Inorg. Chem. **2008**, *47*, 10158−10168

Cu(I) Complexes Bearing the New Sterically Demanding and Coordination Flexible Tris(3-phenyl-1-pyrazolyl)methanesulfonate Ligand and the Water-Soluble Phosphine 1,3,5-Triaza-7-phosphaadamantane or Related Ligands

Riccardo Wanke,[†] Piotr Smoleński,[†] M. Fátima C. Guedes da Silva,[†,‡] Luísa M. D. R. S. Martins,[†,§] and Armando J. L. Pombeiro*[,†]

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU Lisbon, Av. Rovisco Pais, 1049-001 Lisbon, Portugal, Universidade Lusófona de Humanidades e Tecnologias, Campo Grande 376, 1749-024 Lisbon, Portugal, and Departamento de Engenharia Química, ISEL, R. Conselheiro Emídio Navarro, 1950-062 Lisbon, Portugal

Received July 4, 2008

The new sterically hindered scorpionate tris(3-phenylpyrazolyl)methanesulfonate ($Tpms^{Ph}$)$^-$ has been synthesized and its coordination behavior toward a Cu(I) center, in the presence of 1,3,5-triaza-7-phosphaadamantane (PTA), *N*-methyl-1,3,5-triaza-7-phosphaadamantane tetraphenylborate ((mPTA)[BPh_4]) or hexamethylenetetramine (HMT) has been studied. The reaction between Li($Tpms^{Ph}$) (**1**) and [$Cu(MeCN)_4$][PF_6] yields [$Cu(Tpms^{Ph})(MeCN)$] (**2**) which, upon further acetonitrile displacement on reaction with PTA, HMT, or (mPTA)[BPh_4], gives the corresponding complexes [$Cu(Tpms^{Ph})(PTA)$] (**3**), [$Cu(Tpms^{Ph})(HMT)$] (**4**), and [$Cu(Tpms^{Ph})(mPTA)$][PF_6] (**5**). All the compounds have been characterized by ^1H, ^{31}P, ^{13}C, COSY or HMQC-NMR, IR, elemental analysis, and single crystal X-ray diffraction. In the complexes (**3**) and (**5**), which bear a phosphine ligand (i.e., PTA and mPTA, respectively), the new scorpionate ligand shows the typical *N*,*N*,*N*-coordination mode, whereas in (**2**) and (**4**), bearing a N-donor ligand (i.e., MeCN and HMT, respectively), it binds the metal via the N,N,O chelating mode, involving the sulfonate moiety.

Introduction

Copper species are widely present in Nature as mono- or multinuclear metal complexes and play a crucial role in different enzymes and catalytic systems, leading to a currently growing interest in the development of new copper models.[1] In bioinorganic and organometallic chemistry the systems involving this metal represent one of the most relevant areas of investigation.[2]

In pursuit of our recent investigation of the coordination chemistry of N-, P- and O-donor ligands,[3] including the scorpionate-type tris(pyrazolyl)methane,[4] toward copper(I) and (II) centers, we have now focused our attention on the

* To whom correspondence should be addressed. E-mail: pombeiro@ist.utl.pt. Fax: +351−21−846 4455.
† TU Lisbon.
‡ Universidade Lusófona de Humanidades e Tecnologias.
§ Departamento de Engenharia Química, ISEL.

(1) (a) Solomon, E. I.; Sundaram, U. M.; Machonkin, T. E. *Chem. Rev.* **1996**, *96*, 2563–2605. (b) Klinman, J. P. *Chem. Rev.* **1996**, *96*, 2541–2561. (c) Koval, I. A.; Gamez, P.; Belle, C.; Selmeczi, K.; Reedijk, J. *Chem. Soc. Rev.* **2006**, *35*, 814–840. (d) Maheswari, P. U.; Roy, S.; den Dulk, H.; Barends, S.; van Wezel, G.; Kozlevcar, B.; Gamez, P.; Reedijk, J. *J. Am. Chem. Soc.* **2006**, *128*, 710–711. (e) Elsevier, C. J.; Reedijk, J.; Walton, P. H.; Ward, M. D. *Eur. J. Inorg. Chem.* **2003**, *9*, 1669–1674. (f) Elsevier, C. J.; Reedijk, J.; Walton, P. H.; Ward, M. D. *Dalton Trans.* **2003**, *10*, 1869–1880.

(2) (a) Kim, E.; Chufan, E. E.; Kamarai, K.; Karlin, K. D. *Chem. Rev.* **2004**, *104*, 1077–1133. (b) Chen, P.; Gorelsky, S. I.; Ghosh, S.; Solomon, E. I. *Angew. Chem., Int. Ed.* **2004**, *43*, 4132–4140. (c) Koval, I. A.; Belle, C.; Selmeczi, K.; Philouse, C.; Saint-Aman, E.; Schuitema, A. M.; Gamez, P.; Pierre, J. L.; Reedijk, J. *J. Biol. Inorg. Chem.* **2005**, *10*, 739–750. (d) Koval, I. A.; Pursche, D.; Stassen, A. F.; Gamez, P.; Krebs, B.; Reedijk, J. *Eur. J. Inorg. Chem.* **2003**, *9*, 1669–1674. (e) Uber, J. S.; Vogels, Y.; Van Den Helder, D.; Multikainen, I.; Turpeinen, U.; Fu, W. T.; Roubeau, O.; Gamez, P.; Reedijk, J. *Eur. J. Inorg. Chem.*, **2007**, *26*, 4197−4206.

(3) (a) Kirillow, A. M.; Kopylovich, M. N.; Kirillova, M. V.; Haukka, M.; da Silva, M. F. C. G.; Pombeiro, A. J. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4345–4349. (b) Di Nicola, C.; Kabarach, Y. Y.; Kirillov, A. M.; Monari, M.; Pandolfo, L.; Pettinari, C.; Pombeiro, A. J. L. *Inorg. Chem.* **2007**, *46*, 221–230.

(4) (a) Alegria, E. C. B.; Martins, L. M. D. R. S.; Haukka, M.; Pombeiro, A. J. L. *Dalton Trans.* **2006**, *41*, 4954–4961. (b) Alegria, E. C. B.; Martins, L. M. D. R. S.; da Silva, M. F. C. G.; Pombeiro, A. J. L. *J. Organomet. Chem.* **2005**, *690*, 1947–1958.

10.1021/ic801254b CCC: $40.75
Published on Web 10/08/2008

synthesis of a new class of copper complexes bearing a sterically hindered chelating facially binding scorpionate that could modulate the coordination properties of the metal center.

Metal complexes of tris(pyrazolyl)borate (Tp) and derived ligands constitute one of the most extensively studied classes of coordination compounds in inorganic, organometallic, and bioinorganic chemistries,[5,6] and, for instance, several examples of the use of Tp complexes to mimic enzymatic systems have been reported.[7] In contrast, the coordination chemistry of the isoelectronic tris(pyrazolyl)methane ($HC(pz)_3$, Tpm, pz = pyrazolyl) type ligands is much less studied. One reason for the limited research in this area is that the syntheses of the latter ligands, with the exception of Tpm itself, are more difficult than those of the tris(pyrazolyl)borate analogues.[8] A "second generation" of tris(pyrazolyl) ligands, introduced again by Trofimenko,[9] in which the pyrazolyl rings contain bulky substituents, especially at the 3-position, offers the opportunity to tune the coordination behavior toward different metal centers.

More recently, Kläui reported the synthesis of tris(pyrazolyl)methanesulfonate (Tpms) salts and their derivatives as a novel and more hydrophilic class of ligands.[10] Moreover, these ionic functionalized tris(pyrazolyl)methane derivatives exhibit a relevant coordination versatility, acting as either a tripodal or a bipodal ligand (i.e., with N_3-, N_2O-, N_2- or NO-coordination modes) with the possibility of involving the sulfonate moiety in the coordination.[11] This flexibility allows exploring the behavior of the resulting complexes toward further ligand binding to the metal center.

The study we now report is aimed at the synthesis and investigation of the coordination behavior of a new scorpionate that could combine the flexibility and water solubility of the sulfonato-functionalized class with the sterically demanding features of the 3-substituted tris(pyrazolyl) ligands. For these purposes, we designed a new Tpms derivative bearing a phenyl ring at the 3-position of pyrazolyl rings. When ligating a metal center, such a bulky species would be expected to provide a "steric control" on the other coordination position(s) of the complex, selecting the suitable ligands on the opposite side, namely preventing the formation of "sandwich" complexes (with two of such scorpionate ligands).[12] Hence, herein we present the synthesis of the new tris(3-phenylpyrazolyl)methanesulfonate $(Tpms^{Ph})^-$ species, its coordination behavior toward copper(I), and the reactions with the two water soluble phosphines[13] 1,3,5-triaza-7-phosphaadamantane (PTA) and *N*-methyl-1,3,5-triaza-7-phosphaadamantane tetraphenyl borate ((mPTA)[BPh_4]), and the related hexamethylenetetramine (HMT). The coordination chemistry of the aqua-soluble PTA and $(mPTA)^+$ species has received an increased interest in recent years[13b] on account of the enhanced solubility in water of their complexes, a feature of interest for applications in biological systems[14] and aqueous phase catalysis.[15] The new water soluble complexes could represent a potentially active class of catalysts bearing a flexibile labile ligand that would provide a convenient entry to further reactivity studies (i.e., dioxygen activation, coordination of small molecules, development of inorganic enzyme models[7e]).

Experimental Section

General Materials and Experimental Procedures. All syntheses were carried out under an atmosphere of dinitrogen, using standard Schlenk techniques. All solvents were dried, degassed, and distilled prior to use. The reagents [$Cu(MeCN)_4$][PF_6], hexamethylenetetramine (HMT), Na[BPh_4], 3-phenyl-1*H*-pyrazole, and sulfur trioxide-trimethylamine complex were purchased from Aldrich and used without further purification. 1,3,5-triaza-7-phosphaadamantane (PTA) and *N*-methyl-1,3,5-triaza-7-phosphaadamantane iodide ([mPTA]I) were synthesized in accordance with

(5) (a) Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842–1844. (b) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborates Ligands*; Imperial College Press: London, 1999.
(6) (a) McCleverty, J. A.; Meyer, T. J. *Comprehensive Coordination Chemistry II: From Biology to Nanotechnology*; Elsevier: Amsterdam, 2003; Vol. *1*. (b) Byers, P. K.; Canty, A. J.; Skelton, B. W. *Organometallics* **1990**, *9*, 826–832. (c) Bigmore, H. R.; Lawrence, C. S.; Mountford, P.; Tredget, C. S. *Dalton Trans.* **2005**, 635–651. (d) Pettinari, C.; Pettinari, R. *Coord. Chem. Rev.* **2005**, *249*, 525–543. (e) Kitajima, N. *Adv. Inorg. Chem.* **1992**, *39*, 1–77.
(7) (a) Looney, A.; Han, R.; McNeill, K.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4690–4697. (b) Parkin, G. *Chem. Commun.* **2000**, 1971–1985. (c) Vahrenkamp, H. *Acc. Chem. Res.* **1999**, *32*, 589–596. (d) Schneider, J. L.; Carrier, S. M.; Ruggiero, C. E.; Young, V. G.; Tolman, W. B. *J. Am. Chem. Soc.* **1998**, *120*, 11408–11418. (e) Hu, Z.; Williams, R. D.; Tran, D.; Spiro, T. G.; Gorun, S. M. *J. Am. Chem. Soc.* **2000**, *122*, 3556–3557. (f) Beck, A.; Weibert, B.; Burzlaff, N. *Eur. J. Inorg. Chem.* **2001**, *2*, 521–527.
(8) Reger, D. L.; Grattan, T. C. *Synthesis* **2003**, 350–356.
(9) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943–980. (b) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419–531. (c) Kealey, S.; Long, N. J.; Miller, P. W.; White, A. J. P.; Gee, A. D. *Dalton Trans.* **2008**, *20*, 2677–2679.
(10) Kläui, W.; Berghahn, M.; Rheinwald, G.; Lang, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2464–2466.
(11) (a) Kläui, W.; Peters, W.; Rheinwald, G.; Lang, H. *Eur. J. Inorg. Chem.* **2001**, *6*, 1415–1424. (b) Kläui, W.; Berghahn, M.; Shönherr, T.; Rheinwald, G.; Lang, H. *Eur. J. Inorg. Chem.* **2003**, *11*, 2059–2070. (c) Papish, E. T.; Taylor, M. T.; Jernigan, F. E.; Rodig, M. J.; Shewhan, R. R.; Yap, G. P. A.; Jové, F. A. *Inorg. Chem.* **2006**, *45*, 2242–2250. (d) Chenskaya, T. B.; Berghahn, M.; Kunz, P. C.; Frank, W.; Kläui, W. *J. Mol. Struct.* **2007**, *829*, 135–148.
(12) (a) Edwards, P. G.; Harrison, A.; Newman, P. D.; Zhang, W. *Inorg. Chim. Acta* **2006**, *359*, 3549–3556. (b) Trofimenko, S.; Calabrese, J. C.; Domille, P. J.; Thompson, J. S. *Inorg. Chem.* **1989**, *28*, 1091–1101.
(13) (a) Pruchnik, F. P.; Smolenski, P. *Appl. Organomet. Chem.* **1999**, *13*, 829–836. (b) Phillips, A. D.; Gonsalvi, L.; Romerosa, A.; Vizza, F.; Peruzzini, M. *Coord. Chem. Rev.* **2004**, *248*, 955–993.
(14) (a) Romerosa, A.; Campos-Malpartida, T.; Lidrissi, C.; Saoud, M.; Serrano-Ruiz, M.; Perruzzini, M.; Garrido-Cardenas, J. A. G.; Garcia-Maroto, F. G. *Inorg. Chem.* **2006**, *45*, 1289–1298. (b) Romerosa, A.; Saoud, M.; Campos-Malpartida, T.; Lidrissi, C.; Serrano-Ruiz, M.; Peruzzini, M.; Garrido, J. A.; Garcia-Maroto, F. G. *Eur. J. Inorg. Chem.* **2007**, *18*, 2803–2812. (c) Romerosa, A.; Bergamini, P.; Bertolasi, V.; Canella, A.; Cattabriga, M.; Gavioli, R.; Mañas, S.; Mantovani, N.; Pellicani, L. *Inorg. Chem.* **2004**, *43*, 905–913. (d) Bergamini, P.; Bertolasi, V.; Martelli, L.; Canella, A.; Cattabriga, M.; Gavioli, R.; Mañas, S.; Romerosa, A. *Inorg. Chem.* **2007**, *46*, 4267–4276. (e) Scolaro, C.; Geldbach, T. J.; Rochat, S.; Dorcier, A.; Gossens, C.; Bergamo, A.; Cocchietto, M.; Tavernelli, I.; Sava, G.; Rothlisberger, U.; Dyson, P. J. *Organometallics* **2006**, *25*, 756–765. (f) Scolaro, C.; Bergamo, A.; Brescacin, L.; Delfino, R.; Cocchietto, M.; Laurenczy, G.; Geldbach, T. J.; Sava, G.; Dyson, P. J. *J. Med. Chem.* **2005**, *12*, 4161–4171.
(15) (a) *Aqueous Phase Organometallic Catalysis*; Horvath, I. T., Joü, F. Eds.; Wiley-VCH: Weinheim, 1998. (b) Smolenski, P.; Pruchnik, F. P.; Ciunik, Z. T. L. *Inorg. Chem.* **2003**, *42*, 3318–3322. (c) Pruchnik, F. P.; Smolenski, P.; Wajda-Hermanowicz, K. *J. Organomet. Chem.* **1998**, *570*, 63–69.

literature methods,[16] whereas hydrotris(3-phenylpyrazolyl)methane (Tpm^{Ph}) was prepared by modifying a published procedure.[17] C, H, and N analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. ^1H, ^{13}C, and ^{31}P NMR spectra were measured on Bruker 300 and 400 UltraShield™ spectrometers. ^1H and ^{13}C chemical shifts δ are expressed in ppm relative to $Si(Me)_4$ and $\delta(^{31}P)$ relative to 85% H_3PO_4. Coupling constants are in Hz; abbreviations: s, singlet; d, doublet; m, complex multiplet; vt, virtual triplet; br, broad.

Synthesis of HC(3-Phpz)$_3$, Tpm^{Ph}. To a vigorously stirred suspension of 3-phenyl-1*H*-pyrazole (5.00 g, 34.7 mmol) and tetrabutylammonium bromide (0.56 g, 1.70 mmol) in water (70 mL) was added an excess of Na_2CO_3 (22.0 g, 208 mmol) during 30 min. Then chloroform (17 mL) was added, and the final mixture was refluxed for 84 h. The reaction mixture was then cooled to room temperature, and toluene (20 mL) and water (15 mL) were added. The organic phase was separated, washed with water, brine, dried over Na_2SO_4, and evaporated under vacuum to give a brown oil. This crude oil was dissolved in toluene (40 mL) and a catalytic amount (ca. 80 μL, 1.0 mmol) of trifluoroacetic acid (TFA) was added to this solution which was then refluxed for 1 day. After this, the solution was cooled down to room temperature, washed with water (2 × 15 mL) and neutralized with an aqueous solution of $NaHCO_3$. The organic phases were collected, washed with water and brine, then dried over Na_2SO_4 and evaporated. The crude solid was triturated in diisopropyl ether to give an off-white powder of Tpm^{Ph} (3.2 g, 62%). The compound is well soluble in medium and high polarity solvents like Me_2CO, $CHCl_3$, CH_2Cl_2, MeOH, EtOH, and DMSO and insoluble in H_2O. HC(3Phpz)$_3$, $C_{28}H_{22}N_6$ (442.51): calcd C 75.99, N 18.99, H 5.01; found C 75.86, N 18.71, H 5.39. IR (KBr): 3162 (w) 1529 (m, ν(C=N)), 1502 (m), 1456 (s), 1240 (s), 1077 (s), 1050 (s), 809 (s), 756 (s), 693 (s) cm^{-1}. ^1H NMR (300 MHz, acetone-d_6): 8.86 (s, 1H, *H*C), 8.11 (d, 3H, J_{HH} = 2.6 Hz, 5-H (pz)), 7.90 (d, 2H, J_{HH} = 8.1 Hz, *o*-H (Ph)), 7.42 (dd, vt, 6H, *m*-H (Ph)), 7.35 (dd, vt, 3H, *p*-H (Ph)), 6.90 (dd, vt, 3H, J_{HH} = 2.6 Hz, 4-H (pz)).

Synthesis of Li[O$_3$SC(3-Phpz)$_3$], Li(Tpms^{Ph}), (1). A 1.6 M solution of butyllithium (1.6 mL, 2.7 mmol, 1.1 equiv) in hexane was added dropwise to tris(3-phenylpyrazolyl)methane Tpm^{Ph} (1.00 g, 2.26 mmol, 1.0 equiv) in dry tetrahydrofuran (THF) at −65 °C. The solution turned red/brown and was stirred for 1 h at −60 °C. Sulfur trioxide-trimethylamine complex (330 mg, 2.38 mmol, 1.05 equiv) was added at −60 °C, and the reaction was allowed to warm to room temperature overnight. The solvent was evaporated, and the residue was dried under vacuum at room temperature for 2 h. It was then suspended in THF and filtered to yield a white powder of (**1**) (0.66 g, 56%). The compound is well soluble in medium and high polarity solvents like H_2O ($S_{25°C} \approx 90$ mg·mL^{-1}), Me_2CO, $CHCl_3$, MeOH, EtOH, and DMSO, and insoluble in Et_2O. Li[O$_3$SC-(3Ph-pz)$_3$], $C_{28}H_{21}N_6O_3SLi$ (528.51): calcd C 63.63, N 15.90, H 4.01, S 6.07; found C 63.12, N 15.71, H 4.39, S 5.91. IR (KBr): 3437 (s), 3060, 2980, 2882 (m br), 1534 (m, ν(C=N)), 1502 (m), 1456 (s), 1398 (m), 1354 (m), 1266 (s br), 1240 (s br), 1077 (s), 1048 (s, ν(S−O)), 888 (m), 866 (s), 760 (s), 698 (s), 643 (s, ν(C−S)) cm^{-1}. ^1H NMR (300 MHz, acetone-d_6): 8.22 (d, 3H, J_{HH} = 2.7 Hz, 5-H (pz)), 7.77 (d, 6H, J_{HH} = 8.1 Hz, *o*-H (Ph)), 7.37−7.24 (m, 9H, *m*-H and *p*-H (Ph)), 6.83 (d, 3H, J_{HH} = 2.7 Hz, 4-H (pz)). ^{13}C NMR (300 MHz, acetone-d_6): 151.1 (s, 3-C (pz)), 134.4 (s, 5-C (pz)), 133.5 (s, pz-*C* (Ph)), 128.3 (s, o-C (Ph)), 127.6 (s, p-C (Ph)), 125.8 (s, m-C (Ph)), 103.5 (s, 4-C (pz)), 99.9 (s, O_3SC).

Synthesis of (mPTA)[BPh$_4$]. A methanolic solution (25 mL) of Na[BPh_4] (342 mg, 1.00 mmol) was added to a solution (25 mL) of [mPTA]I (300 mg, 1.00 mmol) in the same solvent. The resulting white suspension was stirred for 15 min and the solid was then filtered off, washed with methanol (3 × 10 mL) and dried under vacuum giving a white powder, which was crystallized from acetone/methanol leading to the colorless crystalline product (mPTA)[BPh_4], in about 80% yield. The compound is well soluble in medium polarity solvents like Me_2CO, $CHCl_3$, and CH_2Cl_2, sparingly soluble in H_2O ($S_{25°C}$ = 0.2 mg·mL^{-1}), MeOH, EtOH and DMSO, and insoluble in C_6H_6 and Et_2O. (mPTA)-[BPh_4]·0.25MeOH, $BC_{31,25}H_{36}N_3OP$ (499.41): calcd C 75.16, N 8.41, H 7.21; found C 75.03, N 8.80, H 7.24. IR (KBr): 3052 (m br), 2996 (m br), 2984 (m br), 2965 (m br), 2921(m br), 1580 (m, ν(C=C)), 1478 (m), 1452 (w), 1426 (m), 1311 (m), 1271 (m), 1247 (m), 1123 (m), 1099 (m), 1025 (m), 982 (m), 913 (m), 804 (m), 751 (s), 737 (s, $\nu(BPh_4^-)$), 709 (s, $\nu(BPh_4^-)$), 602 (m), 554 (m) cm^{-1}. ^1H NMR (300 MHz, acetone-d_6): δ 7.34 (br s, 8H, *o*-H (Ph)), 6.92 (dd, vt, J_{HH} = 6.9 Hz 8H, *m*-H (Ph)), 6.78 (dd, vt, 4H, *p*-H (Ph)), 5.13 and 5.04 ($J(H^AH^B)$ = 13.2 Hz, 4H, $NCH^AH^BN^+$), 4.70 and 4.52 ($J(H^AH^B)$ = 14.0 Hz, 2H, NCH^AH^BN), 4.54 (s, 2H, PCH_2N^+), 4.09 and 3.94 ($J(H^AH^B)$ = 15.0 Hz, $^3J(H^A\text{-}P)$ = 15.0 Hz, $^3J(H^B\text{-}P)$ = 9.6 Hz, 4H, PCH^AH^BN), 2.81 (s, 3H, N^+CH_3). $^{31}P\{^1H\}$ NMR (162.0 MHz, acetone-d_6): −85.4 (s). $^{31}P\{^1H\}$ NMR (162.0 MHz, DMSO-d_6): −87.0 (s). $^{13}C\{^1H\}$ and HMQC $^{13}C-^1H$ NMR (100.6 MHz, acetone-d_6): 165.7 - 164.2 (4s, 1-C, BPh_4), 137.0 (s, 2-C, BPh_4), 126.1 - 126.0 (4s, 3-C, BPh_4), 122.3 (s, 4-C, BPh_4), 81.9 (s, NCH_2N^+), 70.6 (s, NCH_2N), 57.3 (dd, vt, $^1J(C-P)$ = 33.6 Hz, PCH_2N^+), 50.4 (s, N^+CH_3), 46.6 (dd, vt, $^1J(C-P)$ = 20.8 Hz, PCH_2N).

Synthesis of [Cu{O$_3$SC(3-Phpz)$_3$}(MeCN)], [Cu(Tpms^{Ph})(MeCN)], (2). Compound (**2**) was prepared by adding 5 mL of a methanolic solution of Li($Tpms^{Ph}$) (78.3 mg, 0.148 mmol) to a [$Cu(MeCN)_4$][PF_6] solution (55.2 mg, 0.148 mmol) in the same solvent (10 mL). The reaction mixture was stirred at room temperature for 10 min and compound (**2**) precipitated as a white powder which was collected by filtration, washed with cold methanol (2 × 5 mL) and dried under vaccum (57 mg, 62%). It is well soluble in medium polarity solvents like Me_2CO, $CHCl_3$ and CH_2Cl_2, less soluble in H_2O ($S_{25°C} \approx 4$ mg·mL^{-1}), MeOH, EtOH, and DMSO, and insoluble in C_6H_6 and Et_2O. (**2**), $C_{30}H_{24}N_7O_3SCu$ (626.17): calcd C 57.55, N 15.66, H 3.86, S 5.12; found. C 57.36, N 15.09, H 3.71, S 4.95. IR (KBr): 3571 (s), 3158, 3126, 3060 (m br), 2930 (m br), 2316 (w br), 1534 (s, ν(C=N)), 1500 (s), 1458 (s), 1372 (m), 1237 (s br), 1045 (s, ν(S−O)), 853 (m), 767 (s), 696 (m), 639 (s, ν(C−S)), 540 (m) cm^{-1}. ^1H NMR (300 MHz, acetone-d_6, 298 K): δ 8.07 (s, br, 3H), 7.95 (d, 6H, J_{HH} = 7.7 Hz, *o*-H (Ph)), 7.52−7.43 (m, 9H, *m*-H and *p*-H (Ph)), 6.94 (d, 3H, J_{HH} = 2.8 Hz, 4-H (pz)), 2.12 (s, 3H, H_3CCN). ^1H NMR (300 MHz, acetone-d_6, 188 K): δ 8.87 (s, br, 1H, 5-H (pz)), 8.09 (d, 4H, J_{HH} = 7.4 Hz, *o*-H (Ph)), 7.99 (d, 2H, J_{HH} = 7.4 Hz, *o*-H (Ph)), 7.63−7.47 (m, 9H, *m*-H and *p*-H (Ph)), 7.35 (s, br, 1H 4-H (pz)), 7.27 (s, br, 2H, 5-H (pz)), 7.00 (s, br, 2H, 4-H (pz)). $^{13}C\{^1H\}$ and HMQC $^{13}C-^1H$ NMR (300 MHz, acetone-d_6, 298 K): 153.7 (s, 3-C (pz)), 135.8 (s, 5-C (pz)), 131.5 (s, pz-*C* (Ph)), 129.1 (s, *p*-C (Ph)), 128.5 (s, *m*-C (Ph)), 126.9 (s, *o*-C (Ph)), 116.18 (s, $NCCH_3$), 104.71 (s, 4-C (pz)), 100.0 (s, O_3SC), 0.91 (s, $NCCH_3$).

(16) (a) Daigle, D. J.; Pepperman, A. B., Jr.; Vail, S. L. *J. Heterocycl. Chem.* **1974**, *11*, 407–408. (b) Daigle, D. J.; Decuir, T. J.; Robertson, J. B.; Darensbourg, D. J. *Inorg. Synth.* **1998**, *32*, 40–45.

(17) (a) Reger, D. L.; Grattan, C. G.; Brown, K. J.; Little, C. A.; Lamba, J. J. S.; Rheingold, A. L.; Sommer, R. D. *J. Organomet. Chem.* **2000**, *607*, 120–128. (b) Reger, D. L.; Collins, J. E.; Jameson, D. L.; Castellano, R. K.; Canty, A. J.; Jin, H. *Inorg. Synth.* **1998**, *32*, 63–65.

X-ray quality single crystals were grown by slow evaporation in air at room temperature of an acetone solution of (**2**).

Synthesis of [Cu{O_3SC(3-Phpz)$_3$}(PTA)], [Cu(Tpms^{Ph})(PTA)], (3). To a methanolic solution (15 mL) of [Cu(MeCN)$_4$][PF_6] (42.0 mg, 0.113 mmol, 1 equiv) was added 5 mL of a solution of Li(Tpms^{Ph}) (60 mg, 0.113 mmol, 1 equiv) in the same solvent. The transparent colorless solution was stirred for 10 min at room temperature to allow the formation in situ of complex (**2**) that remains in solution. Then PTA (16 mg, 0.10 mmol) was slowly added portionwise and stirring of the reaction mixture was continued at room temperature for 1 h. The formed white powder of (**3**) was collected by filtration, washed with cold methanol (2 × 10 mL), then recrystallized from acetone at 4 °C (73.7 mg, 87.5%). Complex (**3**) is well soluble in medium polarity solvents like Me_2CO, $CHCl_3$ and CH_2Cl_2, less soluble in H_2O ($S_{25°C} \approx 6$ mg·mL^{-1}), MeOH, EtOH and DMSO, and insoluble in C_6H_6, and Et_2O. (**3**)·0.5CH_2Cl_2, $C_{34.5}H_{34}ClN_9O_3PSCu$ (784.74): calcd C 52.80, N 16.06, H 4.36, S 4.08; found C 53.36, N 16.19, H 4.50, S 4.01. IR (KBr): 3168 (s), 2943(m br), 1532 (m, ν(C=N)), 1414 (s), 1328 (m), 1246 (s br), 1054 (s, ν(S−O)), 1015 (s), 972 (m), 854 (m), 770 (s), 633 (s, ν(C−S)), 534 (m) cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6, 298 K): 8.50 (s, br, 3H), 7.73 (d, 6H, J_{HH} = 8.0 Hz, *o*-H (Ph)), 7.61 (dd, vt, 6H, *m*-H (Ph)), 7.54 (dd, vt, 3H, *p*-H (Ph)), 6.92 (d, 3H, J_{HH} = 2.8 Hz, 4-H (pz)), 4.16 H^A and 3.96 H^B (J_{AB} = 13.0 Hz, 6H, NC*H*^{A}*H*^{B}N (PTA)), 2.97 (s, br, 6H, PCH_2N (PTA)). ^{1}H NMR (300 MHz, acetone-d_6, 188 K): δ 8.85 (s, br, 3H, 5-H (pz)), 8.02−7.50 (m, 15H, *o*-H, *m*-H and *p*-H (Ph)), 7.12 (s, br, 3H, 4-H (pz)), 4.09 H^A and 3.72 H^B (6H, J_{AB} = 12.0 Hz, NC*H*^{A}*H*^{B}N (PTA)), 2.57 (s, br, 6H, PCH_2N (PTA)). ^{13}C{^{1}H} and HMQC ^{13}C−^{1}H NMR (300 MHz, acetone-d_6, 298 K): 154.4 (s, 3-*C* (pz)), 135.5 (s, 5-C (pz)), 132.3 (s, pz-*C* (Ph)), 129.33 (s, *p*-C (Ph)), 129.29 (s, m-C (Ph)), 127.3 (s, o-*C* (Ph)), 105.6 (s, 4-C (pz)), 72.2 (s, P*C*H_2N), 48.70 (s, N*C*H_2N). ^{31}P{^{1}H}-NMR (acetone-d_6, 298 K): −93.3 (s, br PTA). X-ray quality single crystals were grown by slow evaporation in air at room temperature of an acetone solution of (**3**).

Synthesis of [Cu{O_3SC(3-Phpz)$_3$}(HMT), [Cu(Tpms^{Ph})(HMT)], (4). A solution of Li(Tpms^{Ph}) (78.3 mg, 0.148 mmol) in methanol (15 mL) was added to a [Cu(MeCN)$_4$][PF_6] solution (55.2 mg, 0.148 mmol) in the same solvent (5 mL). The solution was stirred for 10 min to allow the formation in situ of [Cu(Tpms^{Ph})(MeCN)] (**2**) that remains in solution. Then a methanolic solution (8 mL) of hexamethylenetetramine (HMT) (20.8 mg, 0.148 mmol) was added to the reaction mixture and the final solution was stirred at room temperature for 1 h. The white powder of crude (**4**) was collected by filtration, washed with cold methanol (2 × 10 mL), then recrystallized from acetone at 4 °C. The final white microcrystalline solid was dried under vacuum to afford (**4**)·0.5Me_2CO (97 mg, 87%). Complex (**4**) is well soluble in medium polarity solvents like Me_2CO, $CHCl_3$, and CH_2Cl_2, less soluble in H_2O ($S_{25°C} \approx 6$ mg·mL^{-1}), MeOH, EtOH, and DMSO, and insoluble in C_6H_6 and Et_2O. (**4**)·0.5Me_2CO, $C_{35.5}H_{36}N_{10}O_{3.5}SCu$ (754.34): calcd C 56.52, N 18.57, H 4.81, S 4.25; found C 56.24, N 18.23, H 4.63, S 4.05. IR (KBr): 3571 (s), 3151, 3107, 3070 (m br), 2980 (m br), 2951(m br), 2926(m br), 2883 (m br), 1534 (m, ν(C=N)), 1499 (m), 1457 (s), 1376 (m), 1240 (s br), 1046 (s, ν(S−O)), 1023 (s), 991 (m), 852 (m), 760 (s), 705 (m), 637 (s, ν(C−S)), 533 (m) cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6, 298 K): δ 7.94 (d, 6H, J_{HH} = 7.4 Hz, *o*-H (Ph)), 7.84 (s, br, 3H, 5-H (pz)), 7.60−7.52 (m, 12H, *m*-H *p*-H (Ph)), 6.92 (s, br, 3H, 4-H (pz)), 4.29 (s, br, 12H, NCH_2N (HMT)). ^{1}H NMR (300 MHz, acetone-d_6, 188 K): δ 8.91 (s, br, 1H, 5-H (pz)), 8.14 (d, 4H, J_{HH} = 7.0 Hz, *o*-H (Ph)), 7.95 (s, br, 2H, *o*-H (Ph)), 7.76−7.66 (m, 6H, *m*-H (Ph)), 7.45 (m, 3H, *p*-H (Ph)), 7.35 (s, br, 1H, 4-H (pz)), 7.22 (s, br, 2H, 5-H (pz)), 6.90 (s, br, 2H, 4-H (pz)), 4.39 H^A and 4.09 H^B (J_{AB} = 12.0 Hz, 6H, NC*H*^{A}*H*^{B}N (HMT)), 4.19 (s, br, 6H, N^{coord}CH_2N (HMT)). ^{13}C{^{1}H} and HMQC ^{13}C−^{1}H NMR (75.4 MHz, acetone-d_6, 298 K): 153.9 (s, 3-C (pz)), 136.0 (s, 5-C (pz)), 132.47 (s, pz-*C* (Ph)) 129.7 (s, *p*-C (Ph)), 129.2 (s, *m*-C (Ph)), 127.0 (s, *o*-C (Ph)), 104.9 (s, 4-C (pz)), 74.3 (s, br (HMT)). X-ray quality single crystals were grown by slow evaporation in air at room temperature of the acetone solution of (**4**).

Synthesis of [Cu{O_3SC(3-Phpz)$_3$}(mPTA)][PF_6], [Cu(Tpms^{Ph})(mPTA)][PF_6], (5). To a stirred methanolic solution (45 mL) of [Cu(MeCN)$_4$][PF_6] (186 mg, 0.50 mmol) were added 10 mL of a methanolic solution of Li(Tpms^{Ph}) (264 mg, 0.50 mmol). After 10 min to allow the formation in situ of [Cu(Tpms^{Ph})(MeCN)] (**2**) that remains in solution, a dichloromethane solution (10 mL) of (mPTA)[BPh_4] (246 mg, 0.50 mmol) was added. The reaction mixture was stirred at room temperature for 1 h and then concentrated to half-volume under vacuum. The mixture was kept at 4 °C for 2 days. A white microcrystalline solid was collected, washed with cold methanol (2 × 10 mL), and dried under vacuum to yield (**5**) (315 mg, 70%). Complex (**5**) is well soluble in medium polarity solvents like Me_2CO, $CHCl_3$, and CH_2Cl_2, less soluble in H_2O ($S_{25°C} \approx 7.5$ mg·mL^{-1}), MeOH, EtOH, and DMSO, and insoluble in C_6H_6 and Et_2O. (**5**)·1.5CH_2Cl_2, $C_{36.5}H_{39}F_6Cl_3N_9O_3P_2SCu$ (1029.67): calcd C 42.61, N 12.24, H 3.82, S 3.11; found C 42.58, N 12.79, H 4.06, S 3.34. IR (KBr): 3651 (s), 3154 (m br), 3107 (m br), 3075 (m br), 2990 (m br), 2930 (m br), 1535 (m, ν(C=N)), 1450 (m), 1459 (s), 1386 (m), 1355 (m), 1280 (s br), 1247 (s), 1077 (s), 1049 (s, ν(S−O)), 985 (m), 924 (m), 844 (s), 762 (m), 698 (m), 629 (m, ν(C−S)), 558 (m) cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6, 298 K): δ 8.05−7.89 (m, br, 6H+3H, *o*-H (Ph) + 5-H (pz)), 7.61−7.56 (m, 9H, *m*-H *p*-H (Ph)), 6.96 (s, br, 3H, 4-H (pz)), 5.01 (s, br, 4H, NC*H*^{A}*H*^{B}N$^+$), 4.47 and 4.40 (J(H^{A}H^B) = 14.0 Hz, 2H, NC*H*^{A}*H*^{B}N), 3.98 (s, 2H, PCH_2N$^+$), 3.61 and 3.43 (J(H^{A}H^B) = 13 Hz, 4H, PC*H*^{A}*H*^{B}N), 2.79 (s, 3H, N$^+$CH_3). ^{1}H NMR (300 MHz, acetone-d_6, 213 K): δ 8.94 (d, 1H, J_{HH} = 2.83 Hz, 5-H (pz)), 8.04 (d, 4H, J_{HH} = 7.4 Hz, *o*-H (Ph)), 7.95 (d, 2H, J_{HH} = 7.0 Hz, *o*-H (Ph)), 7.72−7.58 (m, 6H, *m*-H (Ph)), 7.52−7.38 (m, 3H, *p*-H (Ph)), 7.35 (d, 1H, 4-H (pz)), 7.28 (d, J_{HH} = 2.70 Hz, 2H, 5-H (pz)), 6.96 (d, 2H, 4-H (pz)), 5.08 and 5.00 (J(H^{A}H^B) = 13.0 Hz, 4H, NC*H*^{A}*H*^{B}N$^+$), 4.56 and 4.36 (J(H^{A}H^B) = 14.0 Hz, 2H, NC*H*^{A}*H*^{B}N), 4.15 (s, 2H, PCH_2N$^+$), 3.78 and 3.20 (J(H^{A}H^B) = 14 Hz, 4H, PC*H*^{A}*H*^{B}N), 2.81 (s, 3H, N$^+$CH_3). ^{31}P{^{1}H} NMR (121.4 MHz, acetone-d_6, 298 K): δ = −70.9 (br s), −144.2 (septet, PF_6). ^{13}C{^{1}H} and HMQC ^{13}C−^{1}H NMR (100.6 MHz, acetone-d_6, 298 K): 155.8 (s, 3-C (pz)), 137.2 (s, 5-C (pz)), 130.5 (s, *p*-C (Ph)), 130.2 (s, *m*-C (Ph)), 128.3 (s, *o*-C (Ph)), 106.3 (s, 4-C (pz)), 81.6 (s, NCH_2N$^+$), 69.9 (s, NCH_2N), 55.8 (s, PCH_2N$^+$), 50.1 (s, N$^+$$CH_3$), 46.7 (s, P$CH_2$N). X-ray quality single crystals were grown by slow evaporation in air at room temperature of an acetone solution of (**5**).

Results and Discussion

1. Syntheses of the Sterically Hindered Scorpionates Tpm^{Ph} and Li(Tpms^{Ph}). Hydrotris(3-phenylpyrazolyl)-methane, Tpm^{Ph} (Figure 1, R= H), was prepared by modifying Reger's procedure[17a] to obtain the pure desired product without chromatographic purification. Hence, at the final stages, we have treated a toluene solution of the crude product with a catalytic amount of trifluoroacetic acid (to isomerize the mixture of regioisomers to the desired 3-isomer compound)[17b] and then triturated the final crude solid in diisopropyl ether to afford the pure Tpm^{Ph} compound.

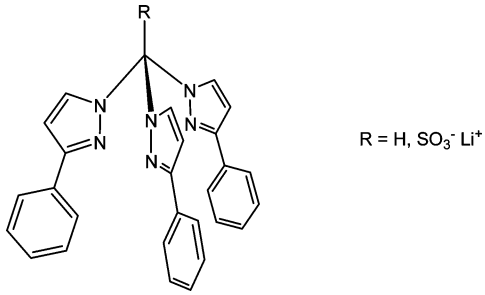
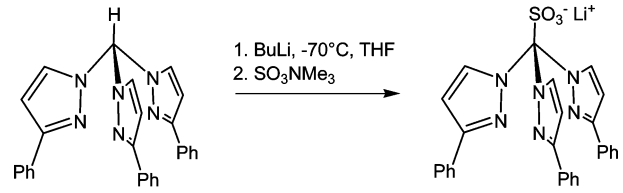


Figure 1. Schematic structures of the tris(3-phenylpyrazolyl)methane compounds Tpm^{Ph} (R = H) and Li($Tpms^{Ph}$) (**1**) (R = SO_3Li).

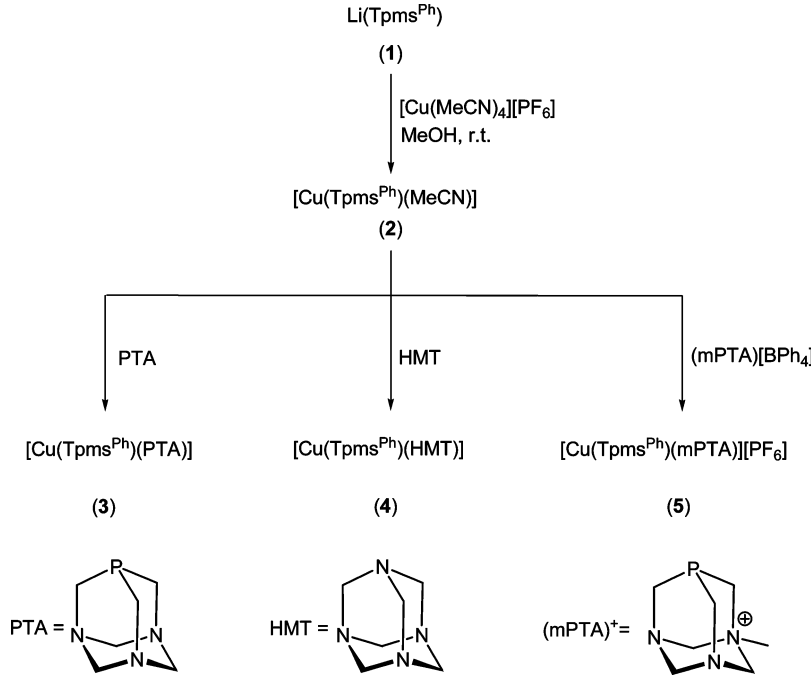
Scheme 1. Synthesis of Tris(3-phenylpyrazolyl)methanesulfonate, as the Lithium Salt Li($Tpms^{Ph}$) (**1**)



Starting from Tpm^{Ph} we were able to prepare the tris(3-phenylpyrazolyl)methanesulfonate species as the lithium salt, Li($Tpms^{Ph}$) (**1**) (Figure 1, R = SO_3Li) in good yield, following a process known[10] for the synthesis of other Tpms, that is, by deprotonation of the methine carbon by BuLi, at low temperature, followed by sulfonation with the SO_3NMe_3 adduct (Scheme 1). Both Tpm^{Ph} and Li($Tpms^{Ph}$) were characterized by ^1H, ^{13}C NMR, and IR spectroscopies, and elemental analyses. As the Tpm^{Ph}, the sulfonate derivative shows a well resolved ^1H NMR spectrum (acetone-d_6) with only one set of resonances for the three equivalent pyrazolyl rings: one pattern of signals for the phenyl protons and a pair of doublets (J_{HH} = 2.7 Hz) at δ 8.22 and 6.83 for the 5-H and 4-H pyrazolyl protons, respectively. Tpm^{Ph} and its sulfonate Li($Tpms^{Ph}$) represent a highly sterically hindered class of scorpionates. Moreover, the sulfonate derivative shows interesting properties in terms of solubility. In fact, in spite of the presence of three phenyl rings, Li($Tpms^{Ph}$) is well soluble in all common polar solvents, that is, MeOH, EtOH, acetone, and water ($S_{25°C} \approx 90$ mg·mL^{-1}), and shows a decreasing solubility in medium polarity solvents and in non-polar ones. We have thus started to investigate its coordination chemistry, as described below.

2. Syntheses of the Cu^I Complexes [Cu($Tpms^{Ph}$)L] [L = MeCN (2), PTA (3), HMT (4)] and [Cu($Tpms^{Ph}$)(mPTA)][PF_6] (5). Reaction of Li($Tpms^{Ph}$) (**1**) with [$Cu(MeCN)_4$][PF_6] in methanol proceeds readily at room temperature to give [Cu($Tpms^{Ph}$)(MeCN)] (**2**) bearing the anionic $Tpms^{Ph}$ ligand and one bound molecule of acetonitrile, in good yield (Scheme 2). The neutral Cu^I complex (**2**) precipitates from the concentrated reaction mixture, as a white solid, which is sparingly soluble in water ($S_{25°C} \approx 4$ mg·mL^{-1}), MeOH, EtOH, or DMSO, and well soluble in Me_2CO, $CHCl_3$, or CH_2Cl_2. It is stable in air when dried but is relatively unstable in solution (after 2−3 days the color changes to green, typical of a Cu^{II} oxidized product). It was characterized, as the compounds (**3**)−(**5**) described below, by NMR and IR spectroscopies, elemental analysis, and X-ray diffraction. The ^1H and ^{13}C NMR and IR spectra of (**2**) confirm the presence of its ligands: the NMR shifted resonances of $Tpms^{Ph}$ and an IR weak and broad NC stretching band at 2316 cm^{-1}, well above that of uncoordinated NCMe, that is, 2253 cm^{-1}. This positive coordination shift [$\Delta\nu_{(NC)}$= 63 cm^{-1}] indicates that the acetonitrile is behaving as a very weak π-acceptor, acting mainly as an effective σ-donor ligand, in accord with related scorpionate complexes.[18]

Scheme 2. Syntheses of the Complexes [Cu($Tpms^{Ph}$)L] [L = MeCN (**2**), PTA (**3**), HMT (**4**)] and [Cu($Tpms^{Ph}$)(mPTA)][PF_6] (**5**)



Treatment of a methanolic solution of (**2**), formed in situ, with PTA (0.9 equiv) in methanol leads to the precipitation of [Cu(Tpms^{Ph})(PTA)] (**3**), as a white solid isolated in high yield (88%). This complex shows a good solubility in acetone and dichloromethane, and it is fairly soluble in water ($S_{25°C} \approx 6$ mg·mL^{-1}). The addition of PTA to the reaction mixture should be slow to yield (**3**) in high purity. Traces of the byproduct [Cu(PTA)$_4$][PF$_6$] are formed when the addition is faster or the phosphine is used in a higher amount, indicating a stronger coordination ability of PTA to Cu(I) in comparison with Tpms^{Ph}. The formation of [Cu(PTA)$_4$][PF$_6$] is evidenced by the quartet ($^1J_{P-Cu} = 760$ Hz) resonance at δ −80 observed by ^{31}P{^{1}H} NMR, which is analogous to that known[19] for [Cu(PTA)$_4$][NO$_3$].

In the ^{1}H NMR spectrum of (**3**) (acetone-d_6), the resonances for the PTA moiety confirm its coordination to copper and appear shifted to lower field relatively to those of the free PTA: the six equivalent protons close to the P-atoms give a broad singlet at δ 2.97, and the other resonances for the protons near the N-atoms display the expected AB pattern at δ 3.96−4.16. The Tpms^{Ph} resonances are given below. The ^{31}P{^{1}H} NMR spectrum shows a single broad signal at δ −93. Further NMR experiments at different temperatures reveal additional information on the behavior of compound (**3**) in solution that will be discussed below. The IR spectrum confirms the presence of Tpms^{Ph} (stretching bands at 1539 (C=N), 1048 (SO) and 643 (CS) cm^{-1})[11d] and PTA (1015, 972 and 950 cm^{-1}, full description in the Experimental Section).

Similarly to the reaction with PTA, the acetonitrile complex (**2**) formed in situ reacts with hexamethylenetetramine (HMT) or *N*-methyl-1,3,5-triaza-7-phosphaadamantane tetraphenyl borate ((mPTA)[BPh$_4$]) to yield the corresponding complexes [Cu(Tpms^{Ph})(HMT)] (**4**) or [Cu(Tpms^{Ph})(mPTA)][PF$_6$] (**5**) (Scheme 2). The ^{1}H NMR spectrum of (**4**) at 188 K shows two types of methylene protons for the ligated HMT (i.e., an AB spin system and a broad singlet) confirming the coordination by one of nitrogen atoms. However, at room temperature, only a broad singlet is observed because of an average effect of a dynamic process (see below, NMR section). The isolation, upon precipitation, of compound (**5**), instead of the [BPh$_4$]$^-$ analogue, indicates that the former is less soluble than the latter. As observed for (**2**), compounds (**3**)−(**5**) are soluble in water ($S_{25°C} \approx$ 6−7 mg·mL^{-1}).

3. X-ray Molecular Structures of Complexes [Cu(Tpms^{Ph})L] [L = MeCN (2), PTA (3), HMT (4)] and [Cu(Tpms^{Ph})(mPTA)][PF$_6$] (5). The molecular structures of compounds (**2**)−(**5**) were determined by single crystal X-ray diffraction experiments. Although the X-ray diffraction structural analysis of compound **5** confirms the formulation proposed (see below) the quality of the crystals, and therefore of the refinement, is very low. The Oak Ridge Thermal Ellipsoid Plot (ORTEP) plots are depicted in Figures 2−5, the ellipsoids being shown at 50% probability and the hydrogen atoms being omitted for clarity. Crystallographic details are given in Table 1, selected bond distances in Table 2, and selected angles in Table 3.

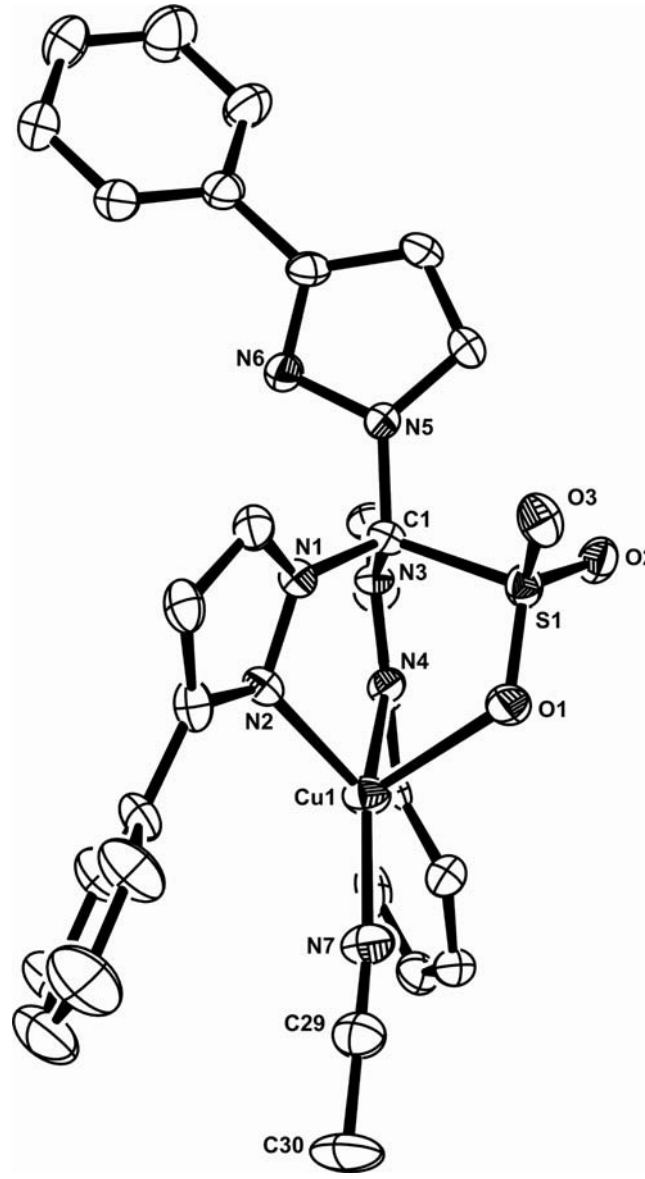


Figure 2. ORTEP plot of [Cu(Tpms^{Ph})(MeCN)] (**2**), with ellipsoids shown at 50% probability.

Single crystals of compounds (**2**) to (**4**) suitable for X-ray diffraction were obtained by slow evaporation in air of acetone solutions. In complexes (**2**) and (**4**) (Figures 2 and 3), the anionic tris(3-phenylpyrazolyl)methanesulfonate group acts as a tridentate ligand with the N,N,O coordination mode to the Cu ion through the two pyrazolyl nitrogens N(2) and N(4) and the oxygen O(1) of the sulfonate moiety. The coordination around each copper is highly distorted tetrahedral with the N2−Cu1−N7 and N4−Cu1−N7 angles of 121.02(12)° and 146.62(12)° for (**2**) or 147.73(14)° and 124.27(14)° for (**4**), and the O1−Cu1−N7 angle of a much lower value (109.82(11)° for (**2**) or 92.38(12)° for (**4**)). Moreover, the Cu(1)−O(1) bond length (2.326(2) Å for (**2**)

(18) (a) Reger, D. L.; Collins, J. E. *Organometallics* **1996**, *15*, 2029–2032. (b) Conry, R. R.; Ji, G.; Tipton, A. A. *Inorg. Chem.* **1999**, *38*, 906–913.

(19) Kirillov, A. M.; Smolenski, P.; da Silva, M. F. C. G.; Pombeiro, A. J. L. *Eur. J. Inorg. Chem.* **2007**, 2686–2692.

Table 1. Crystallographic Data (150 K) for Compounds [Cu(Tpms^{Ph})(MeCN)] (**2**), [Cu(Tpms^{Ph})(PTA)] (**3**), [Cu(Tpms^{Ph})(HMT)] (**4**), and [Cu(Tpms^{Ph})(mPTA)][PF_6] (**5**)

	(**2**)	(**3**)·C_3H_6O	(**4**)	(**5**)·C_3H_6O
empirical formula	$C_{30}H_{24}CuN_7O_3S$	$C_{34}H_{33}CuN_9O_3PS$. C_3H_6O	$C_{37}H_{39}Cu\ N_{10}O_4S$	$C_{35}H_{36}CuN_9O_3PS$, C_3H_6O, F_6P
formula weight	626.18	800.36	783.38	960.37
crystal system	orthorhombic	orthorhombic	orthorhombic	Monoclinic
space group	*Pbcn P2n2ab*	*Pbca*	*Pbca*	*P*21/*n*
a (Å)	15.0997(15)	13.799(3)	11.4692(7)	16.056(6)
b (Å)	13.9691(14)	20.730(5)	21.8702(14)	15.889(6)
c (Å)	28.789(3)	26.676(7)	28.7465(16)	16.279(6)
V (Å^3)	6072.5(11)	7631(3)	7210.6(8)	4123(3)
β (deg)	90	90	90	96.901(2)
Z	8	8	8	4
ρ_{calc} (g cm^{-3})	1.370	1.393	1.443	1.547
μ(Mo Kα) (mm^{-1})	0.831	0.721	0.720	0.738
F (000)	2576	3328	3264	1976
refl. collected/unique	26662/5543	28366/6974	35881/6595	7547/7547
goodness-on-fit on F^2	0.938	0.939	0.997	1.284
R_1 [$I > 2\sigma(I)$] (all data)	0.0474 (0.0904)	0.0615 (0.1721)	0.0555 (0.1315)	0.1573 (0.2349)

Table 2. Selected Bond Distances [Å] for Compounds [Cu(Tpms^{Ph})(MeCN)] (**2**), [Cu(Tpms^{Ph})(PTA)] (**3**), [Cu(Tpms^{Ph})(HMT)] (**4**), and [Cu(Tpms^{Ph})(mPTA)][PF_6] (**5**)

	(**2**)	(**4**)		(**3**)·C_3H_6O	(**5**)·C_3H_6O
Cu(1)−N(2)	2.065(3)	1.968(4)	Cu(1)−N(2)	2.170(4)	2.112(8)
Cu(1)−N(4)	1.996(3)	2.052(3)	Cu(1)−N(4)	2.138(4)	2.099(8)
Cu(1)−O(1)	2.326(2)	2.412(2)	Cu(1)−N(6)	2.099(4)	2.104(8)
C(1)−N(1)	1.458(4)	1.471(5)	C(1)−N(1)	1.446(7)	1.463(13)
C(1)−N(3)	1.465(4)	1.459(5)	C(1)−N(3)	1.465(7)	1.464(13)
C(1)−N(5)	1.429(5)	1.434(5)	C(1)−N(5)	1.446(7)	1.419(13)
Cu(1)−N(7)	1.858(4)	1.956(3)	Cu(1)−P(1)	2.1492(15)	2.139(3)
S(1)−O(1)	1.453(3)	1.452(3)	C(1)−S(1)	1.883(6)	1.893(10)
S(1)−O(2)	1.438(2)	1.441(3)			
S(1)−O(3)	1.446(2)	1.442(3)			
N(7)−C(29)	1.145(6)				

or 2.412(2) Å for (**4**)) is significantly longer than the Cu−O bond in Cu−OSO_2 (2.136(6) Å) and Cu−ONO_2 (2.110(6) Å) in Na_5[Cu(TPPTS)]·$5H_2O$ (TPPTS = tris(*m*-sulfonatophenyl)phosphate) and [$(Ph_3As)_3Cu(NO_3)$], respectively.[20,21] However, it is within the sum of their van der Waals radii and is in accord with other Cu−Tpms complexes.[22] In (**2**) the Cu(1)−N(7) distance of 1.858 Å is comparable to that observed in a analogue acetonitrile copper(I) complexes,[17] although about 0.1 Å shorter than that found in (**4**).

The Cu−N−N−C (where C is at pyrazolyl) torsion angles of the pyrazolyl rings present values from 150.1(2)° (in **2**) to 179.0(3)° (in **4**), whereas the Cu−N−N−C(1) torsion angles (defining[23a] the degree of tilting of the rings with respect to the C_s axis of the molecule) are in the range of 12.3(5)° (in **4**) to 22.5(3)° (in **2**) (Table 3).

In compounds (**3**) and (**5**), the anionic Tpms^{Ph} acts as a tridentate N,N,N-ligand (Figures 4 and 5). The N−Cu−N angles are restrained by the chelate rings to 84.5(3)°−89.06(16)°, while the wider N−Cu−P angles are within the range of 125.24(12)°− 129.9(2)°. In both structures there is a high degree of tilting of the pyrazolyl rings with the Cu−N−N−C(1) torsion angles from 29.6(10)° in (**5**) to 42.2(5)° in (**3**) being drastically higher than those for other scorpionate analogues.[23b] Similarly, we can compare the Cu−N−N−C (where C is at pyrazolyl) torsion angles, averaging 133° for (**3**) and 139° for (**5**), with their analogues in the related Cu(I) complexes [Cu{HC(3-*t*Bupz)$_3$}L][PF_6] (L = CO or NCMe)[18a] with a maximum torsion angle of 171° (L = NCMe). In the present structures, the distortion can tentatively be attributed to steric effects associated to the phenyl substituent in the pyrazolyl rings and to the PTA or $(mPTA)^+$ ligands.

Moreover, the solid state structure of compound (**5**) (Figure 5) exhibits the presence of intramolecular C−H···π interactions specifically between the C(29)−H(22) moiety and the closest phenyl ring (i.e., C(5−10)). The distance between the C−H hydrogen and the centroid of this ring is 2.489 Å,

Table 3. Selected Angles [deg] for Compounds [Cu(Tpms^{Ph})(MeCN)] (**2**), [Cu(Tpms^{Ph})(PTA)] (**3**), [Cu(Tpms^{Ph})(HMT)] (**4**), and [Cu(Tpms^{Ph})(mPTA)][PF_6] (**5**)

	(**2**)	(**4**)		(**3**)·C_3H_6O	(**5**)·C_3H_6O
N2−Cu1−N7	121.02(12)	147.73(14)	N2−Cu1−P1	125.24(12)	127.1(2)
N4−Cu1−N7	146.62(12)	124.27(14)	N4−Cu1−P1	129.05(12)	127.8(2)
O1−Cu1−N7	109.82(11)	92.38(12)	N6−Cu1−P1	128.95(13)	129.9(2)
N2−Cu1−N4	88.65(11)	87.80(14)	N2−Cu1−N4	85.14(16)	86.9(3)
O1−Cu1−N4	86.34(10)	86.63(12)	N4−Cu1−N6	85.06(16)	85.5(3)
O1−Cu1−N2	84.26(9)	84.99(12)	N2−Cu1−N6	89.06(16)	84.5(3)
C1−S1−O1	104.38(16)	103.07(16)			
C1−S1−O3	103.15(15)	104.56(19)	Cu1N2−N1C2	138.2(4)	137.1(7)
C1−S1−O2	103.51(14)	103.32(19)	Cu1N4−N3C11	136.1(4)	141.8(7)
O2−S1−O1	114.81(15)	114.1(2)	Cu1N6−N5C20	126.0(4)	137.3(7)
O2−S1−O3	115.02(14)	115.7(2)	Cu1N2−N1C1	32.9(5)	36.0(9)
O3−S1−O1	113.95(15)	114.04(18)	Cu1N4−N3C1	39.1(5)	29.6(10)
			Cu1N6−N5C1	42.4(5)	33.2(10)
Cu1N4−N3C11	167.9(2)	179.0(3)			
Cu1N2−N1C2	150.1(2)	156.0(3)			
Cu1N4−N3C1	22.5(3)	12.3(5)			
Cu1N2−N1C1	18.0(3)	18.5(5)			

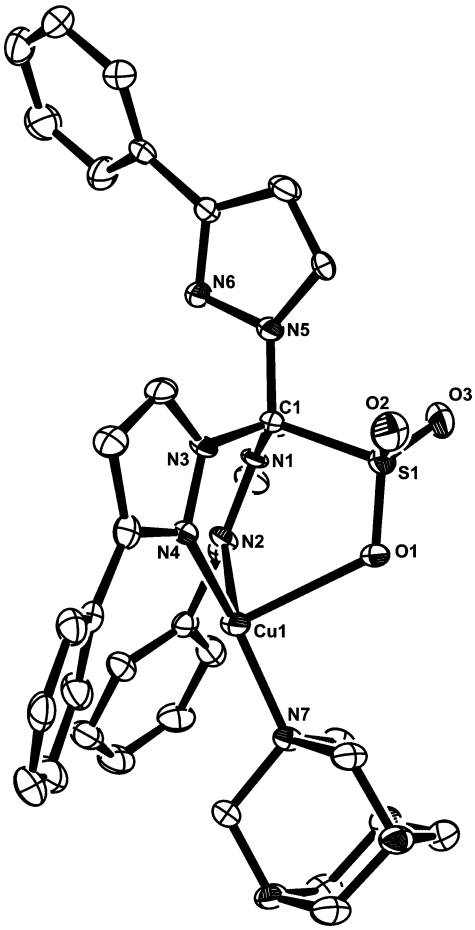


Figure 3. ORTEP plot of [Cu(Tpms^{Ph})(HMT)] (**4**), ellipsoids are shown at 50% probability.

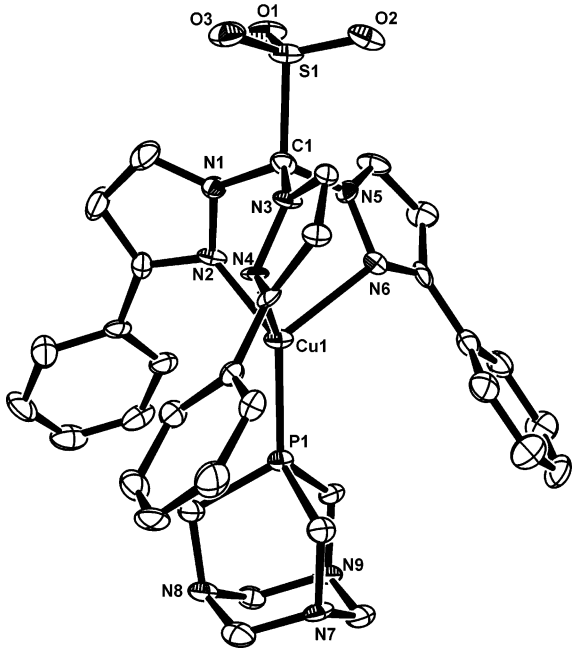


Figure 4. ORTEP plot of [Cu(Tpms^{Ph})(PTA)] (**3**), with ellipsoids shown at 50% probability; one molecule of acetone is omitted for clarity.

indicating a relatively strong non-covalent interaction.[24] Similarly, each of the other two phenyl rings interacts with the corresponding H atom of a methylene group of (mPTA)$^+$ (although at longer 2.520 and 2.594 Å distances), constituting

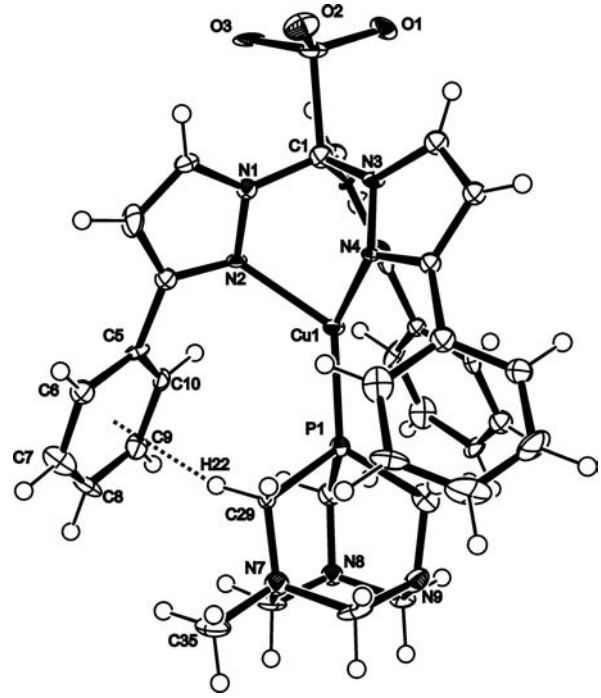


Figure 5. ORTEP plot of [Cu(Tpms^{Ph})(mPTA)][PF$_6$] (**5**), with ellipsoids shown at 50% probability; hydrogen atoms are shown but the [PF$_6$]$^-$ counterion and one molecule of crystallization acetone are omitted for clarity. The dashed line indicates the C−H$\cdots\pi$ intramolecular (2.489 Å) interaction between C(29)−H(22) and the π-phenyl ring (C(5) to C(10)).

Table 4. Selected ^{1}H-NMR (Acetone-d_6) Chemical Shifts (δ) for Compounds [Cu(Tpms^{Ph})(MeCN)] (**2**), [Cu(Tpms^{Ph})(PTA)] (**3**), [Cu(Tpms^{Ph})(HMT)] (**4**), and [Cu(Tpms^{Ph})(mPTA)][PF$_6$] (**5**)

compound		room temperature (δ)	low temperature limit (δ)
(**2**)	4-H	6.94(3H)	7.35(1H),7.00 (2H)
	5-H	8.07(3H)	8.87(1H),7.27 (2H)
(**3**)	4-H	6.92(3H)	7.12(3H)[a]
	5-H	8.50(3H)	8.85(3H)[a]
(**4**)	4-H	6.92(3H)	7.35(1H),6.90 (2H)
	5-H	7.84(3H)	8.91(1H),7.22 (2H)
(**5**)	4-H	6.96(3H)	7.35(1H),6.96(2H)[b]
	5-H	*c*	8.94(1H),7.28(2H)[b]

[a] With a small amount of N_2O-coordination (K_{eq} = [N_3-coordinated species]/[N_2O-coordinated species]= 3.2) at 8.92, 7.35 (for 5-H) and 7.41, 6.97 (for 4-H). [b] With traces of N_3-coordination (K_{eq} = [N_3-coordinated species]/[N_2O-coordinated species]= 0.12) at 8.87 (for 5-H) and 7.08 (for 4-H). [c] Very broad resonance under the phenyl rings resonances at δ about 8.05−7.90, detected by HMQC ^{13}C−^{1}H NMR.

a sort of symmetrical intramolecular interaction that probably helps to stabilize the N,N,N-coordination mode, in the solid state.

In the case of complexes (**2**) and (**4**), bearing N-donor ligands (MeCN and HMT, respectively) that are effective σ-electron donors and not appreciable π-acceptors, the metal tends to prefer the weaker electron-donating N_2O-coordination mode of Tpms^{Ph}. The stronger electron-releasing N_3-coordination of the latter ligand appears to be the preferable one for complexes (**3**) and (**5**) with π-acceptor phosphine ligands, in spite of the stronger steric hindrance associated to this type of coordination in comparison with the N_2O-mode.

(20) Tisato, F.; Refosco, F.; Bandoli, G.; Pilloni, G.; Corani, B. *Inorg. Chem.* **2001**, *40*, 1394–1396.

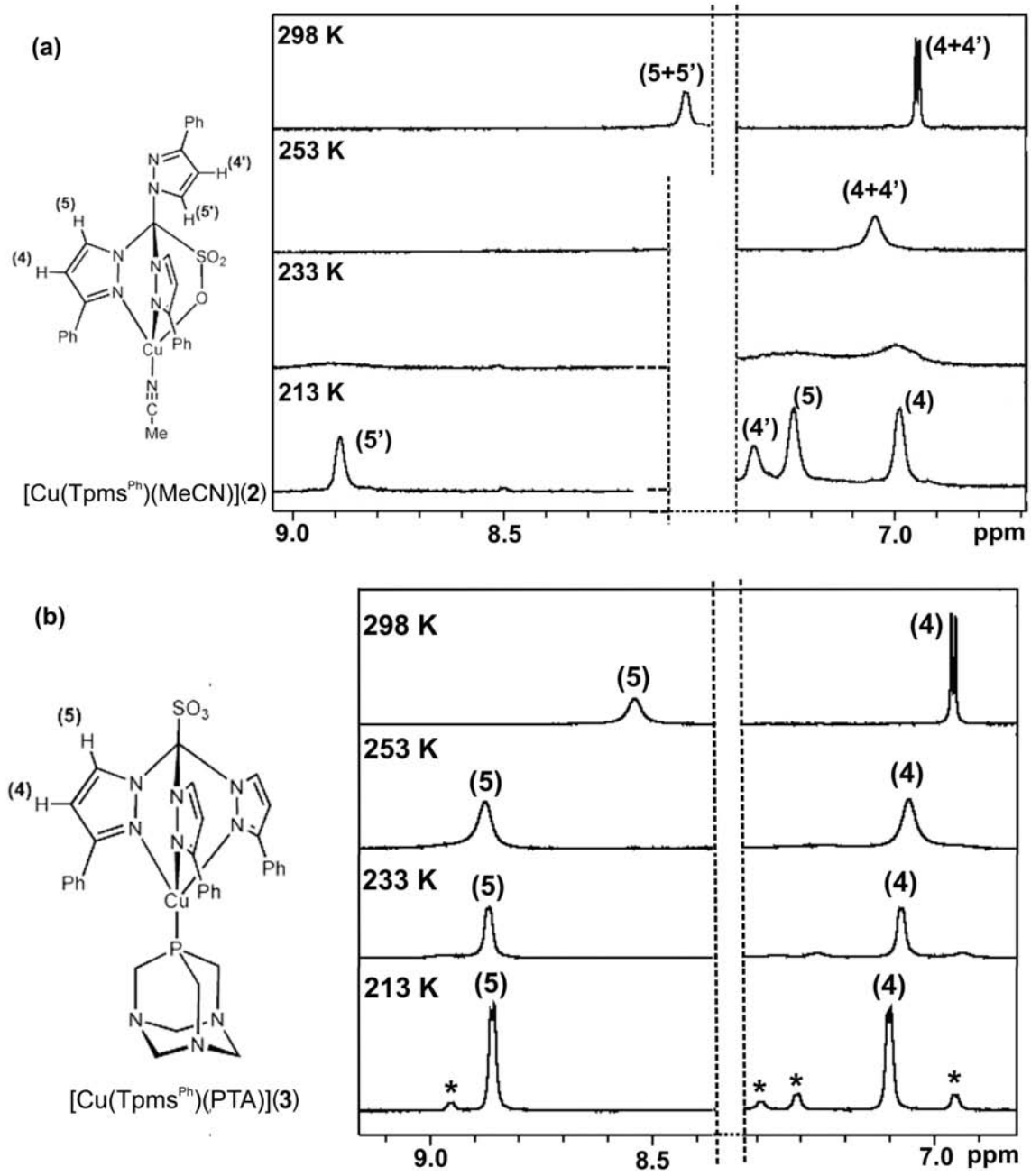


Figure 6. Variable temperature (298−213 K) ^{1}H NMR spectra (selected ppm ranges) for (**2**) (a) and (**3**) (b) in acetone-d_6. (*) indicates traces of the N_2O-coordination isomer.

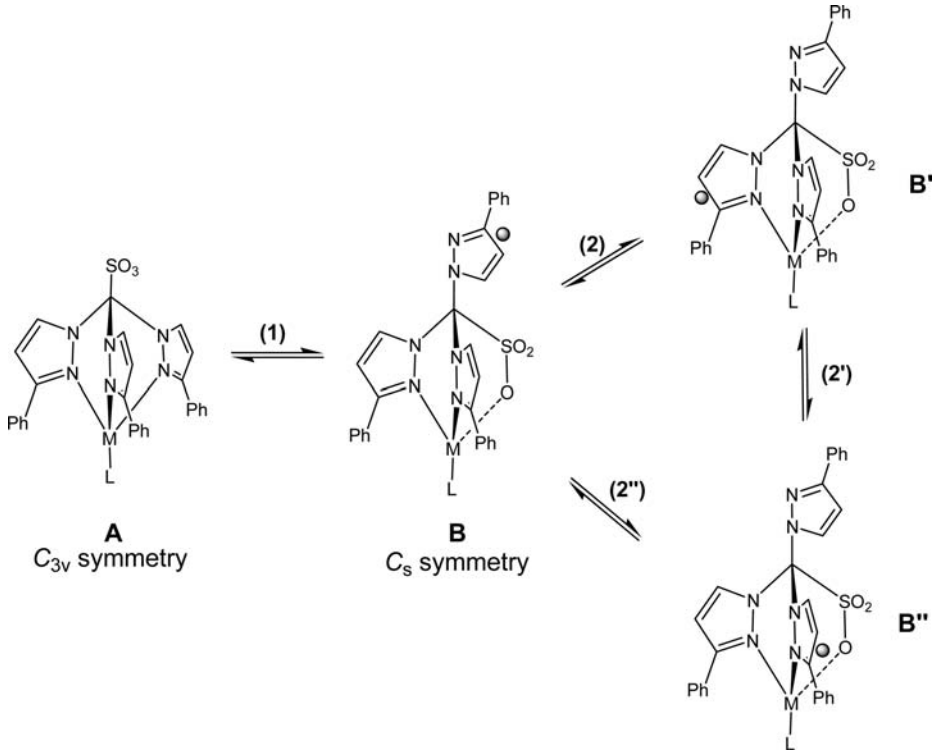
4. NMR Solution Studies. The complexes exhibit fluxional behavior in solution, as shown by variable temperature NMR studies (Table 4) which have allowed to check if the coordination modes of the Tpms^{Ph} ligand observed in the solid state are retained in solution.

Hence, compound (**3**), with the N_3-type coordination in the solid state, as established by X-ray diffraction (see above), in solution (acetone-d_6) at room temperature shows, in the ^{1}H NMR spectrum, the expected resonances for the 4-H and 5-H protons of the three equivalent pyrazolyl rings. This pattern essentially remains upon cooling until 200 K, indicating the preservation of the N_3-coordination at low temperature. Only traces of the pattern associated to the N_2O-coordination were then detected (Figure 6b), as a result of the shift at low temperature, toward this mode, of the equilibrium (1, Scheme 3) between the two coordination forms. In accord, such a type of Tpms coordination equilibrium is known[11a,b] to be temperature dependent.

In contrast, the other complexes ((**2**), (**4**), and (**5**)) display low temperature ^{1}H NMR limit spectra that are consistent with the N_2O-coordination (two equivalent and one nonequivalent pyrazolyl rings, Figure 6a),[11c] which is also the observed one for (**2**) and (**4**) in the solid state. In the case of (**5**), linkage isomerization (1, Scheme 3) of the N_3-mode exhibited in the solid state has occurred in solution (only traces of the N_3-coordination are detected).

However, at room temperature, all complexes (**2**)−(**5**) display ^{1}H NMR spectra that are indicative of the equivalence of the three pyrazolyl rings (Table 4). In the case of (**3**) (see above), this is conceivably due to the N_3-type coordination

Scheme 3. Equilibria between the Two Different $Tpms^{Ph}$ Coordination Modes for Complexes of General Formula $[M(Tpms^{Ph})L]^a$



[a] Type **A**, N_3-coordination, C_{3v}-symmetry; type **B**, N_2O-coordination, C_s-symmetry; also shown is the dynamic process among different N_2O-coordination modes.

(form **A**, Scheme 3) that is retained from the solid state, whereas for the other complexes ((**2**), (**4**), and (**5**)), it can be ascribed to the fast equilibria (2, 2′, and 2″, Scheme 3) among the three forms (**B**, **B′**, and **B″**) with N_2O-coordination. Decreasing the temperature leads to a split to a double pattern with two distinct sets of resonances in the 2:1 ratio (Figure 6a, at 213 K).

The $Tpms^{Ph}$ complexes (**2**) and (**4**), bearing a N-donor ligand (MeCN or HMT, respectively), preserve, in solution, the N_2O-coordination observed in solid state, while for compounds (**3**) and (**5**), with a π-acceptor phosphine ligand (PTA or $(MePTA)^+$, correspondingly), the metal prefers the stronger electron-releasing N_3-coordination mode of $Tpms^{Ph}$. This argument holds specially for (**5**), with the cationic alkylated $(mPTA)^+$ ligand, expected to be, like the protonated PTA,[25] a more effective π-acceptor than PTA in (**3**). In fact, the $^{31}P\{^1H\}$-NMR signal (δ −70.9) of compound (**5**) is shifted to lower field relatively to that (δ −93.3) of complex (**3**). Nevertheless, in solution, the less effective electron-donor N_2O-coordination appears to become dominant, which conceivably results from both steric and electronic effects. The $(mPTA)^+$ ligand would prefer to avoid the more sterically demanding $Tpms^{Ph}$ N_3-binding in accord with the fact that the molecular structure of (**5**) (Figure 5), in the solid state, shows a tilted N_3-bound $Tpms^{Ph}$ ligand to minimize the steric interaction between its phenyl rings and $(mPTA)^+$. Moreover, the cationic phosphine could influence the electrostatic metal interaction with the sulfonate moiety, hampering the charge separation between the positive metal and the negative SO_3^- group, thus favoring the N_2O-mode.

Conclusions

Tris(3-phenylpyrazolyl)methanesulfonate is a new sterically demanding chelating ligand, and its lithium salt, $Li(Tpms^{Ph})$, is a convenient starting material for the synthesis of one-face capping coordination compounds. We have achieved an easy and powerful synthetic procedure to afford a new class of Cu^I complexes bearing this ligand.

It shows the typical tripodal coordination flexibility of tris(pyrazolyl)methanesulfonate derivatives toward the copper atom, that is, the N,N,N or N,N,O coordination modes. From solution NMR and X-ray diffraction experiments we conclude that $Tpms^{Ph}$ tends to adapt its coordination mode to the electronic and steric preferences of the metal center. In fact, compounds (**2**) and (**4**), bearing N-donor ligands (acetonitrile and HMT, respectively) with an expected stronger electron-donor ability display the N_2O coordination, involving the weak electron-donor sulfonate moiety; whereas those containing phosphines with a π-acceptor character (i.e.,

(21) Bowmaker, G. A.; Hart, R. D.; de Silva, E. N.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1997**, *50*, 553–565.
(22) Santini, C.; Pellei, M.; Lobbia, G. G.; Cingolani, A.; Spagna, R.; Cavalli, M. *Inorg. Chem. Commun.* **2002**, *5*, 430–433.
(23) (a) Frohnapfel, D. S.; White, P. S.; Templeton, J. L. *Organometallics* **1997**, *16*, 3737–3750. (b) Reger, D. L.; Gardinier, J. R.; Elgin, J. D.; Smith, M. D. *Inorg. Chem.* **2006**, *45*, 8862–8875.
(24) (a) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, *21*, 3885–3896. (b) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253–4264. (c) Müller-Dethlefs, K.; Hobza, P. *Chem. Rev.* **2000**, *100*, 143–167. (d) Nishio, M. *CrystEngComm* **2004**, *6* (27), 130–158.
(25) (a) Smoleński, P.; Pombeiro, A. J. L. *Dalton Trans.* **2008**, *1*, 87–91. (b) Mebi, C. A.; Frost, B. J. *Organometallics* **2005**, *24*, 2339–2346. (c) Meji, A. M. M.; Otto, S.; Roodt, A. *Inorg. Chim. Acta* **2005**, *358*, 1005–1011.

compounds (**3**) and (**5**)) tend to exhibit the N,N,N capping coordination that provides a more effective electron-release to the metal. Moreover, compound (**5**), bearing the cationic methylated PTA, shows in solution a good affinity for the N_2O coordination mode, with the bound anionic sulfonate moiety, lowering the steric interaction between the $Tpms^{Ph}$ and the phosphine.

The complexes described here are soluble in water, and the flexibility of the new scorpionate ligand, bearing the labile sulfonate group, provides a good example of a versatile ligand able to be employed in further reactivity studies, namely, of metalloenzyme models.

Acknowledgment. This work has been partially supported by the Foundation for Science and Technology (FCT), its POCI 2010 programs (FEDER funded) and the Grants SFRH/BD/23187/2005 (R.W.) and SFRH/BPD/20869/2004 (P.S.) as well as by the Human Resources and Mobility Marie Curie Research Training Network (AQUACHEM project, CMTN-CT-2003-503864).

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC801254B