Discrimination of Octahedral vs Trigonal Bipyramidal Coordination Geometries of Homogeneous Ti(IV), V(V) and Mo(VI) Amino Triphenolate Complexes Through Nitroxyl Radical Units

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Abstract: A new stable radical-containing ligand and the corresponding V(V), Ti(IV) and Mo(VI) complexes have been synthesized and studied by Electron Paramagnetic Resonance (EPR). In order to achieve this goal, a novel strategy for the post-derivatization of a triphenolamine (TPA) ligand has been developed. This has allowed the effective embedding of three TEMPO radicals in the corresponding metal complexes. In these systems, dipolar interactions among the organic radicals are strongly dependent on the geometry assumed in solution: a $|\Delta m_s| = 2$ transition is observed when the geometry of the complexes is octahedral while no signal is detected with trigonal bipyramidal geometries.

Introduction

Homogeneous catalytic reactions are often mediated by ligand-supported metal species and among them, the use of polydentate ligands is the leading strategy for the preparation of robust and catalytically effective systems.^[1] Polydentate ligands confer intrinsically well-defined coordination geometries, which influence the stability and functional properties of the relative metal complexes. In particular, they are able to support the metal in the active state which, in some types of reactivities, corresponds to an expansion of the metal coordination sphere to favor the coordination of the reactant. In oxidation chemistry for example, this type of activation is really common especially for d_0 group metal complexes. This is the case of Polyhedral Oligomeric Silsesquioxane Trisilanolate (POSS) Vanadium V(V) systems, in which the presence of a Lewis Base in solution give an adduct with the metal complex that is more reactive than the starting compound.^[2] In another example, recently reported by us, a Ti(IV) *tris*(2-methylphenolate)amine (TPA) complex shows an increased activity in oxidation reactions when a solvent molecule expands the coordination sphere of the metal.^[3] Typical experiments for the determination of the geometry are VT-NMR and X-ray crystallography, supported when possible by theoretical calculations.

In this study, we envisaged an original method for geometry determination of transition metal complexes in solution. This has been achieved functionalizing polydentate complexes with organic radicals, which have been used as probes in EPR experiments. More in detail, we have prepared Ti(IV), V(V) and Mo(VI) transition metal TPA complexes containing three persistent nitroxyl radicals in their structure, to take advantage of the dipolar interactions that may occur between the radicals depending on the coordination geometry imposed by the metal. The interaction is measured using the characteristic EPR dipolar coupling. Beside the interest on the geometry assumed by TPA complexes in solution that can play a role in their catalytic activities, this study has allowed to set up a novel methodology for the effective post-functionalization of amino triphenolate ligands. This synthetic approach can be widely applied to other amino phenolate systems thus extending the functional properties of these ligands.

Results and Discussion

The interest of our group in TPA ligands resides in their versatility to coordinate transition metals forming robust and catalytic active complexes^[4-7] which, in the solid state, exhibit mainly two main coordination geometries: trigonal bipyramidal (TBP) or octahedral (OCT) (Figure 1).

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Figure 1. TPA ligands adopt a TBP geometry in the case of Ti(IV) and V(V), while OCT geometry is obtained for Mo(VI) complexes.^[5-7]

Scheme 1. Geometries adopted by the ligand in the case of TBP or OCT coordination.

In the case of Ti(IV)^[5] and V(V)^[6] complexes the geometry assumed is most of the times TBP.^[8] In these systems in fact, TPA has four coordination sites, with three equatorial phenolate oxygen atoms and the axial tertiary amine. The residual apical site is an alkoxo group, in the case of Ti(IV), and an oxo moiety for the V(V) complex. OCT geometries have been observed with Mo(VI) ions.^[7] In this case, TPA still occupies four positions, one axial and three equatorials, while the other two positions are occupied by an oxo group in apical position and by an extra anionic ligand (Cl, OR) in equatorial position, *trans* to the central phenoxy TPA arm. It should also be pointed out that these TPA metal complexes are characterized by a propeller-like arrangement of the ligand around the metal. This is more evident observing them along the metal-nitrogen bond (Scheme 1). As consequence TBP complexes are C_3 symmetric. The two enantiomeric helical arrangements interconvert at room temperature, yielding a racemic mixture in solution. In the case of OCT geometry, two different TPAs arrangements have been observed. Some complexes exhibit a pseudo- C_3 symmetric geometry, in which the TPA ligand maintains a propeller-like arrangement around the metal. In other OCT structures, the ligand coordinates the metal in a pseudo- C_6 symmetry. In virtue of this different disposition, the aromatic arms get closer in space (Scheme 1). In order to have a more accurate knowledge of the geometrical structures of TPA complexes in solution and to monitor the possible geometrical switch in the presence of an extra ligand (e.g. a Lewis base), we decided to take advantage of the possible occurrence of dipolar interactions among persistent organic radicals like TEMPO present on the ligand backbone. Indeed, the use of persistent radical have been extensively used as spin labels for the determination of space proximity. By CW EPR it is possible to observe this interaction between nitroxides for distances up to 2 nm.^[9] In order to embed within the TPA three radical moieties we developed a new synthetic strategy based on TPA post-functionalization. The TPA ligand **1** bearing three bulky group in *ortho* position to the phenol group was prepared according to our reported method starting from the commercial 2-*tert*-butylphenol (Scheme 2).^[10]

Scheme 2. Duff reaction on TPA lead to the synthesis of the triformyl system **2**.

As suitable anchoring group for TPA post-functionalization we choose an aldehyde, which was effectively inserted via three-fold formylation via Duff reaction.^[11] Product **2** was obtained in high yields (95%). The presence of the formyl group in the TPA ligands offers the extraordinary possibility to further modify these structures *via*, for example, imine formation or Wittig reaction. The TPA post-modification increases the range of applications of these already versatile tripodal ligands and it is currently investigated in our laboratories. Condensation between **2** and three equivalents of radical 4-amino TEMPO allowed to obtain compound **3**, a TPA ligand functionalized with three nitroxyl radicals linked covalently to the molecular skeleton. The handling of radicals in solution was performed under dark conditions and inert atmosphere, in order to avoid respectively the possible degradation of the radicals and imine bond hydrolysis. Ligand **3** was obtained in good yields (85%) by precipitation from the reaction crude in acetonitrile/ethyl ether.

Synthesis of TEMPO-based TPA Ti(IV), V(V) and Mo(VI) metal complexes

TPA **3** has been used for the synthesis of the corresponding Ti(IV), V(V) and Mo(VI) metal complexes with the procedures reported for ligand **1** (Scheme 3).^[5-7]

Scheme 3. Synthesis of TPA **3** and V(V) **4**, Ti(IV) **5** and Mo(VI) **7** TPA complexes.

Indeed, the corresponding Ti(IV) complex **4** and V(V) complex **5** were prepared in high yields by trans-esterification of the metallic *iso*-propoxides, $\text{VO}(\text{O-}i\text{-Pr})_3$ and $\text{Ti}(\text{O-}i\text{-Pr})_4$. The complexes have been obtained by re-crystallization of the crude mixture in hexane and obtained as dark blue crystals in the case of V(V) complex **4** and a light yellow solid for Ti(IV) **5**. Unfortunately, reaction on TPA **3** with MoO_2Cl_2 in refluxing toluene afforded only a mixture of by-products. However, anionic Mo(VI) complex **7** could be obtained passing through complex **6**, which is obtained from TPA **2** and MoO_2Cl_2 , followed by imine condensation with the amino TEMPO radicals. In this case a yellow-orange solid was obtained after recrystallization. Both synthetic strategies are efficient and afforded the corresponding TPA complexes **4**, **5** and **7** in high yields (92-97%). The new TPAs **2-3** and the corresponding complexes **4-7** were characterized by ESI-MS, FT-IR and Elemental Analysis. In the ESI-MS spectra of **4-7** all experimental isotopic clusters are in agreement with the theoretical ones. The FTIR measurement showed for all the systems the disappearance of the characteristic carbonyl stretching of the aldehyde (1700 cm^{-1}) and the appearance of the stretching peak of the C=N bond ($\sim 1635\text{ cm}^{-1}$). Ligand **3**, and complexes **4**, **5** and **7**, are stable if stored at -20°C under nitrogen atmosphere and dark conditions.

EPR Studies on TEMPO-TPA based Complexes

Electron Paramagnetic Resonance (EPR) spectroscopy is a very powerful and sensitive technique for the characterization of the electronic structures of species with unpaired electrons, either organic radicals or paramagnetic metal cations. In this particular case we use the metal as a template for the TEMPO-based TPA ligands and we study the intramolecular interaction between the radicals, in order to have information on the actual geometry assumed by the metal complexes.

In general, the interaction of the unpaired electron of the radical with the magnetic field is quantized, for this reason only transitions of $|\Delta m_s| = 1$ are allowed. The signal corresponding to this transition gives information about the coupling of the unpaired electron with the atoms $I \neq 0$ of the radical. In nitroxide radicals like TEMPO, when the radical does not interact with its neighbors, the EPR spectrum shows three lines with the same intensity corresponding to the hyperfine coupling interaction with the nitrogen atom. Only under particular conditions (*i.e.* with $|J| \gg |a_N|$) other lines in the spectrum appear, which can be related to the existence of exchange coupling between two or more radicals. Moreover, when the radicals are very close to each other, another signal may occur. This interaction corresponds to a $|\Delta m_s| = 2$ transition and it is called half field signal because appears at half the mean field of the principal

signal ($|\Delta m_s| = 1$ transition). Its intensity is much lower as it is a forbidden transition and appears only at temperatures in which the solution is frozen. The detection of this signal is a clear evidence that the radicals are close enough to present a dipolar interaction. The EPR spectra of 5×10^{-4} M solution of TEMPO-based TPA **3** and corresponding complexes V(V) **4**, Ti(IV) **5** and Mo(VI) **7** in a mixture of dichloromethane/toluene (1:1) at 300 K (Figure 2) showed three lines centered at g values between 2.0062 and 2.0065, with hyperfine coupling constant of ca. $a_N = 15.7$ G, typical for monoradical TEMPO derivatives (see Figures S1 and S2 for the hyperfine coupling constants with the H atoms). All the spectra show a selective broadening of the high-field line due to the hindered motion of the radicals attached to quite large molecules, resulting in incomplete averaging of anisotropic components of the a and g tensors. Three-line spectra pattern indicates that there is no spin exchange interaction between the radicals, as, in the case of two or three interacting TEMPO radicals (*i.e.* with $|J| \gg |a_N|$), five or seven lines should be observed.^[12] Thus, these results indicate that the radicals in the ligand and in the three complexes are distant and they do not interact. However, a more accurate analysis of EPR spectrum of Mo(VI) complex **7** reveals that, together with the three main lines, two weak additional lines are present (marked with arrows in Figure 2). This five-line pattern is explained by the existence of some degree of exchange coupling between two of the three nitroxides. In addition, at 120 K we could observe a $|\Delta m_s| = 2$ transition at half-field in the Mo(VI) complex **7**, while in ligand **3** and complexes V(V) **4** and Ti(IV) **5** we did not or barely observe this forbidden transition (Figure 3). Such a transition indicates weak dipolar interactions between two TEMPO radicals in complex **7**.

Figure 2. EPR spectra of a 10^{-4} M solution of ligand **3** and complexes V(V) **4**, Ti(IV) **5** and Mo(VI) **7** in dichloromethane/toluene (1:1) at 300 K. The inset shows an enlargement of V(V) **4** and Mo(VI) **7** spectra.

Figure 3. EPR frozen solution spectra of ligand **3** and complexes Ti(IV) **4**, V(V) **5** and Mo(VI) **7** at half-field in dichloromethane/toluene (1:1) at 120 K.

The observed EPR behavior can be associated to the structures that complexes V(V) **4**, Ti(IV) **5** and Mo(VI) **7** assume in solution, which seems very similar to the ones observed in the parent complexes crystal structures: TBP in the first two cases (V(V) **4** and Ti(IV) **5** TPA complexes) and OCT in the last one (Mo(VI) **7**). In the free TEMPO-based TPA **3** and TBP complexes **4** and **5**, the TEMPO units are too distant and no dipole-dipole interaction can be detected. On the contrary, the appearance of the $|\Delta m_s| = 2$ transitions at half-field and the weak five-line pattern EPR spectrum observed for complex **7** can be associated to an OCT pseudo- C_s geometry where two of the three arms bearing the TEMPO units can get in proximity. Therefore, the presence of the TEMPO probes allows to detect the formation of complexes with OCT geometries, the unique in which a dipolar interaction can occur between two TEMPO groups.

TEMPO-based TPA Metal Complexes-Lewis Base Adduct: EPR Studies

Because the interaction of the radical probes in the TEMPO-based TPA complexes has been effective for discriminating TPB vs OCT geometries, we tested the behavior of the V(V) **4** and Ti(IV) **5** complexes in the presence of a Lewis base (LB). In previous studies,^[2,3] we registered a strong effect due to the presence of LBs on the reactivity of the systems, the variation of the reactivity observed should occur *via* coordination of the LB to the metal center (V(V) **4** and Ti(IV) **5**), expanding their coordination geometry from TBP to OCT (Scheme 4). On the other side, no effect should be noted in the case of Mo(VI) **7**. The half field transitions were recorded at 120K for the complexes **4**, **5** and **7** (10^{-3} M in dichloromethane:toluene (1:1)) before and after the addition of one equivalent of trioctyl phosphine oxide (Figures 4 (**4**) and 5 (**5**)).

In the case of the V(V) complex **4**, after the addition of one equivalent of trioctyl phosphine oxide, a weak but clear transition at half field was observed (Figure 4). This means that the Lewis base gets coordinated to the metal ion, changing the coordination geometry from TBP to OCT.

The same experiment was performed for Ti(IV) **5** in dichloromethane:toluene (1:1) and no $|\Delta m_s| = 2$ transitions at half-field was detected for the sample without the Lewis base neither after the addition of one or more equivalents of trioctyl phosphine oxide (Fig. 5, Supplementary Figure S3). A plausible explanation is that the addition of the LB results in a pseudo- C_3 symmetry OCT conformation in which the arm are far away one from the other.

Finally, as expected, in the case of Mo(VI) **7** we observed the half-field transition before and after the addition of the Lewis base. This confirms the OCT coordination geometry of Mo(VI) complex **7** also in the presence of the Lewis Base. (Fig. 6).

Scheme 4. Expected geometry switch arising from coordination of a Lewis Base in the case of a TBP complex leading to an OCT geometry.

Figure 4. Half-field EPR spectra for V(V) **4** at 120 K in dichloromethane:toluene (1:1) before (above) and after (below) addition of trioctyl phosphine oxide Lewis base (1 equiv).

Figure 5. Half-field EPR spectra for Ti(IV) **5** at 120 K in dichloromethane:toluene (1:1) before (above) and after (below) adding a Lewis base.

Figure 6. Half-field EPR spectra for Mo(VI) **7** at 120 K in dichloromethane:toluene (1:1) before (above) and after (below) adding a Lewis base.

Conclusions

In this work we report the synthesis and effective use of a new stable nitroxyl TEMPO radical-containing amino triphenolate ligand **3** which has been used to obtain information on the coordination chemistry in solution of the corresponding V(V), Ti(IV) and Mo(VI) complexes. In order to obtain such TEMPO-based complexes a novel method for the functionalization of TPA ligands was developed. This post-functionalization of the ligand opens for newer applications for this class of compounds. Studies by Electron Paramagnetic Resonance (EPR), showed dipolar interactions strongly dependent on the geometry assumed in solution by the modified-TPA containing complexes. In particular a $|\Delta m_s| = 2$ transition is observed when the geometry of the complexes is OCT, while no signal is detected for TBP geometries.

Experimental Section

General remarks. EPR spectra were obtained with an XBand Bruker ELEXYS 500 spectrometer equipped with a TE102 microwave cavity, a Bruker variable temperature unit, a field frequency lock system Bruker ER 033 M and equipped with a NMR Gaussmeter Bruker ER 035 M. The modulation amplitude was kept well below the line width, and the microwave power was well below saturation. All preparations with radicals were performed in dark conditions under inert atmosphere with Schlenk type glassware. Anhydrous solvents were used thoroughly.

Synthesis of 2. In a Schlenk flask, a mixture of 503 mg (1 mmol) of **1**, 140.2 mg (6 mmol) of hexamethylenetetramine and 30 mL of trifluoroacetic acid was stirred for 12 hours at 90°C. The solvent was distilled off to obtain an orange oil. 60 mL of 3 N HCl were then added to the oil and the resulting mixture was stirred at 80°C for three hours. The white precipitate was filtered off, washed with water, recrystallized from ethanol, and dried. The final product **2** was obtained in 95% yield (552 mg). ^1H NMR (250 MHz, CDCl_3): δ 9.81 (s, 1H, CHO), 7.81 (d, 1H, $J = 2.0$ Hz, HAr), 7.59 (d, 1H, $J = 1.9$ Hz, HAr), 4.04 (s, 1H, CH_2N), 1.41 (s, 1H, CH_3) ppm. ^{13}C NMR (200 MHz, CDCl_3) δ 191.00 (CHO), 159.66 (C), 138.76 (C), 131.50 (C), 131.18 (C), 129.54 (CH), 121.49 (CH), 56.65 (CH_2), 34.72 (C), 29.81 (CH_3) ppm. MS (ESI) calcd for $\text{C}_{36}\text{H}_{46}\text{NO}_6$ ($\text{M}+\text{H}$) $^+$ 588.3 found 588.4. Elemental Anal. Calcd. ($\text{C}_{36}\text{H}_{45}\text{NO}_6$): C, 73.57, H, 7.72, N, 2.38. Found: C, 73.32, H, 6.96, N, 2.21.

Synthesis of 3. Ligand **2** (40 mg, 0.07 mmol) and free radical 4-amino-TEMPO (47 mg, 0.27 mmol) were dissolved in CH_3CN (1 mL). The mixture was stirred overnight. The molecular sieves were filtered off and ether was added to the solution until the formation of a pale red precipitate. The mixture was stirred for 10 min and filtered. The solid was washed with THF –hexane (1:10) several times and dried to afford 61 mg of the imine **3** (61 mg, 85%) as a pale red solid. IR (KBr): 2972, 2934, 2866, 1640, 1608, 1520, 1376, 1242, 1175 cm^{-1} . MS (ESI) calcd for $\text{C}_{63}\text{H}_{97}\text{N}_7\text{O}_6$ ($\text{M}+\text{H}$) $^+$ 1047.8, found 1048.8. Elemental Anal. Calcd. ($\text{C}_{63}\text{H}_{96}\text{N}_7\text{O}_6$): C, 72.24, H, 9.24, N, 9.36. Found: C, 72.11, H, 9.15, N, 9.18.

Synthesis of V-TPA complex 4. Compound **3** (13 mg, 0.01 mmol) were dissolved in 400 μL of THF and, under stirring, 3.1 mg (0.01 mmol) of $(i\text{-PrO})_3\text{VO}$ were added. The mixture was let stirring during five minutes and then was left overnight at room temperature, without stirring. Hexane (0.4 mL) was added to the solution and the solvent was then evaporated to afford **4** as a blue solid (13 mg, 96%). IR (KBr): 2971, 2926, 2857, 1636, 1598, 1466, 1431, 1260, 1145 cm^{-1} . MS (ESI) calcd for $\text{C}_{63}\text{H}_{94}\text{N}_7\text{O}_7\text{V}$ ($\text{M}+\text{H}$) $^+$ 1111.6, found 1111.7. Elemental Anal. Calcd. ($\text{C}_{63}\text{H}_{93}\text{N}_7\text{O}_7\text{V}$): C, 68.08, H, 8.43, N, 8.82. Found: C, 67.98, H, 8.21, N, 8.68.

Synthesis of Ti-TPA complex 5. Compound **3** (35 mg, 0.03 mmol) were dissolved in 750 μL of THF and, under stirring, 9.6 mg (0.03 mmol) of $(i\text{-PrO})_3\text{VO}$ were added. The mixture was let stirring during five minutes and then was left overnight at room temperature, without stirring. Hexane (0.8 mL) was added to the solution and the solvent was evaporated to afford **5** as a yellow solid (36.9 mg, 97%). IR (KBr): 2971, 2932, 2865, 1675, 1640, 1599, 1465, 1243, 1146 cm^{-1} . MS (ESI) calcd for $\text{C}_{64}\text{H}_{95}\text{N}_7\text{O}_7\text{Ti}$ ($\text{M}+\text{HCOOH}+\text{H}$) $^+$ 1138.7, found 1138.8. Elemental Anal. Calcd. ($\text{C}_{66}\text{H}_{100}\text{N}_7\text{O}_7\text{Ti}$): C, 68.85, H, 8.75, N, 8.52. Found: C, 70.01, H, 8.79, N, 8.63.

Synthesis of Mo-TPA complex 6. 42 mg (0.2 mmol) of milled MoO_2Cl_2 , 150 mg (0.2 mmol) of the ligand precursor **2** and 88 μL (0.6 mmol) of NEt_3 were mixed with 35 mL of toluene and the stirred suspension was heated to reflux temperature for 18 hours. The resulting intense green solution was filtered through a short pad of silica. Flash chromatography (SiO_2 DCM:MeOH 95:5) yield compound **6** as a violet solid (139 mg 85 % yield). ^1H -NMR (250 MHz, CDCl_3): δ 9.78 (s, 2H, CHO), 9.73 (s, 1H, CHO), 7.75 (d, 3H, $J = 16$ Hz, ArH), 7.53 (d, 3H, $J = 16$ Hz, ArH), 4.09 (d, 2H, $J = 16$ Hz, NCH_2), 3.72

(d, 4H, $J = 16$, NCH_2), 2.85 (m, 6H, NCH_2CH_3), 1.60 (s, 9H), 1.39 (s, 18H), 1.21 (s, 9H). MS (ESI) calcd for $\text{C}_{36}\text{H}_{42}\text{NO}_8\text{Mo}$ (M^-) 714.2 found 714.2. Elemental Anal. Calcd. ($\text{C}_{42}\text{H}_{58}\text{N}_2\text{O}_8\text{Mo}$): C, 61.90, H, 7.17, N, 3.44. Found: C, 61.75, H, 7.02, N, 3.24.

Synthesis of Mo-TPA complex 7. Complex **6** (20 mg, 0.02 mmol) and free radical 4-amino-TEMPO (18 mg, 0.10 mmol) were dissolved in CH_3CN (0.5 mL). The mixture was stirred overnight. Hexane was added to the solution until the formation of a yellow precipitate. The mixture was stirred for 10 min and filtered. The solid was washed hexane and dried to afford 29 mg of the imine **7** (92%) as a yellow solid. IR (KBr): 2972, 2938, 2866, 1637, 1597, 1464, 1243, 1147 cm^{-1} . MS (ESI) calcd for $\text{C}_{63}\text{H}_{93}\text{N}_7\text{O}_8\text{Mo}$ (M^-) 1173.6 found 1173.6. Elemental Anal. Calcd. ($\text{C}_{69}\text{H}_{109}\text{N}_8\text{O}_8\text{Mo}$): C, 65.02, H, 8.62, N, 8.79. Found: C, 64.99, H, 8.12, N, 8.54.

Addition of Lewis Base. One equivalent of trioctylphosphine oxide (0.12 mg, 3×10^{-4} mmol) is added to a 9×10^{-4} M solution of compound **3**, **4** and **7** in dichloromethane:toluene (1:1). The reactions have been followed by EPR.

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- [1] a) C. Moberg, *Angew. Chem. Int. Ed.* **1998**, 37, 248-268; b) O. Wichmann, R. Sillanpää, Ari Lehtonen *Coord. Chem. Rev.* **2012**, 256, 371-392; c) M. M. Hänninen, A. Peuronen, P. Damlin, V. Tyystjärvi, H. Kiveläc, A. Lehtonen *Dalton Trans.* **2014**, 43, 14022-14028; d) A Dupé, K. Hossain, J. A. Schachner, F. Belaj, A. Lehtonen, E. Nordlander, N. C. Mösch-Zanetti *Eur. J. Inorg. Chem.* **2015**, 21, 3572-3579; e) M. Valencia, H. Müller-Bunz, R. A. Gossage, M. Albrecht *Chem. Commun.* **2016**, 52, 3344-3347.
- [2] S. Lovat, M. Mba, H. C. L. Abbenhuis, D. Vogt, C. Zonta, G. Licini, *Inorg. Chem.* **2009**, 48, 4724-4728.
- [3] C. Zonta, G. Licini *Chem. Eur. J.* **2013**, 19, 9438-9441.
- [4] a) G. Licini, M. Mba, C. Zonta, *Dalton. Trans.* **2009**, 5265-5277; b) C. J. Whiteoak, B. Gjoka, E. Martin, M. Martínez Belmonte, E. C. Escudero-Adán, C. Zonta, G. Licini, A. W. Kleij, *Inorg. Chem.* **2012**, 51, 10639-10649; c) C. Zonta, E. Cazzola, M. Mba, G. Licini, *Adv. Synth. Catal.* **2008**, 350, 2503-2506; d) E. Badetti, B. Gjoka, E. M. Nagy, G. Bernardinelli, P. E. Kündig, C. Zonta, G. Licini, *Eur. J. Inorg. Chem.* **2015**, 21, 3478-3484; e) C. Zonta, A. Kolarovic, M. Mba, M. Pontini, E. P. Kündig, G. Licini, *Chirality* **2011**, 23, 796-800.
- [5] M. Mba, L. J. Prins, C. Zonta, M. Cametti, A. Valkonen, K. Rissanen, G. Licini, *Dalton Trans.* **2010**, 39, 7384-7392.
- [6] M. Mba, M. Pontini, S. Lovat, C. Zonta, G. Bernardinelli, E. P. Kündig, G. Licini, *Inorg. Chem.* **2008**, 47, 8616-8618.
- [7] F. Romano, A. Linden, M. Mba, C. Zonta, G. Licini, *Adv. Synth. Catal.* **2010**, 352, 2937-2942.
- [8] As a function of the ligand substituents OCT geometries have been observed also for V(V) oxo compounds. a) S. Groysman, I. Goldberg, M. Kol, Z. Goldschmidt, *Inorg. Chem.* **2005**, 44, 5073-5080; b) C. Redshaw, M. A. Rowan, D. M. Homden, S. H. Dale, M. R. J. Elsegood, S. Matsuic, S. Matsuura, *Chem. Commun.* **2006**, 3329-3331; c) M. Kol, M. Shamis, I. Goldberg, Z. Goldschmidt, S. Alfi, E. Hayut-Salant, *Inorg. Chem. Commun.* **2001**, 4, 177-179; d) A. Lehtonen, V. G. Kessler, *Inorg. Chem. Comm.* **2004**, 7, 691-693; e) A. Lehtonen, R. Sillanpää, *Polyhedron* **2007**, 26, 5293-5300.
- [9] G. I. Likhenshtein, *Spin Labeling Methods in Molecular Biology*; Wiley: New York, **1976**.
- [10] L. J. Prins, M. Mba Blázquez, A. Kolarović, G. Licini, *Tetrahedron Lett.* **2006**, 47, 2735-2738.
- [11] a) A.L Kurlovich, V.A. Tarasevich, N.G Kozlov, *Russian J. Org. Chem.* **2009**, 45, 1503-1508; b) L. F. Lindoy, G. V. Meehan, N. Svenstrup, *Synthesis* **1998**, 7, 1029-1032.
- [12] a) E. Badetti, V. Lloveras, K. Wurst, R. M. Sebastián, A. M. Caminade, J. P. Majoral, J. Veciana, J. Vidal-Gancedo, *Org. Lett.* **2013**, 14, 3490-3493; b) E. Badetti, V. Lloveras, J. L. Muñoz-Gómez, R. M. Sebastián, A. M. Caminade, J. P. Majoral, J. Veciana, J. Vidal-Gancedo, *Macromolecules* **2014**, 47, 7717-7724.