 0.307 mmol) in DME (5 mL) was treated with neat $(CH_3)_3SiN_3$ (0.071 g, 0.62 mmol) dropwise at room temperature. After about 15 s vigorous gas evolution was observed, accompanied by complete decoloration of the solution. The reaction mixture was stirred at room temperature for 2 h. A small amount of colorless insoluble material was separated by filtration, and the resulting solution was concentrated to about 2 mL and layered with 8 mL of heptane. After 2 d at room temperature colorless crystals of **3** separated (0.301 g, 0.25 mmol, 81 %). Elemental analysis (%) calcd for $C_{54}H_{96}N_5O_6Si_2ThLi$: C 53.76, H 8.02, N 5.80; found: C 53.68, H 7.98, N 5.75. ^{1}H NMR (500 MHz, [D$_8$]THF): $\delta = 6.48$, 5.55 (s, each 4 H, CH pyrrolyl), 2.12–1.85 (8 q, overlapping, 16 H, CH_2 ethyl), 0.82, 0.46 (2 t, each 12 H, CH_3 ethyl), 3.27 (s, 24 H, CH_3 dme), 3.42 (s, 16 H, CH_2 dme), 0.14 ppm (s, 18 H, Me_3Si); ^{13}C NMR (125.72 MHz, [D$_8$]THF): $\delta = 116.14$, 102.95 (CH pyrrole), 30.69, 28.60 (CH_2 ethyl), 9.62, 9.86 (CH_3 ethyl), 6.38 (Me_3Si), 59.04 (CH_3 dme), 72.90 (CH_2 dme), 159.00, 151.96, 46.70 ppm (quaternary C).

Crystal data: **1a**: $C_{62}H_{96}N_4O_8ThKLi$, $M_r = 1303.51$, triclinic, $P\bar{1}$, $a = 13.1970(18)$, $b = 13.1904(18)$, $c = 18.966(3)$ Å, $\alpha = 105.855(2)$, $\beta = 94.643(2)$, $\gamma = 92.688(2)°$, $V = 32056.2(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.351$ Mg m^{-3}. Absorption coefficient 2.444 mm^{-1}, $F(000) = 1344$, reflections collected 24688, independent reflections 14011, GOF 1.007, $R = 0.0499$, $wR_2 = 0.1132$. **1b**: $C_{50}H_{66}N_4O_2ThK_2$, $M_r = 1065.31$, orthorhombic, *Pnma*, $a = 15.6699(18)$, $b = 13.202(2)$, $c = 16.3768(19)$ Å, $V = 4927.6(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.436$ Mg m^{-3}. Absorption coefficient 3.236 mm^{-1}, $F(000) = 2152$, reflections collected 34524, independent reflections 6198, GOF 1.030, $R = 0.0429$, $wR_2 = 0.0594$. **2**: $C_{93}H_{149}N_8O_{11}Th_2K_3$, $M_r = 2136.58$, monoclinic, $P2(1)/c$, $a = 13.5302(7)$, $b = 25.3219(13)$, $c = 30.8345(18)$ Å, $\beta = 99.350(2)°$, $V = 10423.9(10)$ Å^3, $Z = 4$, $\phi_{calcd} = 1.361$ Mg m^{-3}. Absorption coefficient 3.025 mm^{-1}, $F(000) = 4352$, reflections collected 30504, independent reflections 21644, GOF 1.040, $R = 0.0916$, $wR_2 = 0.2099$. **3**: $C_{54}H_{196}N_5O_6ThLiSi_2$, $M_r = 1206.52$, monoclinic, $C2/c$, $a = 18.503(3)$, $b = 17.592(3)$, $c = 19.194(3)$ Å, $\beta = 103.046(2)°$, $V = 6086.5(16)$ Å^3, $Z = 4$, $\phi_{calcd} = 1.317$ Mg m^{-3}. Absorption coefficient 2.536 mm^{-1}, $F(000) = 2496$, reflections collected 22358, independent reflections 7136, GOF = 1.019, $R = 0.0223$, $wR_2 = 0.0620$. CCDC-193482, -193483, -193484, and -193485 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: September 16, 2002 [Z50163]

---

[1] See for example a) W. J. Evans, N. T. Allen, J. W. Ziller, *J. Am. Chem. Soc.* **2001**, *123*, 7927; b) W. J. Evans, N. T. Allen, J. W. Ziller, *Angew. Chem.* **2002**, *114*, 369; *Angew. Chem. Int. Ed.* **2002**, *41*, 359; c) W. J. Evans, L. A. Hughes, T. P. Hanusa, *Organometallics* **1986**, *5*, 1285; d) W. J. Evans, L. A. Hughes, T. P. Hanusa, *J. Am. Chem. Soc.* **1984**, *106*, 4270; e) W. J. Evans, T. A. Ulibarri, J. W. Ziller, *J. Am. Chem. Soc.* **1988**, *110*, 6877; f) W. J. Evans, D. K. Drummond, J. W. Grate, H. Zhang, J. L. Atwood, *J. Am. Chem. Soc.* **1987**, *109*, 3928; g) W. J. Evans, J. W. Grate, R. J. Doedens, *J. Am. Chem. Soc.* **1985**, *107*, 1671; h) W. J. Evans, T. A. Ulibarri, *J. Am. Chem. Soc.* **1987**, *109*, 4292; i) W. J. Evans, D. K. Drummond, *J. Am. Chem. Soc.* **1988**, *110*, 2772; j) W. J. Evans, D. K. Drummond, L. R. Chamberlain, R. J. Doedens, S. G. Bott, H. Zhang, J. L. Atwood, *J. Am. Chem. Soc.* **1988**, *110*, 4983; k) W. J. Evans, D. K. Drummond, *J. Am. Chem. Soc.* **1986**, *108*, 7440.

[2] See for example: a) W. J. Evans, J. W. Grate, L. A. Hughes, H. Zhang, J. L. Atwood, *J. Am. Chem. Soc.* **1985**, *107*, 3728; b) H. Schumann, *Angew. Chem.* **1984**, *96*, 475; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 474; c) K. G. Wang, E. D. Stevens, S. P. Nolan, *Organometallics* **1992**, *11*, 1011; d) W. J. Evans, D. K. Drummond, S. G. Bott, J. L. Atwood, *Organometallics* **1986**, *5*, 2389; e) W. J. Evans, D. K. Drummond, *J. Am. Chem. Soc.* **1989**, *111*, 3329; f) T. Dubé, J. Guan, S. Gambarotta, G. P. A. Yap, *Chem. Eur. J.* **2001**, *7*, 374; g) T. Dubé, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 817; h) T. Dubé, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 121; i) J. Guan, T. Dubé, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 4820; j) J. Jubb, S. Gambarotta, *J. Am. Chem. Soc.* **1994**, *116*, 4477; k) T. Dubé, S. Gambarotta, G. P. A. Yap, *Angew. Chem.* **1999**, *111*, 1507; *Angew. Chem. Int. Ed.* **1999**, *38*, 1432; l) T. Dubé, S. Conoci, S. Gambarotta, G. P. A. Yap, G. Vasapollo, *Angew. Chem.* **1999**, *111*, 3890; *Angew. Chem. Int. Ed.* **1999**, *38*, 3657; m) T. Dubé, S. Conoci, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 3716; n) M. Ganesan, M. P. Lalonde, S, Gambarotta, G. P. A. Yap, *Organometallics* **2001**, *20*, 2443.

[3] See for example F. T. Edelmann in *Comprehensive Organometallic Chemistry*, 2nd ed. (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**.

[4] a) H. P. Beck, H. Schuster, *Z. Anorg. Allg. Chem.* **1993**, *619*, 690; b) S. G. Bratsch, J. J. Lagowski, *J. Phys. Chem.* **1986**, *90*, 307.

[5] L. J. Guggenberger, R. A. Jacobson, *Inorg. Chem.* **1968**, *7*, 2257.

[6] The term "synthon" was forged by Corey and used to define "a structural unit within a molecule related to a possible synthetic operation". In coordination and organometallic chemistry, it can be also attributed to molecules that behave as synthetic equivalents of species that unlikely exist. a) P. Diaconescu, P. L. Arnold, T. Baker, D. Mindiola, C. C. Cummins, *J. Am. Chem. Soc.* **2000**, *122*, 6108; b) B. P. Warner, B. L. Scott, C. J. Burns, *Angew. Chem.* **1998**, *110*, 1005; *Angew. Chem. Int. Ed.* **1998**, *37*, 959; c) P. J. Fagan, J. M. Manriquez, T. J. Marks, C. S. Day, S. H. Vollmer, V. W. Day, *Organometallics* **1982**, *1*, 170.

[7] I. Khorobkov, S. Gambarotta, G. P. A. Yap, *Angew. Chem.* **2002**, *114*, 3583; *Angew. Chem. Int. Ed.* **2002**, *41*, 3433.

[8] a) J. S. Parry, G. F. N. Cloke, S. J. Cole, M. B. Hursthouse, *J. Am. Chem. Soc.* **1999**, *121*, 6867, and references therein; b) B. Kannellakopulos, E. Dornberger, F. Baumgaertner, *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 155; c) P. C. Blake, M. F. Lappert, J. L. Atwood, H. Zhang, *J. Chem. Soc. Chem. Commun.* **1986**, 1148; d) M. R. Spirlet, J. Rebizant, J. Goffart, *Acta Crystallogr. Sect. B* **1982**, *38*, 2400.

[9] a) D. M. M. Freckmann, T. Dubé, C. D. Bérubé, S. Gambarotta, G. P. A. Yap, *Organometallics* **2002**, *21*, 1240; b) M. Ganesan, S. Gambarotta, G. P. A. Yap, *Angew. Chem.* **2001**, *113*, 766; *Angew. Chem. Int. Ed.* **2001**, *40*, 788; c) T. Dube, D. M. M. Freckmann, S.

Conoci, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 209.

[10] I. Khorobkov, S. Gambarotta, G. P. A. Yap, unpublished results.

[11] See for example: a) I. Korobkov, S. Gambarotta, G. P. A. Yap, *Organometallics* **2001**, *20*, 2552; b) I. Korobkov, G. Aharonian, S. Gambarotta, G. P. A. Yap, *Organometallics*, in press.

[12] F. A. Cotton, *Inorg. Chem.* **2002**, *41*, 643.

[13] a) M. D. Fryzuk, L. Jafarpour, F. M. Kerton, J. B. Love, S. J. Rettig, *Angew. Chem.* **2000**, *112*, 783; *Angew. Chem. Int. Ed.* **2000**, *39*, 767; b) M. M. Bocharev, *Chem. Rev.* **2002**, *102*, 2089.

[14] a) G. Erker, T. Mühlenbernd, R. Benn, A. Rufinska, *Organometallics* **1986**, *5*, 402; b) G. M. Smith, H. Suzuki, D. C. Sonnenberger, V. W. Day, T. J. Marks, *Organometallics* **1986**, *5*, 549.

0044-8249/03/11507-0842 $ 20.00+.50/0