DOI: 10.1002/anie.201202819

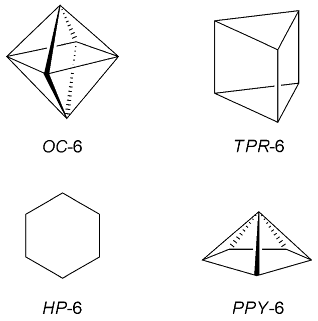
Niobium Complexes

An Organotransition-Metal Complex with Pentagonal-Pyramidal Structure**

*M. Angeles García-Monforte, Miguel Baya, Larry R. Falvello, Antonio Martín, and Babil Menjón**

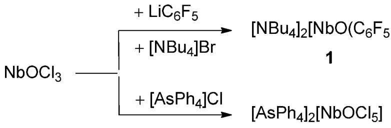
Dedicated to Professor Pablo J. Alonso on the occasion of his 60th birthday

It was Alfred Werner in the late 19th century,[1] who first suggested that six ligands should adopt an octahedral (*OC*-6) geometry around a given central atom. This geometrical arrangement minimizes repulsive effects between six ligands (LCP model) as well as between six valence-electron pairs (VSEPR model).[2] It is no wonder, then, that the many myriads of six-coordinate compounds prepared ever since, almost invariably show an *OC*-6 geometry. There are, however, some examples of alternative geometries currently known (Scheme 1).[3] Thus, a number of compounds containing dithiolato ligands[4] $[M(S_2C_2R_2)_3]^{q-}$ as well as a few homoleptic organo-transition-metal complexes[5] $[MR_6]^{q-}$ that show trigonal-prismatic (*TPR*-6) structures.[6] Hexagonal-planar (*HP*-6) structures have been found in $[Ni(E\mathit{t}Bu)_6]$ compounds (E = P, As),[7] where the nickel center is hosted by a cyclic hexadentate framework. Pentagonal-pyramidal (*PPY*-6) structures have been found mainly in post-transition-element compounds[8–10] including the fascinating species $[XeOF_5]^-$.[8a,b,10] The *PPY*-6 geometry is less frequent in transition-metal compounds, where it has been found mainly associated to either pentadentate ligands[11] or to bidentate ligands of the peroxo type[12] as in $CrO(O_2)_2py$ (py = pyridine).[13] Here we report on what we consider to be the first organo-transition-metal complex with *PPY*-6 structure.[14]



Scheme 1. Idealized geometries in six-coordinate compounds.[3]

The oxohalide compound $NbOCl_3$ reacts with LiC_6F_5 in Et_2O, in the presence of NBu_4Br, to give organoniobium(V) derivative $[NBu_4]_2[NbO(C_6F_5)_5]$ (**1**) in reasonable yield (Scheme 2 and see the Supporting Information for further details). Compound **1** was isolated as a white, air-sensitive solid, and is best kept at −30 °C to avoid thermal degradation. The IR spectrum of **1** shows a sharp signal at 986 cm^{-1}, which was assigned to the ν(NbO) mode, as well as strong bands at 1495, 953 (C–F), and 746 cm^{-1} (X-sensitive mode), which are characteristic of metal-bound C_6F_5 groups.[15]



Scheme 2. Synthetic procedures leading to $[ER_4]^+$ salts of the six-coordinate anions $[NbOX_5]^{2-}$ (X = Cl, C_6F_5) starting from the same precursor species.

The structure of **1**·*n*-hexane was established by single-crystal X-ray diffraction methods. The anion $[NbO(C_6F_5)_5]^{2-}$ (Figure 1)[16] exhibits a *PPY*-6 structure[17] according to the low continuous-shape measure (CShM) value for that geometry: $S(PPY\text{-}6) = 0.76$.[18] The oxo ligand is located in the apical position and is tightly bound to the niobium center. The observed Nb–O bond length (168.5(4) pm) coincides well with the sum of the covalent radii corresponding to a triple bond: $r_3(\mathrm{Nb}) + r_3(\mathrm{O}) = 169$ pm.[19] The *ipso* carbon atoms of the C_6F_5 groups define a nearly regular pentagonal base with long Nb–C bonds (235.6(3) pm average value). The helical arrangement of all five C_6F_5 rings around the Nb–O axis (tilt angles of approximately 75° with respect to the basal plane) makes the $[NbO(C_6F_5)_5]^{2-}$ anion chiral and both *C* and *A* configurations were present in the crystal. This arrangement is related to that found in the seven-coordinate species $[ZrF_2(C_6F_5)_5]^{3-}$, which has a pentagonal-bipyramidal (*PBPY*-7) structure with tilt angles of approximately 65° with respect to the equatorial plane.[20] It is interesting to note that, in the latter compound, the zirconium atom lies in the equatorial

---

[*] Dr. M. A. García-Monforte, Dr. M. Baya, Dr. A. Martín, Dr. B. Menjón
Instituto de Síntesis Química y Catálisis Homogénea (ISQCH)
Universidad de Zaragoza-C.S.I.C.
C/Pedro Cerbuna 12, 50009 Zaragoza (Spain)
E-mail: menjon@unizar.es
Prof. Dr. L. R. Falvello
Instituto de Ciencia de Materiales de Aragón (ICMA)
Universidad de Zaragoza-C.S.I.C.
C/Pedro Cerbuna 12, 50009 Zaragoza (Spain)

[**] This work was supported by the Spanish MICINN (DGPTC)/FEDER (Project CTQ2008-06669-C02-01/BQU) and the Gobierno de Aragón (Grupo Consolidado E21: *Química Inorgánica y de los Compuestos Organometálicos*).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201202819.

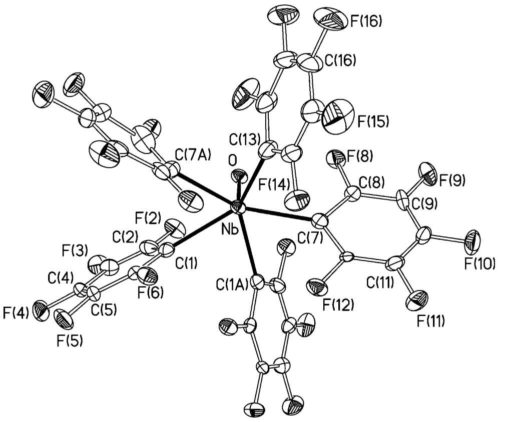
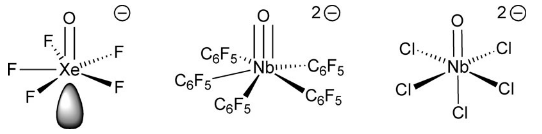


Figure 1. Displacement-ellipsoid diagram (50% probability) of the $[NbO(C_6F_5)_5]^{2-}$ anion as found in single crystals of **1**·*n*-hexane. Selected bond lengths [pm] and angles [°] with estimated standard deviations: Nb–O 168.5(4), average Nb–C 235.6(3), average C-Nb-O 101.4(2), average contiguous C-Nb-C′ 70.4(1).

plane defined by the five donor carbon atoms as expected for a *PBPY*-7 geometry. Even in the formally *PPY*-6 xenon oxyfluoride derivative $NO[XeOF_5]$ (Scheme 3) the xenon atom is only very slightly above the pentagonal plane (2.5(1) pm).[8a] This arrangement can be attributed to the presence of a stereochemically active lone valence-electron pair on the xenon atom in the hypervalent $[XeOF_5]^-$ anion, which can thus be considered as a virtual seven-coordinate species with a pseudo-pentagonal-bipyramidal structure.[8b] On the other hand, the niobium atom in the hypovalent d^0 species **1**, which has no lone valence-electron pairs on the metal, is located 47 pm above the basal plane.



Scheme 3. Structural comparison between related $[AOX_5]^{q-}$ species.

The unusual *PPY*-6 geometry found for the niobium center in **1** is in sharp contrast (Scheme 3) to the common *OC*-6 structure previously established for the homologous derivative $[AsPh_4]_2[NbOCl_5]$.[21] The latter compound is formed following ligand addition to the same oxohalide precursor, $NbOCl_3$ (Scheme 2). The structural difference is particularly conspicuous considering that Cl and C_6F_5 ligands are thought to have similar electronic effects as substituents.[22] It has been suggested, however, that electron-poor metal compounds containing $(\sigma+\pi)$-donor ligands usually follow the VSEPR model, while those containing mainly σ-donor ligands are more prone to adopt non-VSEPR structures.[23] The different coordination polyhedra found for the isoleptic $[NbOX_5]^{2-}$ species (Scheme 3) are in keeping with this proposal, because halides (X = Cl) belong to the first ligand category and σ-organo groups ($X = C_6F_5$) belong to the second. The oxo ligand in $[NbOCl_5]^{2-}$ exerts a considerable *trans* influence on the axial chloride ligand, as the $Nb-Cl_{ax}$ distance (256.5(4) pm) is significantly longer than the average $Nb-Cl_{eq}$ (237.9(4) pm).[24] The oxo ligand in $[NbO(C_6F_5)_5]^{2-}$ is *trans* to a vacant site, which shows no affinity for ligands such as NCMe, CN*t*Bu, and $OCMe_2$. Although it is sensible to assume that the *ortho*-fluorine substituents would shield this vacant site on the metal, there is no evidence to support the existence of any *o*-F···Nb interaction (see below). We believe that the marked *trans*-influence of the triply bonded oxo ligand[25] in **1** together with the mainly σ-donor character of the C_6F_5 ligands are responsible for the unusual geometry observed. Steric effects might also apply, but it has been experimentally established that five C_6F_5 groups are indeed able to adopt a square-pyramidal (*SPY*-5) arrangement even around a light metal atom as in the homoleptic organochromium(III) derivative $[NBu_4]_2[Cr(C_6F_5)_5]$.[26]

The ^{19}F NMR spectrum of **1** in CD_2Cl_2 solution at 183 K (Figure 2b) is in keeping with the solid-state structure. Just one signal is observed for the *para*-fluorine substituents ($\delta_F = -165.7$ ppm) suggesting chemical equivalence of all five C_6F_5 groups. The fact that two signals are observed for the *ortho*-fluorine substituents ($\delta_F = -109.9$ and -115.7 ppm) denotes hindered rotation around the Nb–C bond.[27] The sharply different chemical shifts found for the two kinds of *ortho*-fluorine substituents are in agreement with their substantially different chemical environments. Likewise, two signals are also observed for the *meta*-fluorine substituents ($\delta_F = -164.5$ and -164.7 ppm). When the temperature is raised to 293 K (Figure 2a), the signals corresponding to the *ortho*- and *para*-fluorine substituents maintain their described positions, while those corresponding to the *meta*-fluorine substituents merge into a single signal at the midpoint between them ($\delta_F = -164.6$ ppm). This behavior suggests that a fluxional process takes place upon raising the temperature. Unfortunately, a thorough study of this incipient dynamic process was precluded by the thermal instability of the sample; compound **1** readily decomposes in solution above 293 K.

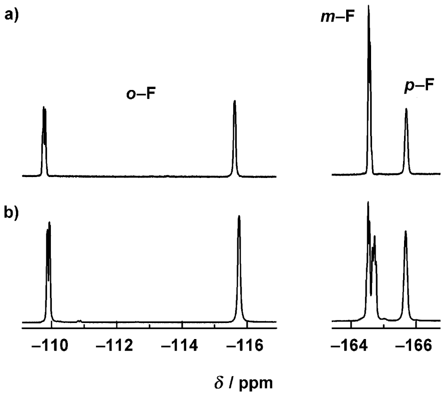


Figure 2. ^{19}F NMR spectrum (470.385 MHz) of **1** in CD_2Cl_2 solution: a) at 293 K and b) at 183 K.

The *PPY*-6 geometry is also energetically favored in the gas phase, according to structural optimizations on the $[NbO(C_6F_5)_5]^{2-}$ anion by density functional theory (DFT) methods (see the Supporting Information for further details). Three bonding orbitals are found to be involved in the Nb–O interaction: 1σ + 2π (Figure S9). The molecular orbital corresponding to the σ bond arises from the overlap of a mainly d_{z^2} orbital (a'_1 symmetry) with the O(p_z) orbital. Interaction between the (d_{xz},d_{yz}) degenerate orbitals of the $Nb(C_6F_5)_5$ fragment (e''_1 symmetry) with the O(p_x,p_y) orbitals of the oxo ligand gives rise to two orthogonal π bonds, which are also degenerate in energy. The triple bond character is in keeping with the short Nb–O bond length and the high *trans*-influence exerted by the strongly bound oxo ligand. No real minimum was found for an *OC*-6 geometric isomer. In the latter polytope, the marked *trans*-influence of the oxo ligand was evidenced by the substantial lengthening of the axial Nb–C bond (up to 268 pm). Another higher-energy polytope (152 kJ mol^{-1} above the *PPY*-6 one) was found to be a seven-coordinate species in which the axial C_6F_5 group shows a marked lateral swing to enable an additional *o*-F–Nb bond (Figure S7). The existence of even secondary *o*-F···Nb interactions in the *PPY*-6 polytope can be ruled out based on structural and electronic grounds. Thus, the moderate swing observed for the C_6F_5 groups in this case (α_2 and α_3 angles in Figure S6) tends to bring the *ortho*-fluorine substituents farther away from the niobium center (see α_2 and α_3 values given in Table S1). Moreover, a topological analysis of the quantum charge-density function (ρ) calculated for the *PPY*-6 polytope (DFT optimized geometry) using the quantum theory of "Atoms In Molecules" (QTAIM) has not afforded the location of bond critical points linking any of the *ortho*-fluorine substituents to the niobium center.

In summary, the six-coordinate organoniobium(V) compound $[NBu_4]_2[NbO(C_6F_5)_5]$ (**1**) is, to the best of our knowledge, the first organotransition-metal complex for which a *PPY*-6 structure has been established (X-ray diffraction). This unusual geometry is not just a solid-state effect, as it seems to be preserved in solution at low temperature (^{19}F NMR spectroscopy) and it is the most energetically favored geometry in the gas phase as well (DFT calculations). Species with the *PPY*-6 geometry had been previously suggested as potential intermediates in ligand rearrangement processes operating in six-coordinate compounds,[28] but later rejected because they were estimated to lie too high in the energy profile.[29] The results herein demonstrate that the *PPY*-6 geometry can indeed be stabilized to such an extent as to become the ground-state structure. This opens up the possibility for *PPY*-6 derivatives to be seriously considered as valid intermediates or transition states in mechanistic pathways, especially in processes involving mainly σ-donor ligands.

Received: April 12, 2012
Revised: June 13, 2012

Keywords: hypovalent compounds · niobium · non-VSEPR structures · organometallic compounds · pentagonal-pyramidal structures

[1] A. Werner, *Z. Anorg. Chem.* **1893**, *3*, 267.

[2] R. J. Gillespie, P. L. A. Popelier, *Chemical Bonding and Molecular Geometry*, Oxford University Press, New York, **2001**.

[3] Intermediate structures such as the so-called bicapped tetrahedron have also been put forward, see: R. Hoffmann, J. M. Howell, A. R. Rossi, *J. Am. Chem. Soc.* **1976**, *98*, 2484.

[4] R. Eisenberg, *Coord. Chem. Rev.* **2011**, *255*, 825.

[5] a) S. El-Kurdi, K. Seppelt, *Chem. Eur. J.* **2011**, *17*, 3956; b) B. Roessler, K. Seppelt, *Angew. Chem.* **2000**, *112*, 1326; *Angew. Chem. Int. Ed.* **2000**, *39*, 1259; c) S. Kleinhenz, V. Pfennig, K. Seppelt, *Chem. Eur. J.* **1998**, *4*, 1687; d) S. Kleinhenz, M. Schubert, K. Seppelt, *Chem. Ber./Recueil* **1997**, *130*, 903; e) V. Pfennig, K. Seppelt, *Science* **1996**, *271*, 626; f) A. Haaland, A. Hammel, K. Rypdal, H. V. Volden, *J. Am. Chem. Soc.* **1990**, *112*, 4547; g) P. M. Morse, G. S. Girolami, *J. Am. Chem. Soc.* **1989**, *111*, 4114.

[6] K. Seppelt, *Acc. Chem. Res.* **2003**, *36*, 147.

[7] a) E. Hey-Hawkins, M. Pink, H. Oesen, D. Fenske, *Z. Anorg. Allg. Chem.* **1996**, *622*, 689; b) R. Ahlrichs, D. Fenske, H. Oesen, U. Schneider, *Angew. Chem.* **1992**, *104*, 312; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 323.

[8] Selected examples within the $Xe^{VI}/I^{V}/Te^{IV}/Sb^{III}/Sn^{II}$ isoelectronic series: a) A. Ellern, K. Seppelt, *Angew. Chem.* **1995**, *107*, 1772; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1586; b) K. O. Christe, D. A. Dixon, J. C. P. Sanders, G. J. Schrobilgen, S. S. Tsai, W. W. Wilson, *Inorg. Chem.* **1995**, *34*, 1868; c) S. Hoyer, K. Seppelt, *J. Fluorine Chem.* **2004**, *125*, 989; d) D. Dakternieks, R. di Giacomo, R. W. Gable, B. F. Hoskins, *J. Am. Chem. Soc.* **1988**, *110*, 6762; e) M. J. Begley, D. B. Sowerby, I. Haiduc, *J. Chem. Soc. Chem. Commun.* **1980**, 64; f) M. C. Poore, D. R. Russell, *J. Chem. Soc. D* **1971**, 18; g) P. F. R. Ewings, P. G. Harrison, T. J. King, A. Morris, *J. Chem. Soc. Chem. Commun.* **1974**, 53.

[9] Selected examples within the Bi^{III}/Pb^{II} isoelectronic series: a) V. Stavila, E. V. Dikarev, *J. Organomet. Chem.* **2009**, *694*, 2956; b) A. E. Koziol, R. C. Palenik, G. J. Palenik, *Inorg. Chim. Acta* **1986**, *116*, L51.

[10] The isoelectronic species $[IOF_5]^{2-}$ has also been assigned a *PPY*-6 structure on the basis of a normal coordinate analysis of the vibrational spectra of its Cs^+ salt: K. O. Christe, W. W. Wilson, D. A. Dixon, J. A. Boatz, *J. Am. Chem. Soc.* **1999**, *121*, 3382.

[11] a) J. L. Sessler, T. Murai, V. Lynch, *Inorg. Chem.* **1989**, *28*, 1333; b) S. M. Nelson, F. S. Esho, M. G. B. Drew, *J. Chem. Soc. Dalton Trans.* **1982**, 407; c) J. Lewis, T. D. O'Donoghue, P. R. Raithby, *J. Chem. Soc. Dalton Trans.* **1980**, 1383; d) M. G. B. Drew, S. G. McFall, S. M. Nelson, *J. Chem. Soc. Dalton Trans.* **1979**, 575; e) S. M. Nelson, S. G. McFall, M. G. B. Drew, A. H. bin Othman, *J. Chem. Soc. Chem. Commun.* **1977**, 370; f) S. M. Nelson, S. G. McFall, M. G. B. Drew, A. H. bin Othman, N. B. Mason, *J. Chem. Soc. Chem. Commun.* **1977**, 167.

[12] a) V. S. Sergienko, *Crystallogr. Rep.* **2004**, *49*, 401 (*Kristallografiya* **2004**, *49*, 467) and references therein; b) J. W. Park, S. M. Koo, *Inorg. Chem.* **1999**, *38*, 4898; c) J.-Y. Piquemal, S. Halut, J.-M. Brégeault, *Angew. Chem.* **1998**, *110*, 1149; *Angew. Chem. Int. Ed.* **1998**, *37*, 1146; d) B. S. Mandimutsira, S.-J. Chen, R. A. Reynolds III, D. Coucouvanis, *Polyhedron* **1997**, *16*, 3911; e) B. S. Mandimutsira, S.-J. Chen, K. D. Demadis, D. Coucouvanis, *Inorg. Chem.* **1995**, *34*, 2267; f) J. Baldas, S. F. Colmanet, M. F. Mackay, *J. Chem. Soc. Chem. Commun.* **1989**, 1890; g) R. K. Thomson, J. A. Bexrud, L. L. Schafer, *Organometallics* **2006**, *25*, 4069; h) J. Beck, J. Strähle, *Z. Anorg. Allg. Chem.* **1987**, *554*, 50.

[13] a) R. Stomberg, *Ark. Kemi* **1964**, *22*, 29; b) B. F. Pedersen, B. Pedersen, *Acta Chem. Scand.* **1963**, *17*, 557; c) R. Stomberg, *Nature* **1962**, *196*, 570.

[14] $[ReOI(MeC{\equiv}CMe)_2]$ has been described as an organorhenium(III) compound (d^4) with pseudotetrahedral structure, where

each π-bound alkyne ligand occupies just one coordination site. This assignment relies on theoretical, crystallographic, and spectroscopic results and is further supported by chemical evidence: a) J. M. Mayer, D. L. Thorn, T. H. Tulip, *J. Am. Chem. Soc.* **1985**, *107*, 7454; a similar structural pattern was observed in the related cationic species $[\mathrm{ReO(MeC{\equiv}CMe)_2(py)}][\mathrm{SbF_6}]$: b) J. M. Mayer, T. H. Tulip, J. C. Calabrese, E. Valencia, *J. Am. Chem. Soc.* **1987**, *109*, 157.

[15] a) R. Usón, J. Forniés, *Adv. Organomet. Chem.* **1988**, *28*, 219; b) E. Maslowsky, Jr., *Vibrational Spectra of Organometallic Compounds*, Wiley, New York, **1977**, pp. 437–442.

[16] CCDC 865292 (**1**·*n*-hexane) 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. The anion of **1** is subjected to a whole-fragment disorder over two equally occupied positions sharing the basal plane (see the Supporting Information). As the *ipso* carbon atoms coincide for each disordered pair, the associated Nb−C bond lengths are not affected by any additional source of error other than that already involved in the indicated standard deviations.

[17] S. Alvarez, D. Avnir, M. Llunell, M. Pinsky, *New J. Chem.* **2002**, *26*, 996.

[18] a) M. Llunell, D. Casanova, J. Cirera, J. M. Bofill, P. Alemany, S. Alvarez, M. Pinsky, D. Avnir, *SHAPE*, Version 1.1b 02t, Universitat de Barcelona and The Hebrew University of Jerusalem; b) M. Pinsky, D. Avnir, *Inorg. Chem.* **1998**, *37*, 5575.

[19] P. Pyykkö, S. Riedel, M. Patzschke, *Chem. Eur. J.* **2005**, *11*, 3511.

[20] M. J. Nelsen, G. S. Girolami, *J. Organomet. Chem.* **1999**, *585*, 275.

[21] U. Müller, I. Lorenz, *Z. Anorg. Allg. Chem.* **1980**, *463*, 110.

[22] W. A. Sheppard, *J. Am. Chem. Soc.* **1970**, *92*, 5419.

[23] M. Kaupp, *Angew. Chem. Int. Ed.* **2001**, *40*, 3535; *Angew. Chem. Int. Ed.* **2001**, *40*, 3535.

[24] When calculating the average length of the Nb−Cl$_{\mathrm{eq}}$ bond in $[\mathrm{AsPh_4}]_2[\mathrm{NbOCl_5}]$, one of the equatorial chloride ligands has been excluded because it is involved in a hydrogen bond with the cation.

[25] a) B. J. Coe, S. J. Glenwright, *Coord. Chem. Rev.* **2000**, *203*, 5; b) W. A. Nugent, J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley, New York, **1988**, section 5.3.3.1, pp. 156–157; c) Y. V. Kokunov, Y. A. Buslaev, *Coord. Chem. Rev.* **1982**, *47*, 15; d) E. M. Shustorovich, M. A. Porai-Koshits, Y. A. Buslaev, *Coord. Chem. Rev.* **1975**, *17*, 1. Please note that "*trans*-influence" has sometimes been termed "structural *trans*-effect" or just "*trans*-effect". For a clear distinction on this confusing terminology, see: e) T. G. Appleton, H. C. Clark, L. E. Manzer, *Coord. Chem. Rev.* **1973**, *10*, 335.

[26] P. J. Alonso, J. Forniés, M. A. García-Monforte, A. Martín, B. Menjón, *Organometallics* **2005**, *24*, 1269.

[27] Similar behavior had been previously observed in the square-pyramidal nitrosyl compound $[\mathrm{N(PPh_3)_2}][\mathrm{Pt(C_6F_5)_4(NO)}]$: I. Ara, J. Forniés, M. A. García-Monforte, B. Menjón, R. M. Sanz-Carrillo, M. Tomás, A. C. Tsipis, C. A. Tsipis, *Chem. Eur. J.* **2003**, *9*, 4094.

[28] D. W. Lahti, J. H. Espenson, *J. Am. Chem. Soc.* **2001**, *123*, 6014.

[29] X. Yang, M. B. Hall, *J. Am. Chem. Soc.* **2007**, *129*, 1560.