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Synthesis and Coordination Chemistry of a New N₄-Polydentate Class of Pyridyl-Functionalized Scorpionate Ligands: Complexes of Fe^{II}, Zn^{II}, Ni^{II}, V^{IV}, Pd^{II} and Use for Heterobimetallic Systems

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The new potentially N₄-multidentate pyridyl-functionalized scorpionates 4-((tris-2,2,2-(pyrazol-1-yl)ethoxy)methyl)pyridine (TpmPy, (1)) and 4-((tris-2,2,2-(3-phenylpyrazol-1-yl)ethoxy)methyl)pyridine (TpmPy^{Ph}, (2)) have been synthesized and their coordination behavior toward Fe^{II}, Ni^{II}, Zn^{II}, Cu^{II}, Pd^{II}, and V^{IV} centers has been studied. Reaction of (1) with Fe(BF₄)₂·6H₂O yields [Fe(TpmPy)₂](BF₄)₂ (3), that, in the solid state, shows the sandwich structure with trihapto ligand coordination via the pyrazolyl arms, and is completely low spin (LS) until 400 K. Reactions of 2 equiv of (1) or (2) with Zn^{II} or Ni^{II} chlorides give the corresponding metal complexes with general formula [MCl₂(TpmPy*)₂] (M = Zn, Ni; TpmPy* = TpmPy, TpmPy^{Ph}) (4–7) where the ligand is able to coordinate through either the pyrazolyl rings (in case of [Ni(TpmPy)₂]Cl₂ (5)) or the pyridyl-side (for [ZnCl₂(TpmPy)₂] (4), [ZnCl₂(TpmPy^{Ph})₂] (6) and [NiCl₂(TpmPy^{Ph})₂] (7)). The reaction of (1) with VCl₃ gives [VOCl₂(TpmPy)] (8) that shows the N₃-pyrazolyl coordination-mode. Moreover, (1) and (2) react with *cis*-[PdCl₂(CH₃CN)₂] to give the disubstituted complexes [PdCl₂(TpmPy)₂] (9) and [PdCl₂(TpmPy^{Ph})₂] (10), respectively, bearing the scorpionate coordinated via the pyridyl group. Compounds (9) and (10) react with Fe(BF₄)₂ to give the heterobimetallic Pd/Fe systems [PdCl₂(μ-TpmPy)₂-Fe](BF₄)₂ (11) and [PdCl₂(μ-TpmPy^{Ph})₂-Fe₂(H₂O)₆](BF₄)₄ (13), respectively. Compound (11) can also be formed from reaction of (3) with *cis*-[PdCl₂(CH₃CN)₂], while reaction of (3) with Cu(NO₃)₂·2.5H₂O generates [Fe(μ-TpmPy)₂-Cu(NO₃)₂](BF₄)₂ (12), confirming the multidentate ability of the new chelating ligands. The X-ray diffraction analyses of compounds (1), (3), (4), (5), and (9) are also reported.

Introduction

Tripodal ligands containing nitrogen-donor heterocycles linked to a bridging carbon atom are widely used for a variety

of applications in coordination and organometallic chemistry.¹ The tris(pyrazolyl)methane HCp₃ (pz = pyrazolyl) (Tpm) ligand has been studied in the past years, and there is a growing interest to develop its multiple coordination modes.² In fact, many works report the functionalization of the central methine carbon atom with groups other than the hydrogen atom, extending the coordination properties of the ligand and opening to a variety of applications,³ in particular in supramolecular chemistry and multimetallic systems. The polydentate character of such a type of ligands has also been investigated.⁴

Within our interest in N-donor ligand chemistry with scorpionate derivatives,⁵ we aimed to design new multidentate tris(pyrazolyl)methane ligands bearing an additional N-donor group pending from the central methine carbon and to study the role of this extra-unit on their coordination behavior, namely, focusing on their potential to form heteronuclear species. Hence, we describe the synthesis of the new

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class of potential tetradentate scorpionates 4-((tris-2,2,2-(pyrazol-1-yl)ethoxy)methyl)pyridine (TpmPy) (**1**) and 4-((tris-2,2,2-(3-phenylpyrazol-1-yl)ethoxy)methyl)pyridine (TpmPy^{Ph}) (**2**) with an additional pyridyl moiety also able to coordinate. Therefore, we report herein the coordination chemistry of these new ligands toward Fe^{II}, Zn^{II}, Ni^{II}, Pd^{II}, and V^{III} centers, and their first application as doubly functionalized ligands to the preparation of heterobimetallic complexes, namely, of Fe^{II}/Pd^{II} and Fe^{II}/Cu^{II} centers.

Experimental Section

General Materials and Experimental Procedures. All syntheses were carried out under an atmosphere of dinitrogen, using standard Schlenck techniques. All solvents were dried, degassed, and distilled prior to use. The reagents Fe(BF₄)₂·6H₂O, NiCl₂·6H₂O, ZnCl₂, 4-bromomethylpyridine hydrobromide (Aldrich), and vanadium trichloride (Acros) were purchased and used without further purification. Tris(pyrazolyl)methane, tris-2,2,2-(pyrazol-1-yl)ethanol, and tris(3-phenyl)pyrazolylmethane were synthesized in accordance with literature methods.^{6,5c} 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, and far-infrared spectra (400–200 cm⁻¹) were recorded on a Vertex 70 spectrophotometer, in polyethylene and cesium iodide pellets. Vibrational frequencies are expressed in cm⁻¹; abbreviations (intensity, shape): s, m and w, strong, medium and weak; s and br, sharp and broad. ¹H, ¹³C NMR spectra were measured on Bruker 300 and 400 UltraShield spectrometers. ¹H and ¹³C chemical shifts δ are expressed in parts per million (ppm) relative to Si(Me)₄. Coupling constants are in hertz (Hz); abbreviations: s, singlet; d, doublet; m, complex multiplet; vt, virtual triplet; br, broad. EPR spectra were recorded on a Bruker ESP 300E X-band spectrometer equipped with an ER 4111 VT variable-temperature unit. ESI⁺/ESI⁻ mass spectra were obtained on a VARIAN 500-MS LC ion trap mass spectrometer (solvents: acetonitrile/methanol; flow: 20 μ L/min; needle spray voltage: \pm 5 kV, capillarity voltage: \pm 100 V; nebulizer gas (N₂): 35 psi; drying gas (N₂): 10 psi; drying gas temperature (N₂): 350 °C). For the MS spectra description, M denotes the complex part of the compound.

Synthesis of 4-((Tris-2,2,2-(pyrazol-1-yl)ethoxy)methyl)pyridine, TpmPy (1**).** Sodium hydride (159 mg, 3.98 mmol, 2 equiv,

60% dispersion in mineral oil) is washed with dry pentane (2 \times 10 mL) and then suspended in dry tetrahydrofuran (THF, 15 mL). A THF (20 mL) suspension of tris-2,2,2-(pyrazol-1-yl)ethanol (482 mg, 1.98 mmol, 1 equiv) and 4-bromomethyl pyridine hydrobromide (502 mg, 1.98 mmol, 1 equiv) is added portionwise to the hydride mixture under nitrogen; during this time, gaseous H₂ is formed. The resulting pale brown milky suspension is refluxed overnight. Then the mixture is allowed to cool down to room temperature and H₂O (20 mL) and Et₂O (20 mL) are added. The organic phase is separated and the aqueous phase is washed with Et₂O (5 mL). The organic phases are collected, washed with brine, and dried over Na₂SO₄, whereafter they are filtered and the solvent removed under vacuum to leave a pale yellow solid that is crystallized in Et₂O to give colorless crystals of (**1**) (518 mg, 78%). Compound (**1**) is well soluble in all common organic solvents, for example, Me₂CO, CHCl₃, CH₂Cl₂, MeOH, EtOH, and dimethyl sulfoxide (DMSO), and less soluble in H₂O (*S*_{25 °C} \approx 10 mg·mL⁻¹). C₁₇H₁₇N₇O (335.36): calcd. C 60.88, N 29.23, H 5.10; found C 61.03, N 29.02, H 5.41. IR (KBr): 3113 (m s), 3041, 2959, 2935 (m s), 2880 (m br), 1601 (s s, ν (C=N)), 1564 (s s, ν (C=N)), 1517 (s s, ν (C=C)), 1426 (m s), 1387 (m br), 1124 (s br), 863 (m s), 753 (s s), 688 (s s), 612 (s s), 489 (m s) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 8.53 (d, 2H, *J*_{HH} = 6.2 Hz, 2-H (py)), 7.67 (d, 3H, *J*_{HH} = 2.5 Hz, 5-H (pz)), 7.40 (d, 3H, *J*_{HH} = 2.5 Hz, 3-H (pz)), 7.06 (d, 2H, *J*_{HH} = 6.2 Hz, 3-H (py)), 6.36 (dd, 3H, *J*_{HH} = 2.5 Hz, 4-H (pz)), 5.20 (s, 2H, CH₂-C(pz)₃), 4.56 (s, 2H, CH₂-py). ¹H NMR (MHz, methanol-*d*₄): δ 8.43 (d, 2H, *J*_{HH} = 5.7 Hz, 2-H (py)), 7.66 (d, 3H, *J*_{HH} = 2.5 Hz, 5-H (pz)), 7.50 (d, 3H, *J*_{HH} = 2.5 Hz, 3-H (pz)), 7.20 (d, 2H, *J*_{HH} = 5.7 Hz, 3-H (py)), 6.41 (dd, 3H, *J*_{HH} = 2.5 Hz, 4-H (pz)), 5.15 (s, 2H, CH₂-C(pz)₃), 4.64 (s, 2H, CH₂-py). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 148.79 (2-C (py)), 145.26 (4-C (py)), 140.46 (3-C (pz)), 129.73 (5-C (pz)), 120.57 (3-C (py)), 105.69 (4-C (pz)), 88.71 (C(pz)₃), 73.11 (s, 2H, CH₂-C(pz)₃), 71.50 (s, 2H, CH₂-py). X-ray quality single crystals were grown by slow cooling to 15 °C of a concentrated diethyl ether solution of (**1**).

Synthesis of 4-((Tris-2,2,2-(3-phenylpyrazol-1-yl)ethoxy)methyl)pyridine, TpmPy^{Ph} (2**).** Sodium hydride (159 mg, 3.98 mmol, 2 equiv, 60% dispersion in mineral oil) is washed with dry pentane (2 \times 10 mL) and then suspended in dry THF (15 mL). A THF (20 mL) suspension of tris-2,2,2-(3-phenylpyrazol-1-yl)ethanol (940 mg, 1.98 mmol, 1 equiv) and 4-bromomethyl pyridine hydrobromide (502 mg, 1.98 mmol, 1 equiv) is added portionwise to the hydride

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mixture under nitrogen. The resulting pale brown milky suspension is refluxed overnight. Then the mixture is allowed to cool down to room temperature, and H₂O (20 mL) and Et₂O (20 mL) are added. The organic phase is separated and the aqueous phase is washed with Et₂O (5 mL). The organic phases are collected, washed with brine, and dried over Na₂SO₄. Filtration and removal of solvent under vacuum leaves a transparent oil that is purified by column chromatography (pentane/acetone 8/2) to give an off white solid (835 mg, 75%) of (2). Compound (2) is stable in air although being slightly hygroscopic. It is well soluble in all common organic solvents, for example, Me₂CO, CHCl₃, CH₂Cl₂, MeOH, EtOH, and DMSO, and is insoluble in H₂O. C₃₅H₂₉N₇O (563.66): calcd. C 74.58, N 17.39, H 5.19; found. C 74.02, N 16.92, H 5.01. IR (KBr): 3132, 3059, 2923, 2853 (w s, ν (C–H)), 1603 (s s, ν (C=N)), 1561 (s s, ν (C=N)), 1530 (s s, ν (C=C)), 1499, 1455 (s s), 1219 (m br), 1124, 1101, 1071, 1042 (m s), 869 (s s), 751 (s s), 692 (s s), 616 (w s), 477 (m s) cm^{−1}. ¹H NMR (CDCl₃, 298 K): δ 8.47 (d, 2H, J_{HH} = 6.0 Hz, 2,6-H (py)), 7.81 (d, 6H, J_{HH} = 7.6 Hz, *o*-H (Ph)), 7.57 (d, 3H, J_{HH} = 2.6 Hz, 5-H (pz)), 7.40 (dd, vt, 6H, J_{HH} = 7.6 Hz, *m*-H (Ph)), 7.33 (dd, vt, 3H, J_{HH} = 7.6 Hz, *p*-H (Ph)), 7.10 (d, 2H, J_{HH} = 6.0 Hz, 3,5-H (py)), 6.67 (d, 3H, J_{HH} = 2.6 Hz, 4-H (pz)), 5.40 (s, 2H, CH₂-C(pz)₃), 4.64 (s, 2H, CH₂-py). ¹H NMR (acetone-*d*₆, 298 K): δ 8.41 (d, 2H, J_{HH} = 5.7 Hz, 2,6-H (py)), 7.86 (d, 6H, J_{HH} = 7.7 Hz, *o*-H (Ph)), 7.78 (d, 3H, J_{HH} = 2.7 Hz, 5-H (pz)), 7.40 (t, 6H, J_{HH} = 7.7 Hz, *m*-H (Ph)), 7.32 (t, 3H, J_{HH} = 7.2 Hz, *p*-H (Ph)), 7.19 (d, 2H, J_{HH} = 6.0 Hz, 3,5-H (py)), 6.88 (d, 3H, J_{HH} = 2.6 Hz, 4-H (pz)), 5.42 (s, 2H, CH₂-C(pz)₃), 4.79 (s, 2H, CH₂-py). ¹³C{¹H} and HMQC ¹³C–¹H NMR (100.6 MHz, CDCl₃, 298 K): δ 153.08 (s, 3-C (pz)), 149.76 (s, 2,6-C (py)), 146.73 (s, 4-C (py)), 132.81 (s, pz-C (Ph)), 132.44 (s, 5-C (pz)), 128.70 (s, *m*-C (Ph)), 128.38 (s, *p*-C (Ph)), 126.03 (s, *o*-C (Ph)), 121.75 (s, 3,5-C (py)), 103.88 (s, 4-C (pz)), 90.17 (s, CH₂-C(pz)₃), 74.07 (s, O-CH₂-C(pz)₃), 72.54 (s, O-CH₂-py). ¹³C NMR (100.6 MHz, acetone-*d*₆, 298 K): δ 153.47 (s, 3-C (pz)), 150.46 (s, 2,6-C (py)), 147.51 (s, 4-C (py)), 133.72 (s, pz-C (Ph)), 133.65 (s, 5-C (pz)), 129.40 (s, *m*-C (Ph)), 129.00 (s, *p*-C (Ph)), 126.52 (s, *o*-C (Ph)), 122.38 (s, 3,5-C (py)), 104.43 (s, 4-C (pz)), 90.99 (s, CH₂-C(pz)₃), 74.32 (s, O-CH₂-C(pz)₃), 72.65 (s, O-CH₂-py).

Synthesis of [Fe(TpmPy)₂](BF₄)₂ (3). To a methanolic solution (2 mL) of Fe(BF₄)₂·6H₂O (50 mg, 0.148 mmol, 1 equiv) is added portionwise a solution of TpmPy (99 mg, 0.296 mmol, 2 equiv) in MeOH (2 mL). The colorless solution turns immediately to pink and after a few minutes a pink solid precipitates. The mixture is stirred under nitrogen for 15 min and then filtered. The solid is washed with methanol (2 × 5 mL) to leave a pale pink solid of (3) (120 mg, 91%). Compound (3) is well soluble in acetonitrile and DMSO, sparingly soluble in CH₂Cl₂, CHCl₃, MeOH, and less soluble in H₂O (*S*_{25 °C} ≈ 4.0 mg·mL^{−1}). (3)·2CH₃CN, C₃₈H₄₀N₁₆O₂FeB₂F₈ (982.30): calcd. C 46.46, N 22.81, H 4.10; found. C 46.50, N 22.98, H 3.99. IR (KBr): 3158, 3126, 3060 (m br), 2918 (m br), 1562 (m s, ν (C=N)), 1518 (m s, ν (C=C)), 1419 (s s), 1341 (s s), 1231 (s br), 1119–1050 (s br, ν (BF₄)), 867 (m s), 770 (s s), 607 (m s), 521 (m s) cm^{−1}. ¹H NMR (CD₃CN, 298 K): δ 8.71–8.40 (m, 5H), 7.53 (br s, 2H), 7.39–7.23 (br m, 3H), 6.57 (br s, 3H), 5.76 (br s, 2H, CH₂-C(pz)₃), 5.24 (br s, 2H, CH₂-py). ¹H NMR (CD₃CN, 233 K): δ 8.65–8.60 (m, 24H, 5-H(pz) + 2,6-H(py)), 8.41 (br s, 6H, 5-H(pz)), 7.53 (d, 12H, J_{HH} = 6.0 Hz, 2,6-H(py)), 7.43 (d, 4H, J_{HH} = 1.6 Hz, 3-H(pz)), 7.40 (d, 2H, J_{HH} = 1.6 Hz, 3-H(pz)), 7.28 (d, 8H, J_{HH} = 1.6 Hz, 3-H(pz)), 7.24 (d, 4H, J_{HH} = 1.6 Hz, 3-H(pz)), 6.55 (m, 6H, 4-H(pz)), 6.52 (m, 12H, 4-H(pz)), 5.73 (br s, 12H, CH₂-C(pz)₃), 5.23 (br s, 12H, CH₂-py). ¹³C{¹H} and HMQC ¹³C–¹H NMR (100.6 MHz, CD₃CN, 298 K): δ 153.08 (s, 3-C (pz)), 149.76 (s, 2,6-C (py)), 146.73 (s, 4-C (py)), 132.81 (s, pz-C (Ph)), 132.44 (s, 5-C (pz)), 128.70 (s, *m*-C (Ph)), 128.38 (s, *p*-C (Ph)), 126.03 (s, *o*-C (Ph)), 121.75 (s, 3,5-C (py)), 103.88 (s, 4-C (pz)), 90.17 (s, CH₂-C(pz)₃), 74.07 (s, O-CH₂-C(pz)₃), 72.54 (s, O-CH₂-py). X-ray quality single crystals were grown by slow evaporation under nitrogen, at room temperature, of an acetonitrile solution of (3).

Synthesis of [ZnCl₂(TpmPy)₂] (4). To a methanolic solution of ZnCl₂ (15 mg, 0.11 mmol, 1 equiv) is added dropwise a solution of (1) (74 mg, 0.22 mol, 2 equiv) in MeOH. The colorless solution is stirred at room temperature for 3 h, during which time a white solid precipitates. The product (4) is filtered off, washed with a small amount of cold methanol and dried (69 mg, 78%). The compound (4) is soluble in CHCl₃, sparingly soluble in MeOH, EtOH, acetone, and acetonitrile, insoluble in Et₂O and less soluble in H₂O (*S*_{25 °C} ≈ 2.5 mg·mL^{−1}). (4)·2CH₃CN·0.5CH₂Cl₂, C_{38.5}H₄₁Cl₃N₁₆O₂Zn (931.60) calcd. C 49.63, H 4.43, N 24.06; found. C. 49.62, H 4.23, N 24.06. IR (KBr): 3155, 2930, 2900 (m s, ν (C–H)), 1621 (s s, ν (C=N)), 1563, 1518 (m s, ν (C=N), ν (C=C)), 1430 (s s), 1390 (s s), 1133, 1112 (s s), 869 (m s), 754 (s s), 614 (m s), 508, 478 (m s) cm^{−1}. MS-EI *m/z*: 434 [ZnCl(TpmPy)]⁺, 367 [Zn(TpmPy)₂]²⁺. ¹H NMR (300 MHz, methanol-*d*₄): δ 8.51 (d, 2H, J_{HH} = 5.7 Hz, 2-H (py)), 7.67 (d, 3H, J_{HH} = 2.5 Hz, 5-H (pz)), 7.50 (d, 3H, J_{HH} = 2.5 Hz, 3-H (pz)), 7.30 (d, 2H, J_{HH} = 5.7 Hz, 3-H (py)), 6.42 (dd, 3H, J_{HH} = 2.5 Hz, 4-H (pz)), 5.17 (s, 2H, CH₂-C(pz)₃), 4.68 (s, 2H, CH₂-py). ¹H NMR (300 MHz, acetone-*d*₆): δ 8.67 (d, 2H, J_{HH} = 5.7 Hz, 2-H (py)), 7.67 (d, 3H, J_{HH} = 2.3 Hz, 5-H (pz)), 7.56 (d, 3H, J_{HH} = 2.4 Hz, 3-H (pz)), 7.52 (d, 2H, J_{HH} = 5.7 Hz, 3-H (py)), 6.41 (dd, vt, 3H, J_{HH} = 2.4 Hz, 4-H (pz)), 5.25 (s, 2H, CH₂-C(pz)₃), 4.83 (s, 2H, CH₂-py). ¹³C{¹H}-NMR (100.6 MHz, acetone-*d*₆, 298 K): δ 153.04 (s, 4-C (py)), 149.54 (s, 2,6-C (py)), 142.05 (s, 3-C (pz)), 133.70 (s, pz-C (Ph)), 132.16 (s, 5-C (pz)), 123.85 (s, 3,5-C (py)), 107.24 (s, 4-C (pz)), 90.84 (s, CH₂-C(pz)₃), 74.61 (s, O-CH₂-C(pz)₃), 72.12 (s, O-CH₂-py).

Synthesis of [Ni(TpmPy)₂]Cl₂ (5). To a water solution of NiCl₂·6H₂O (22 mg, 0.09 mmol, 1 equiv) is added portionwise (1) (61 mg, 0.18 mol, 2 equiv). The solid partially dissolves during the addition. After addition, the blue-violet solution is stirred at room temperature overnight, after which time the solvent is left to evaporate. The product crystallizes from the concentrated mixture as pale violet crystals that are separated by filtration (57 mg, 80%). The compound (5) is soluble in CHCl₃, sparingly soluble in MeOH, EtOH, acetone, and acetonitrile, insoluble in Et₂O and well soluble in H₂O (*S*_{25 °C} ≈ 50 mg·mL^{−1}). (5)·H₂O C₃₄H₃₆Cl₂N₁₄O₃Ni (818.35) calcd. C 49.90, H 4.43, N 23.96; found. C. 49.57, H 4.21, N 24.09. IR (KBr): 2965, 2927 (m s, ν (C–H)), 1568, 1522 (m s, ν (C=N), ν (C=C)). MS-EI *m/z*: 364 [Ni(TpmPy)₂]²⁺. X-ray quality single crystals were grown by slow evaporation of a concentrated methanol solution of (5).

Synthesis of [ZnCl₂(TpmPy^{Ph})₂] (6). To a methanolic solution of ZnCl₂ (15 mg, 0.11 mmol, 1 equiv) is added dropwise a solution of (2) (124 mg, 0.22 mmol, 2 equiv) in MeOH. An immediate precipitation of a pale yellow solid occurs. The mixture is stirred for 10 min, then the solid is filtered off and washed with a small amount of cold methanol, to yield a pale yellow solid of (6) (113 mg, 80%). The compound is well soluble in CHCl₃ and acetone, moderately soluble in MeOH, EtOH, and acetonitrile and less soluble in H₂O (*S*_{25 °C} ≈ 0.8 mg·mL^{−1}). (6)·CH₃OH, C₇₁H₆₂Cl₂N₁₄O₃Zn (1295.66) calcd. C 65.81, H 4.82, N 15.13; found. C. 65.74, H 4.67, N 15.31. IR (KBr): 3148, 3060, 2928 (w s, ν (C–H)), 1620 (s s, ν (C=N)), 1531 (m s, ν (C=C)), 1500 (m s, ν (C=C)), 1456 (s s), 1222 (s br), 871, 776, 694 (s s), 616 (w s), 477 (m s) cm^{−1}. *far*-IR (Cesium Iodide): 336–301 cm^{−1} (m s, ν (Zn–Cl)). MS-EI *m/z*: 564 [TpmPy^{Ph} + H]⁺, 662 [ZnCl(TpmPy^{Ph})]⁺. ¹H NMR (CDCl₃, 298 K): δ 8.56 (d, 2H, J_{HH} = 6.0 Hz, 2,6-H (py)), 7.76 (d, 6H, J_{HH} = 7.5 Hz, *o*-H (Ph)), 7.44 (d, 3H, J_{HH} = 2.6 Hz, 5-H (pz)), 7.40–7.28 (m, 11H, *m*-H, *p*-H (Ph) + 3,5-H (py)), 6.34 (d, 3H, J_{HH} = 2.6 Hz, 4-H (pz)), 5.40 (s, 2H, CH₂-C(pz)₃), 4.73 (s, 2H, CH₂-py). ¹H NMR (acetone-*d*₆, 298 K): δ 8.55 (d, 2H, J_{HH} = 6.2 Hz, 2,6-H (py)), 7.83 (d, 6H, J_{HH} = 7.0 Hz, *o*-H (Ph)), 7.76 (d, 3H, J_{HH} = 2.6 Hz, 5-H (pz)), 7.53 (d, 2H, J_{HH} = 6.0 Hz, 3,5-H (py)), 7.38 (dd, vt, 6H, J_{HH} = 7.6 Hz, *m*-H (Ph)), 7.31 (dd, vt, 3H, J_{HH} = 7.6 Hz, *p*-H (Ph)), 6.86 (d, 3H, J_{HH} = 2.6 Hz, 4-H (pz)), 5.47 (s, 2H, CH₂-C(pz)₃), 4.97 (s, 2H, CH₂-py). ¹³C{¹H}-NMR

(100.6 MHz, CDCl₃, 298 K): δ 153.22 (s, 3-C (pz)), 151.90 (s, 4-C (py)), 148.46 (s, 2,6-C (py)), 132.46 (s, pz-C (Ph)), 132.27 (s, 5-C (pz)), 128.79 (s, m-C (Ph)), 128.55 (s, p-C (Ph)), 125.94 (s, o-C (Ph)), 122.97 (s, 3,5-C (py)), 104.08 (s, 4-C (pz)), 89.91 (s, CH₂-C(pz)₃), 74.37 (s, O-CH₂-C(pz)₃), 71.83 (s, O-CH₂-py). ¹³C NMR (100.6 MHz, acetone-*d*₆, 298 K): δ 153.69 (s, 3-C (pz)), 153.28 (s br, 4-C (py)), 149.35 (s, 2,6-C (py)), 133.78 (s, pz-C (Ph)), 132.06 (s, 5-C (pz)), 129.58 (s, m-C (Ph)), 129.19 (s, p-C (Ph)), 126.66 (s, o-C (Ph)), 123.88 (s, 3,5-C (py)), 104.67 (s, 4-C (pz)), 90.37 (s, CH₂-C(pz)₃), 75.14 (s, O-CH₂-C(pz)₃), 72.40 (s, O-CH₂-py).

Synthesis of [NiCl₂(TpmPy^{Ph})₂] (7). To a methanolic solution of NiCl₂·6H₂O (22 mg, 0.09 mmol, 1 equiv) is added dropwise a solution of (2) (104 mg, 0.18 mmol, 2 equiv) in MeOH. An immediate precipitation of an off white solid occurs. The mixture is stirred for 10 min, then the solid is filtered off and washed with a small amount of cold methanol, to yield (7) (92 mg, 81%). The compound is well soluble in CHCl₃ and acetone, moderately soluble in MeOH, EtOH, and acetonitrile, and less soluble in H₂O (*S*_{25 °C} ≈ 1.0 mg·mL⁻¹). (7), C₇₀H₅₈Cl₂N₁₄O₂Ni (125.92) calcd. C 66.89, H 4.65, N 15.60; found: C. 67.03 H 4.82, N 15.19. IR (KBr): 3148, 3061, 2926 (w s, ν (C-H)), 1617 (s s, ν (C=N)), 1531 (m s, ν (C=C)), 1500 (m s, ν (C=C)), 1456 (s s), 1221 (s br), 871, 751, 693 (s s), 619 (w s), 489 (m s) cm⁻¹. MS-EI *m/z*: 564 [TpmPy^{Ph} + H]⁺, 656 [NiCl(TpmPy^{Ph})]⁺.

Synthesis of [VOCl₂(TpmPy)] (8). To a solution of vanadium trichloride (0.20 g, 1.27 mmol, 1 equiv) in THF (15 mL) is added (1) (0.430 g, 1.27 mmol, 1 equiv) in THF (10 mL). The resulting pale blue solution is stirred overnight. The final pale blue solution is concentrated and upon addition of Et₂O a pale blue solid precipitates. The solid is collected by filtration, washed with Et₂O, and dried in vacuum (313 mg, 52%). The compound (8) is soluble in DMSO, moderately soluble in MeOH and EtOH, and less soluble in H₂O (*S*_{25 °C} ≈ 5.0 mg·mL⁻¹). (8) VO₂Cl₂C₁₇H₁₇N₇ (473.21) calcd. C 43.15, H 3.62, N 20.72. found: C 42.92, H 3.53, N 20.81. IR (KBr): 3170, 3148 (s s, ν (C-H)), 1519–1517 (s br, ν (C=C)), ν (C=N)), 971 (m, ν (V=O)). *far*-IR (polyethylene): 391 and 348 cm⁻¹ (m s, ν (V-Cl)). EPR (DMSO, r.t.): *a* = 101.6 G, *g* = 1.9989. MS-EI *m/z*: 406 [VOCl₂(TpmPy) - pz]⁺, 339 [VOCl₂(TpmPy) - 2pz]⁺.

Synthesis of [PdCl₂(TpmPy)₂] (9). To a dichloromethane solution (8 mL) of (1) (78 mg, 0.23 mmol, 2 equiv) is added dropwise a suspension of *cis*-[PdCl₂(CH₃CN)₂] (30 mg, 0.11 mmol, 1 equiv) in dichloromethane. The yellow resulting solution is stirred at room temperature for 1 h, during which time a pale yellow solid precipitates. The product is filtered off, washed with a small amount of cold CH₂Cl₂, and dried, yielding a pale yellow powder of (9) (70 mg, 75%). The compound is soluble in CH₂Cl₂, CHCl₃, and DMSO, sparingly soluble in MeOH and acetonitrile, and less soluble in H₂O (*S*_{25 °C} ≈ 0.8 mg·mL⁻¹). (9) C₃₄H₃₄Cl₂N₁₄O₂Pd, (848.06) calcd. C 48.15, H 4.04, N 23.12. found: C 48.06, H 3.94, N 23.15. IR (KBr): 3128, 3050, 2923, 2851 (w s, ν (C-H)), 1619 (m s, ν (C=N)), 1561, 1517 (s s, ν (C=N)), ν (C=C)), 1428, 1390 (s s), 1323 (s s), 1133, 1111, 1064 (s s), 867 (s s), 753 (s s), 616 (m s), 505 (m s) cm⁻¹. *far*-IR (polyethylene): 361 (m s, ν (Pd-Cl)), 308–296 cm⁻¹ (m s, ν (Pd-Cl)). MS-EI *m/z*: 811 [Pd(TpmPy)₂Cl]⁺. ¹H NMR (300 MHz, CDCl₃, 298 K): δ 8.68 (d, 2H, *J*_{HH} = 6.7 Hz, 2,6-H (py)), 7.67 (s, vd, 3H, 5-H (pz)), 7.34 (d, 3H, *J*_{HH} = 2.6 Hz, 3-H (pz)), 7.07 (d, 2H, *J*_{HH} = 6.0 Hz, 3,5-H (py)), 6.36 (m, vdd, 3H, 4-H (pz)), 5.22 (s, 2H, CH₂-C(pz)₃), 4.61 (s, 2H, CH₂-py). ¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 298 K): δ 153.11 (s, 2,6-C (py)), 150.25 (s, 4-C (py)), 141.75 (s, 3-C (pz)), 130.77 (s, 5-C (pz)), 122.54 (s, 3,5-C (py)), 107.01 (s, 4-C (pz)), 89.85 (s, CH₂-C(pz)₃), 74.72 (s, O-CH₂-C(pz)₃), 71.78 (s, O-CH₂-py). ¹³C{¹H}-NMR (100.6 MHz, DMSO-*d*₆, 298 K): δ 152.61 (s, 2,6-C (py)), 150.75 (s, 4-C (py)), 141.01 (s, 3-C (pz)), 131.15 (s, 5-C (pz)), 122.60 (s, 3,5-C (py)), 106.57 (s, 4-C (pz)), 89.17 (s, CH₂-C(pz)₃), 73.16 (s, O-CH₂-C(pz)₃), 70.30 (s, O-CH₂-py). X-ray quality single

crystals were grown by slow evaporation of a concentrated dichloromethane solution of (9).

Synthesis of [PdCl₂(TpmPy^{Ph})₂] (10). To a dichloromethane solution (10 mL) of (2) (104 mg, 0.18 mmol, 2 equiv) is added dropwise a suspension of *cis*-[PdCl₂(CH₃CN)₂] (24 mg, 0.09 mmol, 1 equiv) in dichloromethane. The pale yellow resulting solution is stirred at room temperature for 1 h. The solvent is removed under vacuum, and the residue is washed with a small amount of cold methanol (2 mL), filtered off, and dried yielding a pale yellow powder of (10) (80 mg, 68%). The compound is well soluble in CH₂Cl₂, CHCl₃, CH₃CN, and DMSO, moderately soluble in MeOH and EtOH, and insoluble in H₂O. (10), C₇₀H₅₈N₁₄O₂PdCl₂, (1304.65) calcd. C 65.66, H 2.68, N 15.31. found: C 65.89, H 2.91, N 15.02. IR (KBr): 3147, 3060, 2925, 2850 (w s, ν (C-H)), 1621 (m s, ν (C=N)), 1531 (s s, ν (C=N)), ν (C=C)), 1500, 1456 (s s), 1221 (s br), 1134, 1102, 1073, 1044 (m s), 871 (s s), 752 (s s), 694 (s s), 627 (w s), 503 (m s) cm⁻¹. *far*-IR (polyethylene): 365 (s s, ν (Pd-Cl)). MS-EI *m/z*: 1268 [PdCl(TpmPy^{Ph})₂]⁺, 1304 [PdCl₂(TpmPy^{Ph})₂]⁺. ¹H NMR (CDCl₃, 298 K): δ 8.63 (d, 2H, *J*_{HH} = 6.7 Hz, 2,6-H (py)), 7.81 (d, 6H, *J*_{HH} = 7.9 Hz, *o*-H (Ph)), 7.48 (d, 3H, *J*_{HH} = 2.6 Hz, 5-H (pz)), 7.41 (dd, vt, 6H, *J*_{HH} = 7.6 Hz, *m*-H (Ph)), 7.33 (dd, vt, 3H, *J*_{HH} = 7.6 Hz, *p*-H (Ph)), 7.10 (d, 2H, *J*_{HH} = 6.6 Hz, 3,5-H (py)), 6.66 (d, 3H, *J*_{HH} = 2.6 Hz, 4-H (pz)), 5.40 (s, 2H, CH₂-C(pz)₃), 4.64 (s, 2H, CH₂-py). ¹³C{¹H} and HMQC ¹³C-¹H NMR (100.6 MHz, CDCl₃, 298 K): δ 153.25 (s, 3-C (pz)), 152.97 (s, 2,6-C (py)), 150.36 (s, 4-C (py)), 132.69 (s, pz-C (Ph)), 132.31 (s, 5-C (pz)), 128.77 (s, m-C (Ph)), 128.47 (s, p-C (Ph)), 126.05 (s, *o*-C (Ph)), 122.54 (s, 3,5-C (py)), 104.06 (s, 4-C (pz)), 90.10 (s, CH₂-C(pz)₃), 74.56 (s, O-CH₂-C(pz)₃), 71.79 (s, O-CH₂-py).

Synthesis of [PdCl₂(μ -TpmPy)₂Fe(BF₄)₂] (11). **Method (b, Scheme 6).** To a yellow/brown solution of *cis*-[PdCl₂(CH₃CN)₂] (12 mg, 0.046 mmol) in dichloromethane (5 mL) is added dropwise an acetonitrile solution (5 mL) of [Fe(TpmPy)₂](BF₄)₂ (3) (41 mg, 0.045 mmol, 1 equiv). The resulting mixture is stirred at room temperature for 1 h, during which time a pale orange-pink solid precipitates. The solid is filtered off, washed with acetonitrile and dried, yielding (11) (38 mg, 78%).

Method (b', Scheme 6). To a dichloromethane solution (8 mL) of [PdCl₂(TpmPy)₂] (9) (25 mg, 0.030 mmol) is added dropwise a solution of Fe(BF₄)₂·6H₂O (10 mg, 0.030 mmol, 1 equiv) in methanol. The pale pink resulting mixture is stirred at room temperature for 1 h. The product is filtered off, washed with a small amount of methanol, and dried, yielding a pale pink powder of (11) (23 mg, 69%). (11)·4H₂O, C₃₄H₄₂N₁₄B₂F₈FeO₆PdCl₂, (1149.58) calcd. C 35.52, H 3.68, N 17.05 found: C 35.36, H 3.22, N 17.10. IR (KBr): 3138, 2900 (w s, ν (C-H)), 1621 (s s, ν (C=N)), 1519–1513 (m br, ν (C=N)), ν (C=C)), 1420 (s s), 1339 (s s), 1231 (s s), 1106–1036 (s br, ν (BF₄)), 866 (m s), 766 (m br) cm⁻¹. MS-EI *m/z*: 811/813 [PdCl(TpmPy)₂]⁺, 990 [{PdCl₂(TpmPy)Fe]₂(BF₄)₂]²⁺. ¹H NMR (CD₃CN, 313 K): δ 8.78 (d, 2H, *J*_{HH} = 6.0 Hz, 2,6-H (py)), 8.58 (s br, 3H, 5-H (pz)), 7.58 (d, 2H, *J*_{HH} = 6.0 Hz, 3,5-H (py)), 7.30 (s br, 3H, 3-H (pz)), 6.57 (s, br, 3H, 4-H (pz)), 5.78 (s, 2H, CH₂-C(pz)₃), 5.31 (s, 2H, CH₂-py). ¹H NMR (CD₃CN, 253 K): δ 8.72 (d br, 2H, 2,6-H (py)), 8.62 (s br, 2H, 5-H (pz)), 8.41 (s br, 1H, 5-H (pz)), 7.58 (d br, 2H, 3,5-H (py)), 7.40 (s br, 1H, 4-H (pz)), 7.27 (s br, 2H, 4-H (pz)), 6.56 (s, br, 1H, 4-H (pz)), 6.51 (s, 2H, 2H, 4-H (pz)), 5.78 (s, 2H, CH₂-C(pz)₃), 5.30 (s, 2H, CH₂-py).

Synthesis of [Fe(μ -TpmPy)₂Cu(NO₃)₂](BF₄)₂ (12). To an acetonitrile solution (5 mL) of [Fe(TpmPy)₂](BF₄)₂ (3) (89 mg, 0.1 mmol, 1 equiv), a solution of Cu(NO₃)₂·2.5H₂O (23 mg, 0.1 mmol, 1 equiv) in acetonitrile (2 mL) is added. An immediate precipitation of a pale violet solid occurs. It is filtered off under nitrogen, washed with a small amount of cold acetonitrile (1 mL) and dried to leave compound (12) (75 mg, 69%). (12)·2H₂O, C₃₄H₃₈N₁₆B₂CuF₈FeO₁₀, (1119.27) calcd. C 36.34, H 3.40, N 19.94. found: C 36.47, H 3.30, N 20.02. IR (KBr): ν = 3137 (m s, C-H), 1620 (m s, ν (N=C)), 1517–1515 (m br,

Table 1. Crystallographic Data for Compound TpmPy (1), [Fe(TpmPy)₂](BF₄)₂ (3), [ZnCl₂(TpmPy)₂] (4), [Ni(TpmPy)₂]Cl₂ (5), and [PdCl₂(TpmPy)₂] (9)

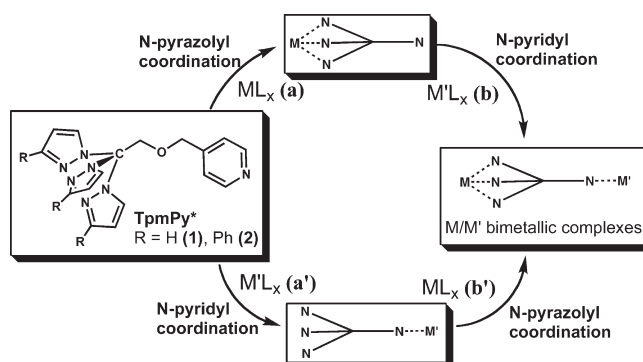
	1	3	4	5	9
crystal shape	block white	block red	cube colorless	prism pink	plate colorless
empirical formula	C ₁₇ H ₁₇ N ₇ O	C ₃₄ H ₃₄ FeN ₁₄ O ₂ 2(BF ₄)	C ₃₄ H ₃₄ Cl ₂ N ₁₄ O ₂ Zn	C ₃₄ H ₃₄ N ₁₄ NiO ₂	C ₃₄ H ₃₄ Cl ₂ N ₁₄ O ₂ Pd
formula weight	335.38	900.22	807.02	729.46	848.05
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	8.3750(11)	14.8596(12)	20.5210(12)	13.126(11)	13.266(3)
<i>b</i> (Å)	9.6879(11)	13.0034(10)	15.8868(17)	22.194(18)	9.2463(19)
<i>c</i> (Å)	10.6197(14)	20.7112(17)	11.0942(12)	20.15(2)	16.451(3)
α	92.074(7)	90.00	90.00	90.00	90.00
β	106.285(8)	105.932(3)	92.334(3)	104.03(4)	111.280(7)
γ	91.599(7)	90.00	90.00	90.00	90.00
<i>V</i> (Å ³)	825.88(18)	3848.2(5)	3613.9(6)	5695(9)	1880.3(7)
<i>Z</i>	2	4	4	4	2
ρ_{calc} (g cm ⁻³)	1.349	1.554	1.483	0.851	1.498
μ (Mo K α) (mm ⁻¹)	0.091	0.485	0.882	0.374	0.688
<i>F</i> (000)	352	1840	1664	1520	864
reflections collected	18468	24714	26666	43838	12587
reflections unique	4997	6808	7610	12516	3233
<i>R</i> _{int}	0.031	0.1116	0.057	0.098	0.1462
goodness-of-fit on <i>F</i> ² ^a	0.999	0.912	1.021	0.847	1.081
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^b	<i>R</i> ₁ = 0.0425 <i>wR</i> ₂ = 0.1094	<i>R</i> ₁ = 0.0618 <i>wR</i> ₂ = 0.1574	<i>R</i> ₁ = 0.0374 <i>wR</i> ₂ = 0.0880	<i>R</i> ₁ = 0.0675 <i>wR</i> ₂ = 0.1608	<i>R</i> ₁ = 0.0827 <i>wR</i> ₂ = 0.1817
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0572 <i>wR</i> ₂ = 0.1200	<i>R</i> ₁ = 0.1324 <i>wR</i> ₂ = 0.2117	<i>R</i> ₁ = 0.0641 <i>wR</i> ₂ = 0.1068	<i>R</i> ₁ = 0.1464 <i>wR</i> ₂ = 0.1806	<i>R</i> ₁ = 0.2602 <i>wR</i> ₂ = 0.2787

^a Refinement Method: Full-matrix least-squares on *F*². ^b *R*₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$. *wR*₂ = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

$\nu(\text{N}=\text{C})$, $\nu(\text{C}=\text{C})$), 1384 (s s), 1107 (m s), 1082 (m s), 1035 (s s), 866 (s s), 767 (m s), 606 (w s) cm⁻¹. MS-EI *m/z*: 731 [Fe(TpmPy)₂-Cu₂(TpmPy)](BF₄)(NO₃)₃]²⁺, 363 [Fe(TpmPy)₂]²⁺.

Synthesis of [PdCl₂(μ -TpmPy^{Ph})₂Fe₂(H₂O)₆](BF₄)₄ (13). To an acetonitrile suspension (7 mL) of [PdCl₂(TpmPy^{Ph})₂] (10) (30 mg, 0.023 mmol, 1 equiv) is added dropwise a solution of Fe(BF₄)₂·6H₂O (8 mg, 0.024 mmol, 1 equiv) in acetonitrile. The yellow resulting mixture is stirred at room temperature for 1 h, during which time a pale yellow solid precipitated. The product is filtered off, washed with a small amount of acetonitrile and dried, yielding a pale yellow powder of (13) (23 mg, 59%). (13)·2((CH₃)₂CO)·0.5CH₃CN, C₇₇H_{83.5}N_{14.5}B₂F₈Fe₂O₁₀PdCl₂, (1834.72). calcd. C 50.40, H 4.59, N 11.07. found: C 50.33, H 4.87, N 11.02. IR (KBr): 3441 (w s, $\nu(\text{OH})$), 3147, 3058, 2924 (w s, $\nu(\text{C}-\text{H})$), 1643 (w br, $\delta(\text{OH})$), 1620 (m s, $\nu(\text{C}=\text{N})$), 1531 (s s, $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{C})$), 1499, 1455 (s s), 1429, 1392 (m s), 1220 (s br), 1134, 1133–1043 (s br, $\nu(\text{BF}_4)$), 871 (s s), 750 (s s), 693 (s s) cm⁻¹. MS-EI *m/z*: 1268 [PdCl(TpmPy^{Ph})₂]⁺, 1366 [PdCl(TpmPy^{Ph})₂Fe](CH₃CN)⁺. ¹H NMR (CDCl₃, 298 K): δ 8.61 (d, 2H, *J*_{HH} = 6.4 Hz, 2,6-H (py)), 7.78 (d, 6H, *J*_{HH} = 7.6 Hz, *o*-H (Ph)), 7.46 (d, 3H, *J*_{HH} = 2.6 Hz, 5-H (pz)), 7.40 (dd, vt, 6H, *J*_{HH} = 7.6 Hz, *m*-H (Ph)), 7.33 (dd, vt, 3H, *J*_{HH} = 7.6 Hz, *p*-H (Ph)), 7.11 (d, 2H, *J*_{HH} = 6.6 Hz, 3,5-H (py)), 6.65 (d, 3H, *J*_{HH} = 2.6 Hz, 4-H (pz)), 5.40 (s, 2H, CH₂-C(pz)), 4.67 (s, 2H, CH₂-py). ¹³C{¹H} and HMQC ¹³C-¹H NMR (100.6 MHz, CDCl₃, 298 K): δ 153.34 (s, 3-C (pz)), 153.07 (s, 2,6-C (py)), 149.91 (s, 4-C (py)), 132.76 (s, pz-C (Ph)), 132.39 (s, 5-C (pz)), 128.82 (s, *m*-C (Ph)), 128.53 (s, *p*-C (Ph)), 126.12 (s, *o*-C (Ph)), 122.62 (s, 3,5-C (py)), 104.12 (s, 4-C (pz)), 89.25 (s, CH₂-C(pz)), 73.92 (s, O-CH₂-C(pz)), 70.89 (s, O-CH₂-py).

Crystal Structure Determinations. Single crystals of TpmPy (1), [Fe(TpmPy)₂](BF₄)₂ (3), [ZnCl₂(TpmPy)₂] (4), [Ni(TpmPy)₂]Cl₂ (5), and [PdCl₂(TpmPy)₂] (9) were obtained as indicated above. Intensity data were collected at 150 K, using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-K α

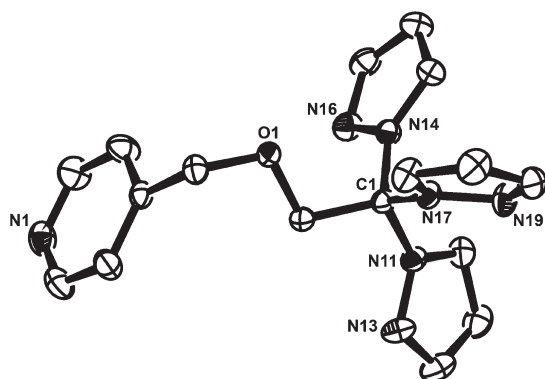
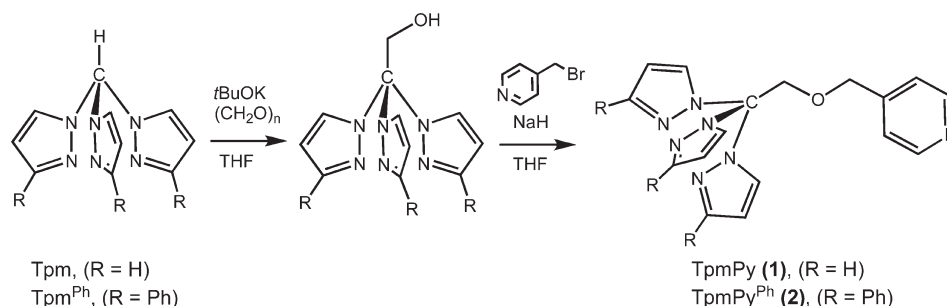
Scheme 1. Possible Coordination Pathways of TpmPy* (TpmPy (1) for R = H; TpmPy^{Ph} (2) for R = Ph)

(λ = 0.71073) radiation. Data were collected using ω scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT^{7a} on all the observed reflections. Absorption corrections were applied using SADABS.^{7a} Structures were solved by direct methods by using the SHELXS-97 package^{7b} and refined with SHELXL-97.^{7c} Calculations were performed using the WinGX System-Version 1.80.03.^{7d} All hydrogen atoms were inserted in calculated positions. Least-squares refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed. For (5) there is disordered solvent in the structure. Attempts were made to model it, but were unsuccessful. PLATON/SQUEEZE^{7e} was used to correct the data. Crystal data and refinement parameters are shown in Table 1. CCDC numbers 776297 to 776301 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.

Results and Discussion

We investigated possible coordination pathways to explore the versatility of these new ligands (Scheme 1): on the one

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Scheme 2. Synthesis of the N₄-Scorpionates TpmPy (**1**) and TpmPy^{Ph} (**2**)**Figure 1.** ORTEP plot of TpmPy (**1**), ellipsoids are shown at 50% of probability. Hydrogen atoms are omitted for clarity.

hand, we studied the coordination chemistry of the tripodal “scorpionate” face of the ligand (step (a)); on the other hand, we explored the reactivity of the pyridyl moiety of the new ligands toward metal centers known to have a good affinity for pyridine (step (a')). The following steps ((b) and (b')) would account for the further coordination ability of the ligand toward the synthesis of heterobimetallic systems.

1. Syntheses and Characterization of the New Scorpionates TpmPy and TpmPy^{Ph}. We were able to synthesize 4-((tris-2,2,2-(pyrazol-1-yl)ethoxy)methyl)pyridine (TpmPy (**1**); Scheme 2, R = H) in good yield by using Tpm as a starting material, by following a two-step synthetic process. From a known⁶ functionalization of Tpm that provides tris-2,2,2-(pyrazol-1-yl)ethanol, we have reacted the latter, upon deprotonation with sodium hydride, with 4-bromomethylpyridine to obtain the desired compound. The reaction proceeds easily and gives (**1**) in good purity, without the need of chromatographic purification.

Similarly, we prepared the “bulky” analogue bearing phenyl groups as substituents at the 3-position of the pyrazolyl rings (TpmPy^{Ph} (**2**); Scheme 2, R = Ph). Compound (**2**) can be easily purified by column chromatography at the final stage.

These products have been characterized by ¹H, ¹³C NMR, and IR spectroscopies, elemental analyses and, in the case of (**1**), also by X-ray diffraction analysis; its molecular structure is depicted in Figure 1. In this respect, the most striking feature of (**1**) is the small O–C_{methylene}–C_{ipso}–C_{ortho} torsion angle (118.31°, see Table 2) which widens considerably upon coordination (see below). Both compounds (**1**) and (**2**) exhibit well resolved ¹H NMR spectra (CDCl₃) with only one set of resonances for the three equivalent pyrazolyl rings (δ 7.67 and 6.36 for (**1**) or δ 7.57 and 6.67 for (**2**), for 5-H and 4-H

of the pyrazolyl rings, respectively) and, in the case of (**2**), one pattern of signals for the phenyl protons (δ 7.81, 7.40, and 7.33 for the *ortho*, *meta*, and *para* protons, respectively). The resonances of the pyridyl ring protons appear as a pair of doublets (*J*_{HH} = 6.0 Hz) at δ 8.53 and 7.06 for (**1**) and at δ 8.47 and 7.10 for (**2**).

Compound (**1**) is well soluble in all common organic solvents (i.e., Et₂O, CH₂Cl₂, CH₃Cl, MeOH, EtOH, and acetone) and moderately soluble in water (*S*_{25 °C} ≈ 10 mg·mL⁻¹) as a free base, while upon protonation of the pyridine nitrogen becomes well water-soluble as a salt. Compound (**2**) is not soluble in water, but is soluble in the usual organic solvents (i.e., Et₂O, CH₂Cl₂, CH₃Cl, MeOH, acetonitrile, and acetone). Compounds (**1**) and (**2**) represent a new type of N₄-scorpionate derivatives, bearing not only the common three pyrazolyl rings but also one pyridyl group, thus possibly being able to bind different metal centers, with distinct affinities to the N-pyrazolyl and the N-pyridyl donor sites, allowing also to investigate their competition for such N-ligating functions. TpmPy^{Ph} (**2**), being sterically hindered on the pyrazolyl-side, should be an important candidate to the synthesis of half-sandwich complexes with metals that normally would form the full sandwich complex with two tridentate scorpionate ligands.⁸

2.1. Reaction of TpmPy (1**) with Fe^{II}: Synthesis and Characterization of [Fe(TpmPy)₂](BF₄)₂ (**3**).** Fe^{II} is a metal ion with one of the highest affinities for scorpionates and tends to form full sandwich complexes.⁹ Accordingly, reaction of 2 equiv of TpmPy (**1**) with Fe(BF₄)₂·6H₂O in methanol proceeds readily at room temperature to give [Fe(TpmPy)₂](BF₄)₂ (**3**) bearing two ligated TpmPy (Scheme 3).

Compound (**3**) is moderately soluble in CH₂Cl₂, MeOH, DMSO, and DMF, and is well soluble in acetonitrile.

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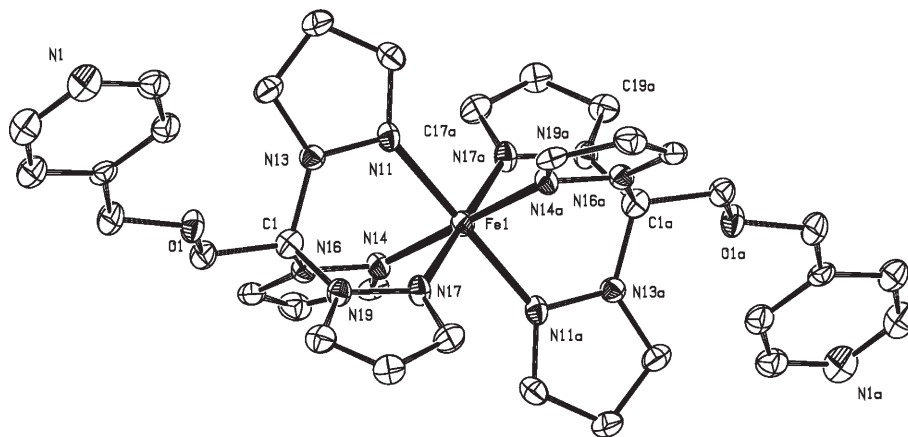
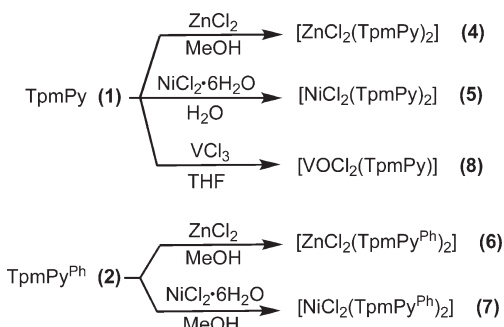


Figure 2. ORTEP plot of the Fe1 molecule in $[\text{Fe}(\text{TpmPy})_2](\text{BF}_4)_2$ (**3**), where the ellipsoids are shown at 50% of probability. The hydrogen atoms and the tetrafluoroborate counterions are omitted for clarity. Symmetry operation to generate equivalent atoms: $2-x, -y, 1-z$.

Scheme 4. Syntheses of $[\text{MCl}_2(\text{TpmPy}^*)_2]$ ($\text{M} = \text{Ni}^{\text{II}}, \text{Zn}^{\text{II}}, \text{TpmPy}^* = \text{TpmPy}, \text{TpmPy}^{\text{Ph}}$) (**4–7**) and $[\text{VOCl}_2(\text{TpmPy})]$ (**8**). Pyridyl-Coordination: (**4**), (**6**), (**7**); Pyrazolyl-Coordination: (**5**), (**8**)



The observed intermolecular π – π interactions in (**3**) are also affected by the different conformations of the two molecules. Indeed, in the Fe1 molecules, the pyridyl rings and vicinal pyrazol rings interact with centroid/centroid distances of 3.510 Å and the ring planes make angles of 5.11°; conversely, in the molecules of Fe2, such type of interactions leads to centroid/centroid distances of 3.843 Å and angles of 11.41° between the ring planes (see Supporting Information, Figure S.4). These interactions could stabilize the packing and the coordination mode through the three pyrazolyl rings.

2.2. Reactions of TpmPy (1) and TpmPy^{Ph} (2) with Ni^{II}, Zn^{II}, and V^{III}: Syntheses and Characterizations of $[\text{MCl}_2(\text{TpmPy}^*)_2]$ ($\text{M} = \text{Ni}^{\text{II}}, \text{Zn}^{\text{II}}, \text{TpmPy}^* = \text{TpmPy}, \text{TpmPy}^{\text{Ph}}$) (4–7**) and $[\text{VOCl}_2(\text{TpmPy})]$ (**8**).** Reactions of (**1**) and (**2**) with Zn^{II} or Ni^{II} metal salts can, in principle, give full- or half-sandwich complexes¹⁰ through the tripodal

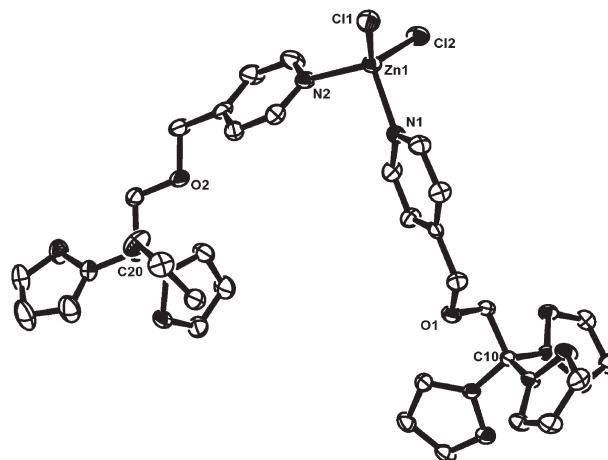


Figure 3. ORTEP plot of $[\text{ZnCl}_2(\text{TpmPy})_2]$ (**4**), ellipsoids are shown at 50% of probability. Hydrogen atoms are omitted for clarity.

coordination of one or two scorpionates via the pyrazolyl rings, but the competition of the pyridyl arm for the metal can also occur in view of the known¹¹ metal affinity for this group.

Reaction of 2 equiv of TpmPy (**1**) with ZnCl₂ in methanol affords $[\text{ZnCl}_2(\text{TpmPy})_2]$ (**4**) (Scheme 4). The compound is well soluble in CH₂Cl₂ and sparingly soluble in MeOH and EtOH. The ESI-MS spectrum shows ionic fragments corresponding to $[\text{ZnCl}(\text{TpmPy})]^+$ and $[\text{Zn}(\text{TpmPy})_2]^{2+}$.

The X-ray diffraction analysis of the solid-state structure of (**4**) shows a metal tetrahedral-type coordination with the two TpmPy ligands binding through the pyridyl rings, whereas the pyrazolyl groups remain uncoordinated (Figure 3, Tables 1 and 2). This mode of TpmPy coordination is preserved in solution. In fact, in the ¹H NMR spectrum, the pyridyl resonances are shifted to lower field (by ca. 0.1 ppm) relatively to those of the free ligand (i.e., 8.51, 7.30 for (**4**) and 8.43, 7.20 for (**1**), in methanol-*d*₄, corresponding to 2,6-H and 3,5-H of the pyridyl ring, respectively), whereas the pyrazolyl resonances remain almost unchanged. Moreover, NMR experiments at variable temperature confirm the equivalence^{5c} of the three uncoordinated pyrazolyl rings. In accordance, the IR spectrum displays a shift of $\nu_{\text{C=N}}$ assigned to the pyridyl rings to higher wavelengths compared to free (**1**) (i.e., 1601 or 1621 cm^{−1} for (**1**) or (**4**), respectively, Supporting Information, Table S.1).

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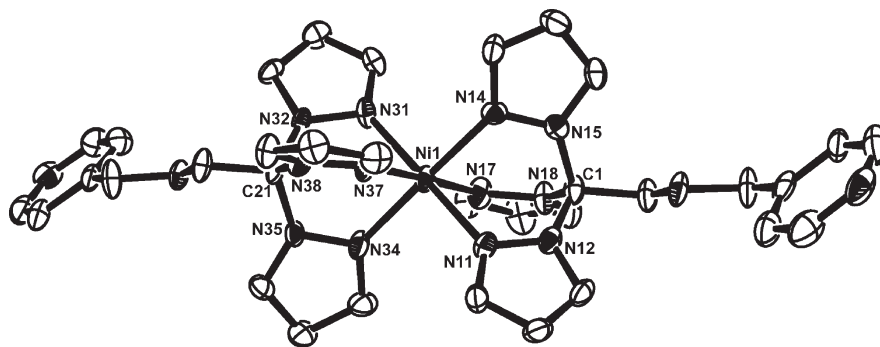


Figure 4. ORTEP plot of $[\text{Ni}(\text{TpmPy})_2]\text{Cl}_2$ (**5**), where the ellipsoids are shown at 50% of probability and the hydrogen atoms and the two chlorides are omitted for clarity.

The tetrahedral coordination around the zinc is slightly distorted with the internal angles of $100.69(8)^\circ$ for $\text{N1}-\text{Zn1}-\text{N2}$ and $119.77(3)^\circ$ for $\text{Cl1}-\text{Zn1}-\text{Cl2}$, that is, the larger angle concerns the chloride ligands. The $\text{Zn}-\text{N}$ bond lengths are identical ($2.058(2)$ Å and $2.053(2)$ Å), like the $\text{Zn}-\text{Cl}$ distances, thus showing a symmetrical elongation of the ideal tetrahedral geometry. The $\text{O}-\text{C}_{\text{methylene}}-\text{C}_{\text{ipso}}-\text{C}_{\text{ortho}}$ torsion angles in (**4**) are markedly disparate (135.26 and 177.97° , Table 2), in contrast to the other complexes that present a different coordination geometry (see below). π interactions are also apparent (see Supporting Information, Figure S.5); the distance between the $\text{N37}-\text{N39}$ pyrazolyl plane and the vicinal N2 pyridine plane is 4.054 Å (centroid-centroid) allowing a weak offset face-to-face stacking fashion.

In contrast to the case of Zn^{II} , Ni^{II} chloride reacts with 2 equiv of (**1**) to give (Scheme 4) the corresponding sandwich complex $[\text{Ni}(\text{TpmPy})_2]\text{Cl}_2$ (**5**) bearing two trihapto TpmPy ligands coordinated via the pyrazolyl rings, as shown by X-ray diffraction analysis (Figure 4, Tables 1 and 2). The octahedral N_6 -coordination of nickel(II) is consistent with the ^1H NMR spectrum that shows its typical paramagnetic nature (octahedral Ni^{II} , $S = 1$). Compound (**5**) is well soluble in water ($S_{25^\circ\text{C}} \approx 50 \text{ mg} \cdot \text{mL}^{-1}$), MeOH, and EtOH, and sparingly soluble in CHCl_3 , CH_2Cl_2 , and acetonitrile.

Similar to compound (**3**), the X-ray diffraction analysis of (**5**) confirms the scorpionate sandwich structure. The $\text{Ni}-\text{N}$ distances are very close (2.038 – 2.068 Å range), and the degree of tilting of the pyrazolyl rings is very low (i.e., $\text{Ni}-\text{N}-\text{N}-\text{C}$ torsion angles are within the range of 165.90° – 178.04°). The disparity of the $\text{O}-\text{C}_{\text{methylene}}-\text{C}_{\text{ipso}}-\text{C}_{\text{ortho}}$ torsion angles is only of 6.5° (Table 2). The main intermolecular interactions detected in (**5**) involve $\text{C}-\text{H} \cdots \pi$ interactions (see Supporting Information, Figure S.6). Each pyrazolyl hydrogen atoms H14 and H34 from one molecule is aimed at the π -clouds of the N2 and N1 pyridine rings, respectively, of a vicinal one; the $\text{H} \cdots \text{centroid}$ distances for these interactions are of 2.599 and 2.728 Å with $\text{C}-\text{H} \cdots \text{centroid}$ angles of 156.49 and 154.28° .

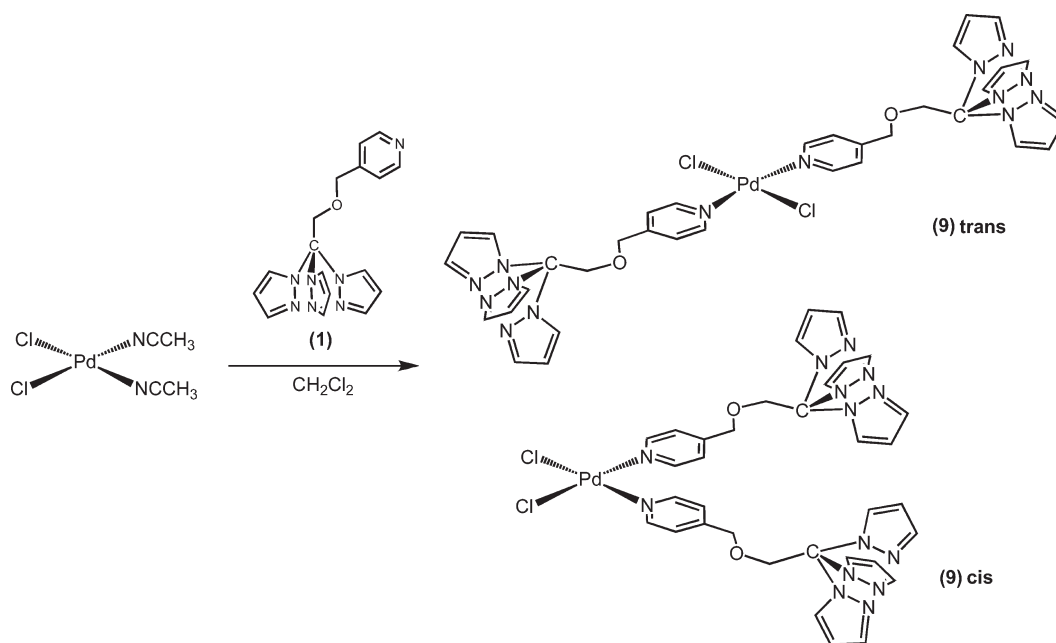
Similarly to the previous synthetic procedures, we studied the reactions of Zn^{II} and Ni^{II} chlorides with TpmPy^{Ph} (**2**). The latter, being sterically hindered at the pyrazolyl-side, is expected to coordinate preferably through the pyridyl moiety. In fact, reaction of (**2**) with ZnCl_2 in methanol leads readily to the quantitative precipitation of $[\text{ZnCl}_2(\text{TpmPy}^{\text{Ph}})_2]$ (**6**) which has been

characterized by IR, *far*-IR, NMR, MS, and elemental analysis. Like its TpmPy analogue (**4**), complex (**6**) bears the scorpionate ligands bound via the pyridyl groups. Its ^1H NMR spectrum shows, in fact, the equivalence of its three pyrazolyl rings (without a significant shift relative to the free ligand) and a lower field coordination shift (of 0.14 and 0.33 ppm) for the pyridyl protons. The 2-, 6- and 4- pyridyl carbons appear low field shifted in the ^{13}C NMR spectrum, as for the analogue (**4**). This feature appears to be common to all the complexes that exhibit pyridyl-coordination, as will be discussed below (see also Supporting Information, Figure S.2). Compound (**6**) is very soluble in CHCl_3 , CH_2Cl_2 , acetone, and moderately soluble in MeOH, while is insoluble in water.

Reaction of 2 equiv of TpmPy^{Ph} (**2**) with NiCl_2 in methanol proceeds readily leading to the precipitation of $[\text{NiCl}_2(\text{TpmPy}^{\text{Ph}})_2]$ (**7**) that also bears the scorpionate ligands coordinated through the pyridyl moieties. Hence, the pyrazolyl N_6 -coordination mode observed for (**5**), with unsubstituted tris(pyrazolyl)methane ligands, is sterically hindered for (**7**). The mass spectrum (EI) of (**7**) shows a pattern of fragmentation that is equivalent to that of its zinc analogue (**6**) (e.g., peaks at m/z 656 and 662 for $[\text{Ni}(\text{TpmPy}^{\text{Ph}})\text{Cl}]^+$ and $[\text{Zn}(\text{TpmPy}^{\text{Ph}})\text{Cl}]^+$, respectively). The IR spectra of (**6**) and (**7**) show almost identical profiles for the 1800 – 400 cm^{-1} region, in particular the shifted band at 1617 cm^{-1} ascribed to $\nu_{\text{C}=\text{N}}$ of the coordinated pyridyl moiety (see Supporting Information, Figure S.7 and Table S.1). The ^1H NMR spectrum of (**7**) shows broad resonances where it is possible to distinguish those assigned to the pyrazolyl rings, while those of the pyridyl moiety collapse because of the proximity of the metal center.

The reaction of TpmPy (**1**) with V^{III} chloride (Scheme 4) also proceeds readily with the precipitation, as a pale blue powder, of $[\text{VOCl}_2(\text{TpmPy})]$ (**8**) with the N_3 -pyrazolyl coordination. The compound has been characterized by MS, IR, *far*-IR, and EPR spectroscopies, and elemental analysis. The IR spectrum confirms the conceivable N_3 -pyrazolyl coordination mode of the scorpionate, typical for this type of compounds,¹² since $\nu_{\text{C}=\text{N}}$ appears at

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Scheme 5. Synthesis of $[\text{PdCl}_2(\text{TpmPy})_2]$ (**9**)

wavenumbers that are consistent with the coordinated-pyrazolyl rings (i.e., $1519\text{--}1517\text{ cm}^{-1}$, see also Supporting Information, Table S.1), whereas for the pyridyl-coordinated compounds $\nu_{\text{C}=\text{N}}$ usually shifts to higher wavenumbers (i.e., in the range of $1617\text{--}1621\text{ cm}^{-1}$, see below and Supporting Information, Table S.1). The EPR spectrum shows the expected signal (i.e., with a eight-line pattern, $g = 1.9989$) for a vanadium(IV) (d^1 , $I = 7/2$, $S = 1/2$).¹²

2.3. Reaction with Pd^{II} : Synthesis and Characterization of $[\text{PdCl}_2(\text{TpmPy})_2]$ (9**) and $[\text{PdCl}_2(\text{TpmPy}^{\text{Ph}})_2]$ (**10**).** Palladium(II) complexes bearing heterocyclic N-donor ligands are well-known, and the coordination chemistry of Pd-based complexes with pyrazoles, imidazoles and pyridines ligands has been fully developed.¹³ Pd^{II} reacts easily with bis(pyrazolyl)methane (Bpm) and tris(pyrazolyl)methane (Tpm) to give typical square planar N,N-coordination compounds (involving two ligated pyrazolyl rings, and leaving one free in the case of Tpm). Moreover, the recognized affinity¹⁵ of this metal with the pyridyl N-donor group encouraged us to investigate its coordination chemistry toward these new “pyridyl-based” scorpionates.

Reaction of *cis*- $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ with 2 equiv of (**1**) in dichloromethane gives the disubstituted product $[\text{PdCl}_2(\text{TpmPy})_2]$ (**9**) in quantitative yield (Scheme 5). The compound is stable and soluble in organic solvents such as CH_2Cl_2 and CHCl_3 , but in DMSO undergoes a partial decomposition. In the ^1H NMR spectrum the remarkable shift to lower field (by ca. 0.15 ppm) of the pyridyl resonances relatively to those of the free ligand confirms

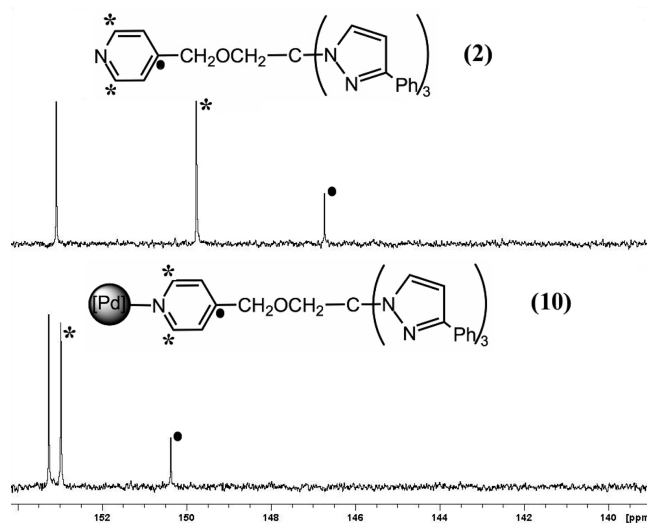


Figure 5. Shift of 2,6-C (*) and 4-C (•) pyridyl carbon resonances in ^{13}C NMR (400 MHz) spectra (CDCl_3) upon coordination of free (**2**) to Pd^{II} in $[\text{PdCl}_2(\text{TpmPy}^{\text{Ph}})_2]$ (**10**).

the coordination through the pyridyl moiety, whereas the pyrazolyl groups remain equivalent.

The phenyl substituted analogue, $[\text{PdCl}_2(\text{TpmPy}^{\text{Ph}})_2]$ (**10**), was prepared similarly, upon reaction of *cis*- $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ with (**2**). In this case, the coordination through the pyridyl moiety is expected to be even more favorable than for the unsubstituted (**9**), since the pyrazolyl-side is highly hindered by the phenyl substituents. Compound (**10**) shows NMR coordination shifts comparable to those of (**9**). For instance, similarly to (**9**), the ^{13}C NMR (400 MHz) spectrum of (**10**) shows the 2,6- and 4-pyridyl carbon resonances (at δ 152.9 and 150.4, respectively) shifted to lower field (by 3.1 and 3.7 ppm, correspondingly) relatively to the free ligand. This behavior supports the expected deshielding upon pyridyl coordination, confirming that the *ortho* and the *para* positions are more influenced than the *meta* position (Figure 5).

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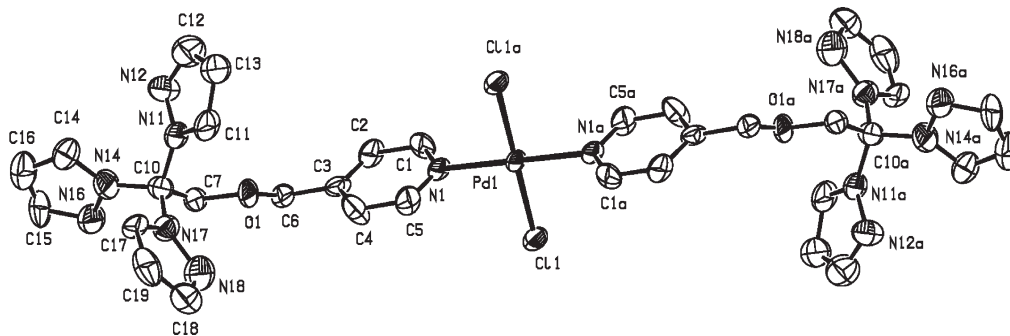
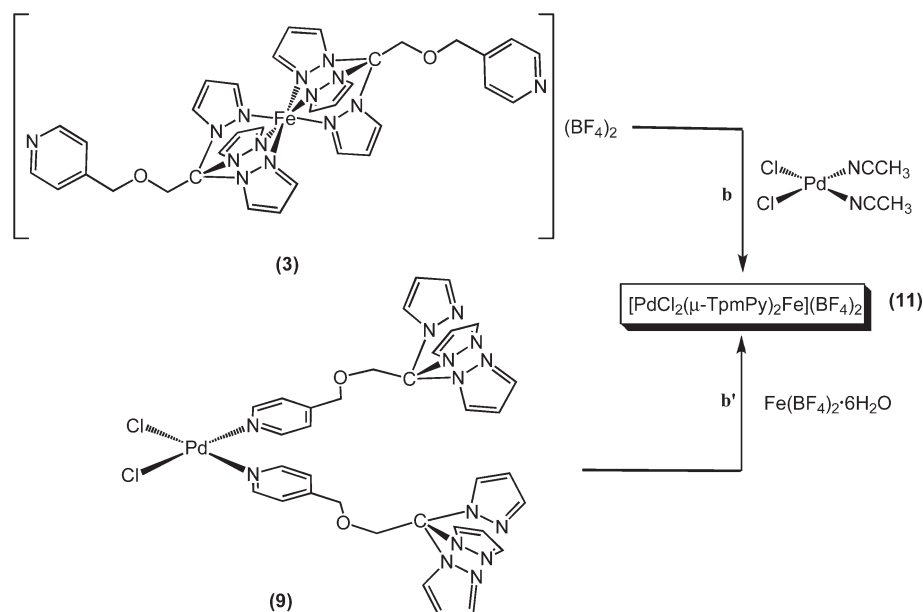


Figure 6. ORTEP plot of *trans*-[PdCl₂(TpmPy)₂] (**9**), where the ellipsoids are shown at 50% of probability. Hydrogen atoms are omitted for clarity. Symmetry code to generate equivalent atoms: 2 - *x*, 2 - *y*, -*z*.

Scheme 6. Synthetic Pathways for [PdCl₂(*μ*-TpmPy)₂Fe](BF₄)₂ (**11**)



Similarly, the IR spectra of (**9**) and (**10**) show a displacement to higher wavenumbers of the $\nu_{\text{C=N}}$ frequency compared to that of the corresponding free ligands (**1**) and (**2**) (from 1601 to 1619 and from 1603 to 1621 cm^{-1} , for the (**1**)/(**9**) and (**2**)/(**10**) pairs, respectively; see Supporting Information, Table S.1 and Figure S.8(a)). The mass spectra of (**9**) and (**10**) confirm the presence of two scorpionate ligands, and the far-IR spectra reveals the bands ascribed to Pd–Cl stretching (Supporting Information, Figure S.8(b)).¹⁶ For (**9**), the $\nu_{\text{Pd-Cl}}$ at 308 and 296 cm^{-1} , typical for a *cis*-isomer, appear shifted to higher wavenumbers in comparison to those of the starting compound *cis*-[PdCl₂(CH₃CN)₂] (255 and 242 cm^{-1}) suggesting a higher π -electron acceptor character for the coordinated pyridyl species than that of the acetonitrile ligand. Moreover, another band is detected at 361 cm^{-1} , being ascribed to the *trans* isomer, also present in the solid state. On the other hand,

the analogue (**10**) shows just a single strong band at 365 cm^{-1} , corresponding to the *trans* isomer, which is preferably formed because of the steric hindrance of TpmPy^{Ph}. Attempted chromatographic separation of the two isomers of (**9**) resulted in decomposition of the compound.

Furthermore, the *trans* isomer of (**9**) was identified in the X-ray diffraction analysis (from very poor quality crystals) that displays an almost perfect square-planar geometry around the Pd(II) ion, with the two scorpionates in *trans* position (Figure 6) and the N(1)–Pd(1)–Cl(1) angles of 89.6(3)° (Table 2).

3.0. Applications of TpmPy (1**) and TpmPy^{Ph} (**2**) to the Synthesis of Bimetallic Complexes, [PdCl₂(*μ*-TpmPy)₂Fe](BF₄)₂ (**11**), [Fe(*μ*-TpmPy)₂Cu(NO₃)₂](BF₄)₂ (**12**), and [PdCl₂(*μ*-TpmPy^{Ph})₂Fe₂(H₂O)₆](BF₄)₄ (**13**).** To investigate the multidentate ability of the new scorpionates of this work and the versatility of the new complexes prepared, we explored the “second” coordination step (**b** and **b'**, Scheme 1) of the latter compounds.

Reaction of equimolar amounts of [Fe(TpmPy)₂](BF₄)₂ (**3**) and *cis*-[PdCl₂(CH₃CN)₂] gives [PdCl₂(*μ*-TpmPy)₂Fe](BF₄)₂ (**11**) (Scheme 6(b)), which alternatively can be obtained upon an equimolar reaction of [PdCl₂(TpmPy)₂] (**9**) with Fe(BF₄)₂·6H₂O (Scheme 6(b')).

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Compound (**11**) has been characterized by IR and NMR spectroscopies, MS, and elemental analysis. Besides, its variable temperature ^1H NMR spectra indicate a fluxional behavior, in solution, suggesting a dynamic equilibrium between different structures.

Similarly, reaction of $[\text{Fe}(\text{TpmPy})_2](\text{BF}_4)_2$ (**3**) with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ leads to the immediate precipitation of a pale violet solid of $[\text{Fe}(\mu\text{-TpmPy})_2\text{Cu}(\text{NO}_3)_2](\text{BF}_4)_2$ (**12**), where each pyridyl moiety is coordinated to Cu^{II} . This compound is well soluble in MeOH and sparingly soluble in CH_3CN , while it decomposes in H_2O after a few hours. The ^1H NMR spectrum confirms the presence of paramagnetic Cu^{II} , where the pyridyl resonances appear more affected by the metal electronic state. In the mass spectrum (EI) of (**12**), the peak at m/z 713, assigned to the double charged $[\{\text{Fe}(\mu\text{-TpmPy})_2\text{Cu}_2(\text{TpmPy})(\text{NO}_3)_3\}(\text{BF}_4)]^{+2}$ fragment, suggests the possible formation of higher nuclearity species.

In contrast with the synthesis of the full sandwich compound (**11**), the reaction of $[\text{PdCl}_2(\text{TpmPy}^{\text{Ph}})]$ (**10**) with $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ gives the hydrated half sandwich complex $[\text{PdCl}_2(\mu\text{-TpmPy}^{\text{Ph}})_2\text{Fe}_2(\text{H}_2\text{O})_6](\text{BF}_4)_4$ (**13**) bearing each iron coordinated by the three pyrazolyl rings of just one bridging TpmPy^{Ph} . Steric hindrance of the bulky TpmPy^{Ph} prevents the formation of the N_6 -sandwich coordination at Fe^{II} (which occurs for compound (**11**)) leaving three coordination positions available for small ligands, such as water.^{8a} The ^1H NMR spectrum of (**13**) is consistent with that of its precursor (**10**), and shows a modest shift of the pyrazolyl resonances on account of coordination to iron(II).

The possibility of those compounds to arrange in polymeric structures could not be ruled out and eventually thwarted the crystallization attempts and prevented their complete characterization.

Conclusion

We prepared a new multifunctional class of scorpionates bearing a pyridyl group pending from the methine carbon, TpmPy and TpmPy^{Ph} , and studied their coordination chemistry with different metal centers. In the case of Fe^{II} , NMR and X-ray analyses of compound (**3**) reveal, by comparison with the Tpm analogous complex, that the pyridyl moiety promotes the stabilization of the LS state of Fe^{II} up to 400 K

in the solid state. In the cases of Ni^{II} , Zn^{II} , and Pd^{II} , the extra N-donor pyridyl group shows a good affinity to the metal centers: the new pyridyl-based complexes of Ni, Zn, and Pd (i.e., compounds (**4**), (**6**), (**7**), (**9**), and (**10**), respectively) provide relevant examples in this field.

Moreover, by increasing the bulkiness of the pyrazolyl groups by introducing a phenyl substituent (as in (**2**)), the coordination through the pyridyl-side is forced: the two nickel complexes (**5**) and (**7**) (i.e., bearing the ligating scorpionates in the N_3 -pyrazolyl and N-pyridyl coordination modes, respectively) provide a good comparison model of steric inducement.

In general, the ^1H and ^{13}C NMR, IR, and far-IR spectroscopies allowed to confirm the coordination modes of the new scorpionate ligands in their metal complexes. In particular, ^{13}C NMR and IR spectra are of diagnostic value to distinguish between pyrazolyl- and pyridyl-coordination (Supporting Information, Figures S.1, S.2, S.7, S.8 and Table S.1). Hence, a significant low field shift (ca. $\Delta\delta$ 2–3 ppm) for the 2-, 6- and 4-pyridyl carbons in the ^{13}C NMR spectra is indicative of pyridyl coordination which also affects the pyridyl IR $\nu_{\text{C}=\text{N}}$ values that shift to higher wavenumbers (i.e., falling within the range of 1617–1621 cm^{-1} , Supporting Information, Table S.1). The consistency of these behaviors illustrates an easy pattern for the characterization of these new complexes.

The multifunctional ligands are particularly adequate to the easy synthesis of heterobimetallic units, such as those of the current study. This represents a first application of this class of multidentate ligands that are expected to be able to coordinate to a wide variety of metal centers and to generate polymetallic species for further studies, for example, in supramolecular and solid-supported chemistries, besides the various fields of common applications of scorpionate compounds.

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Supporting Information Available: Further details are given in Figures S.1–S.8 and Table S.1. This material is available free of charge via the Internet at <http://pubs.acs.org>.