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Synthesis and Coordination Chemistry of a New N_4-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 N_4-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^{III} centers has been studied. Reaction of (**1**) with $Fe(BF_4)_2 \cdot 6H_2O$ yields $[Fe(TpmPy)_2](BF_4)_2$ (**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 $[MCl_2(TpmPy^*)_2]$ (M = Zn, Ni; TpmPy* = TpmPy, $TpmPy^{Ph}$) (**4**−**7**) where the ligand is able to coordinate through either the pyrazolyl rings (in case of $[Ni(TpmPy)_2]Cl_2$ (**5**)) or the pyridyl-side (for $[ZnCl_2(TpmPy)_2]$ (**4**), $[ZnCl_2(TpmPy^{Ph})_2]$ (**6**) and $[NiCl_2(TpmPy^{Ph})_2]$ (**7**)). The reaction of (**1**) with VCl_3 gives $[VOCl_2(TpmPy)]$ (**8**) that shows the N_3-pyrazolyl coordination-mode. Moreover, (**1**) and (**2**) react with *cis*-$[PdCl_2(CH_3CN)_2]$ to give the disubstituted complexes $[PdCl_2(TpmPy)_2]$ (**9**) and $[PdCl_2(TpmPy^{Ph})_2]$ (**10**), respectively, bearing the scorpionate coordinated via the pyridyl group. Compounds (**9**) and (**10**) react with $Fe(BF_4)_2$ to give the heterobimetallic Pd/Fe systems $[PdCl_2(\mu\text{-}TpmPy)_2\text{-}Fe](BF_4)_2$ (**11**) and $[PdCl_2(\mu\text{-}TpmPy^{Ph})_2Fe_2(H_2O)_6](BF_4)_4$ (**13**), respectively. Compound (**11**) can also be formed from reaction of (**3**) with *cis*-$[PdCl_2(CH_3CN)_2]$, while reaction of (**3**) with $Cu(NO_3)_2 \cdot 2.5H_2O$ generates $[Fe(\mu\text{-}TpmPy)_2\text{-}Cu(NO_3)_2](BF_4)_2$ (**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 $HCpz_3$ (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 $Fe(BF_4)_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $ZnCl_2$, 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, ^{13}C NMR spectra were measured on Bruker 300 and 400 UltraShield spectrometers. ^1H and ^{13}C 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 μL/min; needle spray voltage: ±5 kV, capillarity voltage: ±100 V; nebulizer gas (N_2): 35 psi; drying gas (N_2): 10 psi; drying gas temperature (N_2): 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 × 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 H_2 is formed. The resulting pale brown milky suspension is refluxed overnight. Then the mixture is allowed to cool down to room temperature and H_2O (20 mL) and Et_2O (20 mL) are added. The organic phase is separated and the aqueous phase is washed with Et_2O (5 mL). The organic phases are collected, washed with brine, and dried over Na_2SO_4, whereafter they are filtered and the solvent removed under vacuum to leave a pale yellow solid that is crystallized in Et_2O to give colorless crystals of (**1**) (518 mg, 78%). Compound (**1**) is well soluble in all common organic solvents, for example, Me_2CO, $CHCl_3$, CH_2Cl_2, MeOH, EtOH, and dimethyl sulfoxide (DMSO), and less soluble in H_2O ($S_{25\ °C} \approx 10\ mg \cdot mL^{-1}$). $C_{17}H_{17}N_7O$ (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, $CDCl_3$): 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, CH_2-C(pz)$_3$), 4.56 (s, 2H, CH_2-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, CH_2-C(pz)$_3$), 4.64 (s, 2H, CH_2-py). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): 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, CH_2-C(pz)$_3$), 71.50 (s, 2H, CH_2-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)ethanol, $HOCH_2C(pz^{Ph})_3$ (pz^{Ph} = 3-phenyl-pyrazolyl). Tris(3-phenyl-pyrazol-1-yl)methane (300 mg, 0.68 mmol, 1 equiv) is dissolved in dry THF (8 mL) and potassium *tert*-butoxide (197 mg, 1.76 mmol, 2.6 equiv) is added portionwise. After 5 min *para*-formaldehyde (52 mg, 1.74 mmol, 2.6 equiv) is added and the resulting mixture stirred at room temperature overnight. Water (10 mL) is added, and the mixture extracted with diethyl ether (3 × 20 mL). The organic extracts are combined, washed with brine, and dried over sodium sulfate. The mixture is filtered off, and the solvent is removed in vacuum leading to an off white powder (286 mg, 89%). The compound is well soluble in all common organic solvents, for example, Me_2CO, $CHCl_3$, CH_2Cl_2, MeOH, EtOH, and DMSO, less soluble in H_2O. $C_{29}H_{24}N_6O$ (472.55): calcd. C 73.71, N 17.78, H 5.12; found. C 73.89, N 18.01, H 5.33 IR (KBr): 3056, 2963, 2923 (m s), 2877 (m br), 1544 (m s, ν(C=N)), 1514 (s s, ν(C=C)), 1440 (m s), 1354 (m br), 1137 (s br), 862 (m s), 743 (s s), 648 (m s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.83 (d, 6H, J_{HH} = 8 Hz, o-H (Ph)), 7.41 (dd, vt, 6H, J_{HH} = 8 Hz, m-H(Ph)), 7.38 (dd, vt, 3H, J_{HH} = 8 Hz, *p*-H (Ph)), 7.19 (d, 3H, J_{HH} = 2.6 Hz, 5-H (pz)), 6.67 (dd, 3H, J_{HH} = 2.6 Hz, 4-H (pz)), 5.29 (s, 2H, CH_2). $^{13}C\{^1H\}$ and HMQC $^{13}C-^1H$ NMR (100.6 MHz, $CDCl_3$): δ 153.68 (s, 3-C (pz)), 132.47 (s, pz-*C* (Ph)), 131.78 (s, 5-C (pz)), 128.81 (s, m-C (Ph)), 128.67 (s, p-C (Ph)), 126.17 (s, o-C (Ph)), 104.16 (s, 4-C (pz)), 90.04 (s, CH_2-C(pz)$_3$), 68.15 (s, O-CH_2-C(pz)$_3$).

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 × 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 H_2O (20 mL) and Et_2O (20 mL) are added. The organic phase is separated and the aqueous phase is washed with Et_2O (5 mL). The organic phases are collected, washed with brine, and dried over Na_2SO_4. 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, Me_2CO, $CHCl_3$, CH_2Cl_2, MeOH, EtOH, and DMSO, and is insoluble in H_2O. $C_{35}H_{29}N_7O$ (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 ($CDCl_3$, 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, CH_2-C(pz)$_3$), 4.64 (s, 2H, CH_2-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, CH_2-C(pz)$_3$), 4.79 (s, 2H, CH_2-py). $^{13}C\{^1H\}$ and HMQC $^{13}C-^1H$ NMR (100.6 MHz, $CDCl_3$, 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, CH_2-*C*(pz)$_3$), 74.07 (s, O-*C*H_2-C(pz)$_3$), 72.54 (s, O-*C*H_2-py). ^{13}C 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, CH_2-*C*(pz)$_3$), 74.32 (s, O-*C*H_2-C(pz)$_3$), 72.65 (s, O-*C*H_2-py).

Synthesis of [Fe(TpmPy)$_2$](BF$_4$)$_2$ (3). To a methanolic solution (2 mL) of $Fe(BF_4)_2\cdot 6H_2O$ (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 CH_2Cl_2, $CHCl_3$, MeOH, and less soluble in H_2O ($S_{25\,°C} \approx 4.0$ mg·mL^{-1}). (**3**)·2CH_3CN, $C_{38}H_{40}N_{16}O_2FeB_2F_8$ (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(BF_4)), 867 (m s), 770 (s s), 607 (m s), 521 (m s) cm^{-1}. ^1H NMR (CD_3CN, 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, CH_2-C(pz)$_3$), 5.24 (br s, 2H, CH_2-py). ^1H NMR (CD_3CN, 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, CH_2-C(pz)$_3$), 5.23 (br s,12H, CH_2-py). $^{13}C\{^1H\}$ and HMQC $^{13}C-^1H$ NMR (100.6 MHz, CD_3CN, 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, CH_2-*C*(pz)$_3$), 74.07 (s, O-*C*H_2-C(pz)$_3$), 72.54 (s, O-*C*H_2-py). X-ray quality single crystals were grown by slow evaporation under nitrogen, at room temperature, of an acetonitrile solution of (**3**).

Synthesis of [ZnCl$_2$(TpmPy)$_2$] (4). To a methanolic solution of $ZnCl_2$ (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 $CHCl_3$, sparingly soluble in MeOH, EtOH, acetone, and acetonitrile, insoluble in Et_2O and less soluble in H_2O ($S_{25\,°C} \approx 2.5$ mg·mL^{-1}). (**4**)·2CH_3CN·0.5CH_2Cl_2, $C_{38.5}H_{41}Cl_3N_{16}O_2Zn$ (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, CH_2-C(pz)$_3$), 4.68 (s, 2H, CH_2-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, CH_2-C(pz)$_3$), 4.83 (s, 2H, CH_2-py). $^{13}C\{^1H\}$-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, CH_2-*C*(pz)$_3$), 74.61 (s, O-*C*H_2-C(pz)$_3$), 72.12 (s, O-*C*H_2-py).

Synthesis of [Ni(TpmPy)$_2$]Cl$_2$ (5). To a water solution of $NiCl_2\cdot 6H_2O$ (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 $CHCl_3$, sparingly soluble in MeOH, EtOH, acetone, and acetonitrile, insoluble in Et_2O and well soluble in H_2O ($S_{25\,°C} \approx 50$ mg·mL^{-1}). (**5**)·H_2O $C_{34}H_{36}Cl_2N_{14}O_3Ni$ (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 [ZnCl$_2$(TpmPy^{Ph})$_2$] (6). To a methanolic solution of $ZnCl_2$ (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 $CHCl_3$ and acetone, moderately soluble in MeOH, EtOH, and acetonitrile and less soluble in H_2O ($S_{25\,°C} \approx 0.8$ mg·mL^{-1}). (**6**)·CH_3OH, $C_{71}H_{62}Cl_2N_{14}O_3Zn$ (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 ($CDCl_3$, 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, CH_2-C(pz)$_3$), 4.73 (s, 2H, CH_2-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, CH_2-C(pz)$_3$), 4.97 (s, 2H, CH_2-py). $^{13}C\{^1H\}$-NMR

(100.6 MHz, $CDCl_3$, 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, CH_2-*C*$(pz)_3$), 74.37 (s, O-*C*H_2−C$(pz)_3$), 71.83 (s, O-*C*H_2-py). ^{13}C 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, CH_2-*C*$(pz)_3$), 75.14 (s, O-*C*H_2-C$(pz)_3$), 72.40 (s, O-*C*H_2-py).

Synthesis of [$NiCl_2$(TpmPy^{Ph})$_2$] (7). To a methanolic solution of $NiCl_2\cdot 6H_2O$ (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 $CHCl_3$ and acetone, moderately soluble in MeOH, EtOH, and acetonitrile, and less soluble in H_2O ($S_{25\ °C} \approx 1.0$ mg·mL^{-1}). (**7**), $C_{70}H_{58}Cl_2N_{14}O_2Ni$ (1256.92) 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 [$VOCl_2$(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 Et_2O a pale blue solid precipitates. The solid is collected by filtration, washed with Et_2O, and dried in vacuum (313 mg, 52%). The compound (**8**) is soluble in DMSO, moderately soluble in MeOH and EtOH, and less soluble in H_2O ($S_{25\ °C} \approx 5.0$ mg·mL^{-1}). (**8**) $VO_2Cl_2C_{17}H_{17}N_7$ (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 [$VOCl_2$(TpmPy) − pz]$^+$, 339 [$VOCl_2$(TpmPy) − 2pz]$^+$.

Synthesis of [$PdCl_2$(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*-[$PdCl_2(CH_3CN)_2$] (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 CH_2Cl_2, and dried, yielding a pale yellow powder of (**9**) (70 mg, 75%). The compound is soluble in CH_2Cl_2, $CHCl_3$, and DMSO, sparingly soluble in MeOH and acetonitrile, and less soluble in H_2O ($S_{25\ °C} \approx 0.8$ mg·mL^{-1}). (**9**) $C_{34}H_{34}Cl_2N_{14}O_2Pd$, (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)$_2$Cl]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$, 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, C*H*$_2$-C$(pz)_3$), 4.61 (s, 2H, C*H*$_2$-py). ^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 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, CH_2-*C*$(pz)_3$), 74.72 (s, O-*C*H_2−C$(pz)_3$), 71.78 (s, O-*C*H_2-py). ^{13}C{^{1}H}-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, CH_2-*C*$(pz)_3$), 73.16 (s, O-*C*H_2-C$(pz)_3$), 70.30 (s, O-*C*H_2-py). X-ray quality single crystals were grown by slow evaporation of a concentrated dichloromethane solution of (**9**).

Synthesis of [$PdCl_2$(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*-[$PdCl_2(CH_3CN)_2$] (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 CH_2Cl_2, $CHCl_3$, CH_3CN, and DMSO, moderately soluble in MeOH and EtOH, and insoluble in H_2O. (**10**), $C_{70}H_{58}N_{14}O_2PdCl_2$, (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 [$PdCl_2$(TpmPy^{Ph})$_2$]$^+$. ^{1}H NMR ($CDCl_3$, 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, C*H*$_2$-C$(pz)_3$), 4.64 (s, 2H, C*H*$_2$-py). ^{13}C{^{1}H} and HMQC ^{13}C−^{1}H NMR (100.6 MHz, $CDCl_3$, 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, CH_2-*C*$(pz)_3$), 74.56 (s, O-*C*H_2-C$(pz)_3$), 71.79 (s, O-*C*H_2-py).

Synthesis of [$PdCl_2$(μ-TpmPy)$_2$Fe](BF_4)$_2$ (11). Method (b, Scheme 6). To a yellow/brown solution of *cis*-[$PdCl_2(CH_3CN)_2$] (12 mg, 0.046 mmol) in dichloromethane (5 mL) is added dropwise an acetonitrile solution (5 mL) of [Fe(TpmPy)$_2$]-(BF_4)$_2$ (**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 [$PdCl_2$(TpmPy)$_2$] (**9**) (25 mg, 0.030 mmol) is added dropwise a solution of $Fe(BF_4)_2\cdot 6H_2O$ (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**)·4H_2O, $C_{34}H_{42}N_{14}B_2F_8$-FeO_6PdCl_2, (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(BF_4)), 866 (m s), 766 (m br) cm^{-1}. MS-EI *m*/*z*: 811/813 [PdCl(TpmPy)$_2$]$^+$, 990 [{$PdCl_2$(TpmPy)Fe}$_2$(BF_4)$_2$]$^{+2}$. ^{1}H NMR (CD_3CN, 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, C*H*$_2$-C$(pz)_3$), 5.31 (s, 2H, C*H*$_2$-py). ^{1}H NMR (CD_3CN, 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, br, 2H, 4-H(pz)), 5.78 (s, 2H, C*H*$_2$-C$(pz)_3$), 5.30 (s, 2H, C*H*$_2$-py).

Synthesis of [Fe(μ-TpmPy)$_2$Cu(NO_3)$_2$](BF_4)$_2$ (12). To an acetonitrile solution (5 mL) of [Fe(TpmPy)$_2$](BF_4)$_2$ (**3**) (89 mg, 0.1 mmol, 1 equiv), a solution of $Cu(NO_3)_2\cdot 2.5H_2O$ (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**)·$2H_2O$, $C_{34}H_{38}N_{16}B_2CuF_8FeO_{10}$ (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**), $[Fe(TpmPy)_2](BF_4)_2$ (**3**), $[ZnCl_2(TpmPy)_2]$ (**4**), $[Ni(TpmPy)_2]Cl_2$ (**5**), and $[PdCl_2(TpmPy)_2]$ (**9**)

	1	**3**	**4**	**5**	**9**
crystal shape	block	block	cube	prism	plate
	white	red	colorless	pink	colorless
empirical formula	$C_{17}H_{17}N_7O$	$C_{34}H_{34}FeN_{14}O_2$ $2(BF_4)$	$C_{34}H_{34}Cl_2N_{14}O_2Zn$	$C_{34}H_{34}N_{14}NiO_2$	$C_{34}H_{34}Cl_2N_{14}O_2Pd$
formula weight	335.38	900.22	807.02	729.46	848.05
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P21/c$	$P21/c$	$P21/c$	$P21/c$
a (Å)	8.3750(11)	14.8596(12)	20.5210(12)	13.126(11)	13.266(3)
b (Å)	9.6879(11)	13.0034(10)	15.8868(17)	22.194(18)	9.2463(19)
c (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
V (Å^3)	825.88(18)	3848.2(5)	3613.9(6)	5695(9)	1880.3(7)
Z	2	4	4	4	2
ρ_{calc} (g cm^{-3})	1.349	1.554	1.483	0.851	1.498
μ(Mo Kα) (mm^{-1})	0.091	0.485	0.882	0.374	0.688
F (000)	352	1840	1664	1520	864
reflections collected	18468	24714	26666	43838	12587
reflections unique	4997	6808	7610	12516	3233
R_{int}	0.031	0.1116	0.057	0.098	0.1462
goodness-of-fit on F^2 [a]	0.999	0.912	1.021	0.847	1.081
final R indices [$I > 2\sigma(I)$][b]	R_1 = 0.0425	R1 = 0.0618	R1 = 0.0374	R1 = 0.0675	R1 = 0.0827
	wR_2 = 0.1094	wR_2 = 0.1574	wR_2 = 0.0880	wR_2 = 0.1608	wR_2 = 0.1817
R indices (all data)	R_1 = 0.0572	R1 = 0.1324	R1 = 0.0641	R1 = 0.1464	R1 = 0.2602
	wR_2 = 0.1200	wR_2 = 0.2117	wR_2 = 0.1068	wR_2 = 0.1806	wR_2 = 0.2787

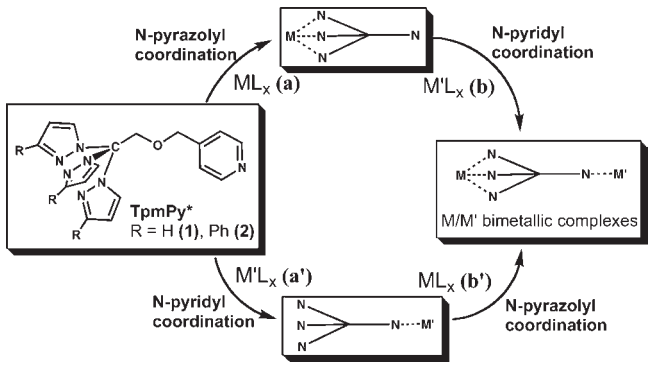
[a] Refinement Method: Full-matrix least-squares on F^2. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

ν(N═C), ν(C═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 [{$Fe(TpmPy)_2$-$Cu_2(TpmPy)$}$(BF_4)(NO_3)_3]^{+2}$, 363 $[Fe(TpmPy)_2]^{+2}$

Synthesis of $[PdCl_2(\mu\text{-}TpmPy^{Ph})_2Fe_2(H_2O)_6](BF_4)_4$ (13). To an acetonitrile suspension (7 mL) of $[PdCl_2(TpmPy^{Ph})_2]$ (**10**) (30 mg, 0.023 mmol, 1 equiv) is added dropwise a solution of $Fe(BF_4)_2 \cdot 6H_2O$ (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**)$\cdot 2((CH_3)_2CO)\cdot 0.5CH_3CN$, $C_{77}H_{83.5}N_{14.5}B_2F_8Fe_2O_{10}PdCl_2$, (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, ν(OH)), 3147, 3058, 2924 (w s, ν(C−H)), 1643 (w br, δ(OH)), 1620 (m s, ν(C═N)), 1531 (s s, ν(C═N), ν(C═C)), 1499, 1455 (s s), 1429, 1392 (m s), 1220 (s br), 1134, 1133−1043 (s br, $\nu(BF_4)$), 871 (s s), 750 (s s), 693 (s s) cm^{-1}. MS-EI m/z: 1268 $[PdCl(TpmPy^{Ph})_2]^+$, 1366 $[PdCl(TpmPy^{Ph})_2Fe](CH_3CN)^+$. ^{1}H NMR ($CDCl_3$, 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, CH_2-C(pz)$_3$), 4.67 (s, 2H, CH_2-py). $^{13}C\{^1H\}$ and HMQC $^{13}C-^1H$ NMR (100.6 MHz, $CDCl_3$, 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, CH_2-*C*(pz)$_3$), 73.92 (s, O-*C*H_2-C(pz)$_3$), 70.89 (s, O-*C*H_2-py).

Crystal Structure Determinations. Single crystals of TpmPy (**1**), $[Fe(TpmPy)_2](BF_4)_2$ (**3**), $[ZnCl_2(TpmPy)_2]$ (**4**), $[Ni(TpmPy)_2]Cl_2$ (**5**), and $[PdCl_2(TpmPy)_2]$ (**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−Kα (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.

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

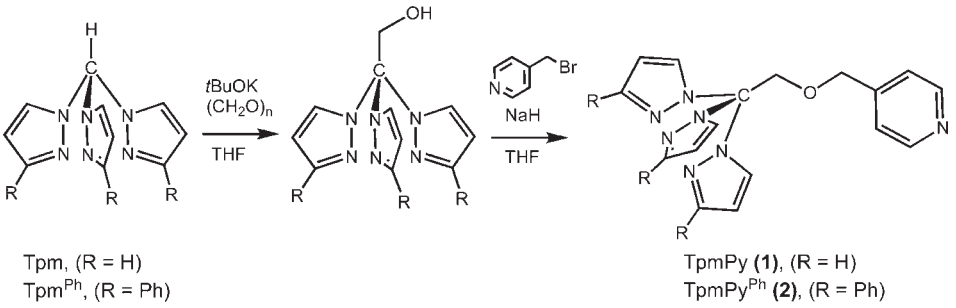


Results and Discussion

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

(7) (a) *APEX2 & SAINT*. Bruker, AXS Inc.: Madison, WI, 2004. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467. (c) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *A64*, 112–122. (d) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837. (e) Spek, A. L. *Acta Crystallogr., Sect. C* **1990**, *46*, C34.

Scheme 2. Synthesis of the N_4-Scorpionates TpmPy (**1**) and $TpmPy^{Ph}$ (**2**)



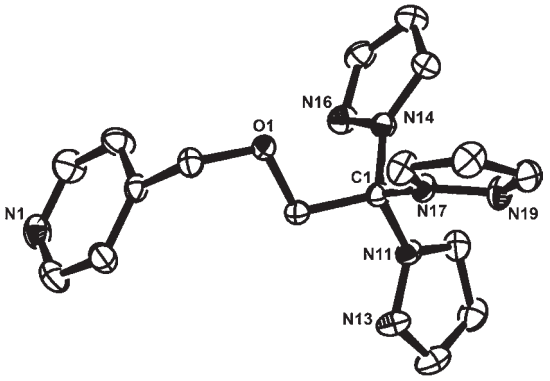


Figure 1. ORTEP plot of TpmPy (**1**), ellipsoids are shown at 50% of probability. Hydrogen atoms are omitted for clarity.

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 known[6] 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, ^{13}C 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 ($CDCl_3$) 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., Et_2O, CH_2Cl_2, CH_3Cl, MeOH, EtOH, and acetone) and moderately soluble in water ($S_{25\ °C} \approx 10\ mg \cdot mL^{-1}$) 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., Et_2O, CH_2Cl_2, CH_3Cl, MeOH, acetonitrile, and acetone). Compounds (**1**) and (**2**) represent a new type of N_4-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 $[Fe(TpmPy)_2](BF_4)_2$ (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 $Fe(BF_4)_2 \cdot 6H_2O$ in methanol proceeds readily at room temperature to give $[Fe(TpmPy)_2](BF_4)_2$ (**3**) bearing two ligated TpmPy (Scheme 3).

Compound (**3**) is moderately soluble in CH_2Cl_2, MeOH, DMSO, and DMF, and is well soluble in acetonitrile.

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Table 2. List of selected bond distances [Å] and angles [deg] for compound TpmPy (**1**), $[Fe(TpmPy)_2](BF_4)_2$ (**3**), $[ZnCl_2(TpmPy)_2]$ (**4**), $[Ni(TpmPy)_2]Cl_2$ (**5**), and $[PdCl_2(TpmPy)_2]$ (**9**)

	1		**3**		**4**		**5**		**9**
C1−N11	1.4543(13)	C1−N13	1.468(6)	Zn1−N1	2.058(2)	Ni1−N14	2.050	Pd1−N1	2.037(10)
C1−N14	1.4573(13)	C1−N16	1.466(7)	Zn1−N2	2.053(2)	Ni1−N17	2.037	Pd1−Cl1	2.315(3)
C1−N17	1.4541(13)	C1−N19	1.466(7)	Zn1−Cl1	2.2103(7)	Ni1−N11	2.063	N1−Pd1−Cl1	89.6(3)
C1−C2	1.5315(15)	C1−C101	1.518(7)	Zn1−Cl2	2.2401(7)	O1−C4−C5−C6[a]	137.03	O1−C6−C3−C2[a]	137.91
O1−C3−C4−C8[a]	118.31	Fe1−N11	1.965(4)	Cl1−Zn1−Cl2	119.77(3)	O2−C23−C24−C28[a]	143.53		
		Fe1−N14	1.954(4)	Cl2−Zn1−N1	108.33(6)				
		Fe1−N17	1.949(4)	N1−Zn1−N2	100.69(8)				
		N17−Fe1−N14	87.71(17)	N2−Zn1−Cl1	115.51(6)				
		N17−Fe1−N11	87.98(17)	Cl2−Zn1−N2	104.80(6)				
		N14−Fe1−N11	86.67(17)	Cl1−Zn1−N1	105.94(6)				
		N24−Fe2−N21	85.72(18)	O1−C6−C3−C2[a]	177.97				
		N24−Fe2−N27	87.93(17)	O2−C26−C23−C24[a]	135.26				
		N21−Fe2−N27	86.34(17)						
		O1−C202−C203−C204[a]	176.76						
		O1−C102−C103−C104[a]	166.62						

[a] Refers to the $O-C_{methylene}-C_{ipso}-C_{ortho}$ torsion angle.

Scheme 3. Synthesis of $[Fe(TpmPy)_2](BF_4)_2$ (**3**)

$$Fe(BF_4)_2{\cdot}6H_2O \xrightarrow[MeOH]{TpmPy,\ 2\ eq.} [Fe(TpmPy)_2](BF_4)_2 \quad \textbf{(3)}$$

It forms a pink powder and purple single crystals, as usual for low spin (LS) Fe^{II} scorpionates at room temperature.[9] Studies of the spin transition properties of related $Fe^{II}-Tpm$ complexes, such as $[Fe(Tpm)_2](BF_4)_2$, $[Fe(Tpm^{Me2})_3)_2](BF_4)_2$ (Tpm^{Me2} = tris(3,5-dimethylpyrazolyl)methane), and their borate analogues $[Fe(Tp)_3)_2](BF_4)_2$ (Tp = tris(pyrazolyl)borate), $[Fe(Tp^{Me2})_3)_2](BF_4)_2$, ($Tp^{Me2}$ = tris(3,5-dimethylpyrazolyl)borate), have been reported, indicating that complexes of this type show a temperature dependence spin crossover.[9d−f] Compound (**3**) is LS in the solid state and in solution at room temperature and keeps this spin state upon heating (to 400 or 325 K, respectively); its solution ^1H NMR spectrum (CD_3CN) at room temperature (298 K) appears as a typical one for a diamagnetic complex, and increasing the temperature until 325 K does not lead to any relevant modification, in contrast with what is observed for the tris(pyrazolyl)methane analogue $[Fe(Tpm)_2](BF_4)_2$ which shows an electronic spin transition from LS ($S = 0$) to HS ($S = 2$), in solution, above 223 K.[9d] For the latter compound, the LS state in the solid state at room temperature starts to change to the HS state upon heating above 295 K, whereas in solution at room temperature it shows the contemporary presence of LS and HS.

These different behaviors should be accounted for by the differences between the ligands (i.e., Tpm and TpmPy). The pyridyl moiety, as possible competing coordination site, could influence, in solution, the electronic state of the metal. In fact, variable temperature ^1H NMR experiments (CD_3CN) of (**3**) allow to distinguish all the resonances. The analysis of the complex pattern of resonances, through two-dimensional NMR experiments (i.e., ^1H-COSY, $^1H/^{13}C$-HSQC and HMBC), indicates the unequivalence of the three pyrazolyl rings and suggests the competition of the pyridyl ring, in solution, for the iron center.

The solid-state structure of (**3**) has been determined by single crystal X-ray diffraction analysis and consists of two crystallographically independent molecules, each one with the TpmPy coordinated through the three pyrazolyl rings, leaving uncoordinated the pyridyl moieties (Figure 2, and Tables 1 and 2). The conformations of the pyridine arms differ in the molecules of (**3**). While those of Fe2 practically lay in one pyrazolyl plane of the molecule, as confirmed by the value of the $O-C_{methylene}-C_{ipso}-C_{ortho}$ torsion angle of 176.76°, those of Fe1 are considerably deviated having such a torsion angle of 166.66° (see Table 2 and Supporting Information, Figure S.3), although not as low as that of the free ligand (see above). Such a peculiarity apparently affects the Fe−N−N−C torsion angles, which are in the 171.90−178.05° range for Fe1 and in a narrower one (174.21−177.10°) for Fe2. As reported for other systems,[9e] the minimum degree of tilting of the pyrazolyl rings from an ideal C_{3v} axis is typical for Fe^{II}-Tpm, LS, sandwich complexes: the Fe−N−N−C torsion angles, in an ideal case, would be 180° and the metal atom would reside in the planes defined by the pyrazolyl rings; for compound (**3**) the indicated angles confirm the pure LS electronic state of the Fe^{II} center.

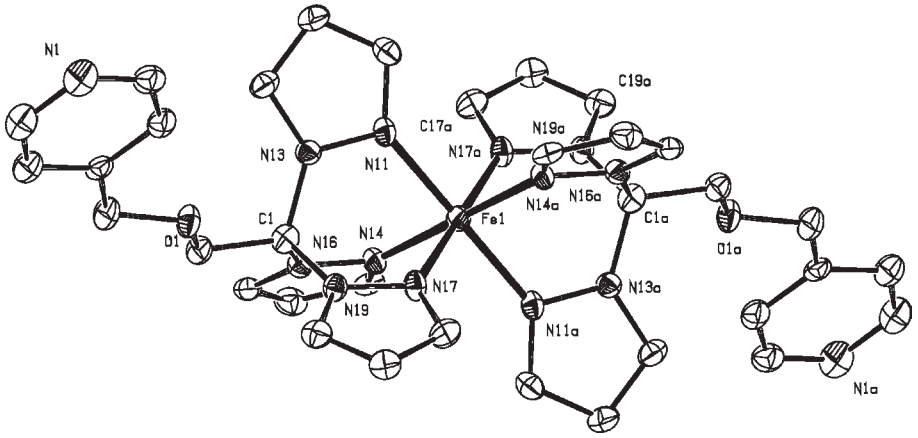
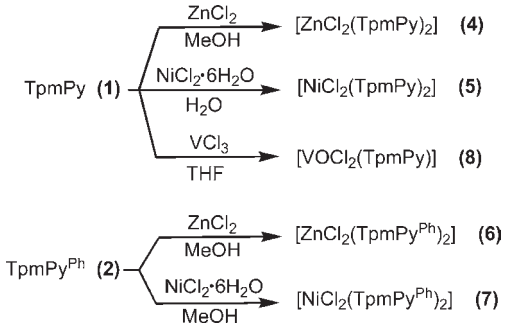


Figure 2. ORTEP plot of the Fe1 molecule in $[Fe(TpmPy)_2](BF_4)_2$ (**3**), where the ellipsoids are shown at 50% of probability. The hydrogen atoms and the tetrafluoroborate counterions are omitted for clarity. Symmetry operation to generate equivalent atoms: $2-x, -y, 1-z$.

Scheme 4. Syntheses of $[MCl_2(TpmPy^*)_2]$ (M = Ni^{II}, Zn^{II}; TpmPy* = TpmPy, $TpmPy^{Ph}$) (**4**−**7**) and $[VOCl_2(TpmPy)]$ (**8**). Pyridyl-Coordination: (**4**), (**6**), (**7**); Pyrazolyl-Coordination: (**5**), (**8**)



The observed intermolecular $\pi-\pi$ 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 $[MCl_2(TpmPy^*)_2]$ (M = Ni^{II}, Zn^{II}; TpmPy* = TpmPy, $TpmPy^{Ph}$) (4−7) and $[VOCl_2(TpmPy)]$ (8). Reactions of (**1**) and (**2**) with Zn^{II} or Ni^{II} metal salts can, in principle, give full- or half-sandwich complexes[10] through the tripodal 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 known[11] metal affinity for this group.

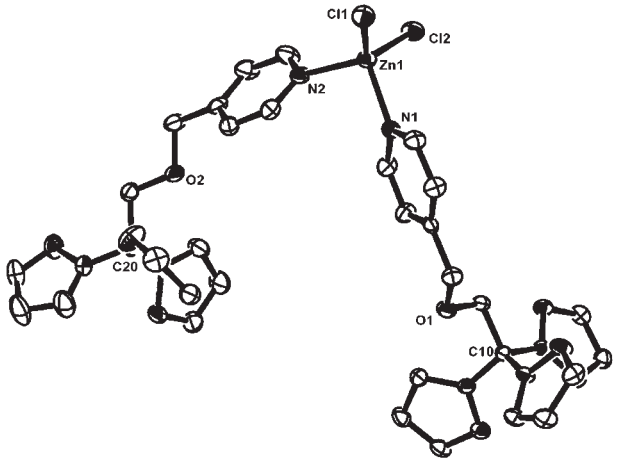


Figure 3. ORTEP plot of $[ZnCl_2(TpmPy)_2]$ (**4**), ellipsoids are shown at 50% of probability. Hydrogen atoms are omitted for clarity.

Reaction of 2 equiv of TpmPy (**1**) with $ZnCl_2$ in methanol affords $[ZnCl_2(TpmPy)_2]$ (**4**) (Scheme 4). The compound is well soluble in CH_2Cl_2 and sparingly soluble in MeOH and EtOH. The ESI-MS spectrum shows ionic fragments corresponding to $[ZnCl(TpmPy)]^+$ and $[Zn(TpmPy)_2]^{2+}$.

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 $\nu_{C=N}$ 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).

(10) (a) Zvargulis, E. S.; Buys, I. E.; Hambley, T. W. *Polyhedron* **1995**, *14*, 2267–2273. (b) Supuran, C. T.; Claramunt, R. M.; Lavandera, J. L.; Elguero, J. *Biol. Pharm. Bull.* **1996**, *19*, 1417–1422. (c) Titze, C.; Hermann, J.; Vahrenkamp, H. *Chem. Ber.* **1995**, *128*, 1095–1103. (d) Trofimenko, S. *J. Am. Chem. Soc.* **1970**, *92*, 5118–5126. (e) Reger, D. L.; Little, C. A.; Smith, M. D.; Long, G. J. *Inorg. Chem.* **2002**, *41*, 4453–4460. (f) Astley, T.; Gulbis, J. M.; Hitchman, M. A.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1993**, 509–515. (g) Hammes, B. S.; Carrano, C. J. *Inorg. Chem.* **1999**, *38*, 3562–3568.

(11) (a) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1977**, *16*, 1119–1127. Blackmore, I. J.; Gibson, V. C.; Hitchcock, P. B.; Rees, C. W.; Williams, D. J.; White, A. J. P. *J. Am. Chem. Soc.* **2005**, *127*, 6012–6020. (b) Westerhausen, M.; Kneifel, A. N.; Kalish, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 96–98. (c) Bacchi, A.; Bosetti, E.; Carcelli, M. *CrystEngComm* **2007**, *9*, 313–318. (d) Long, G. J.; Clarke, P. J. *Inorg. Chem.* **1978**, *17*, 1394–1401. Wu, C. D.; Zhang, L.; Lin, W. *Inorg. Chem.* **2006**, *45*, 7278–7285.

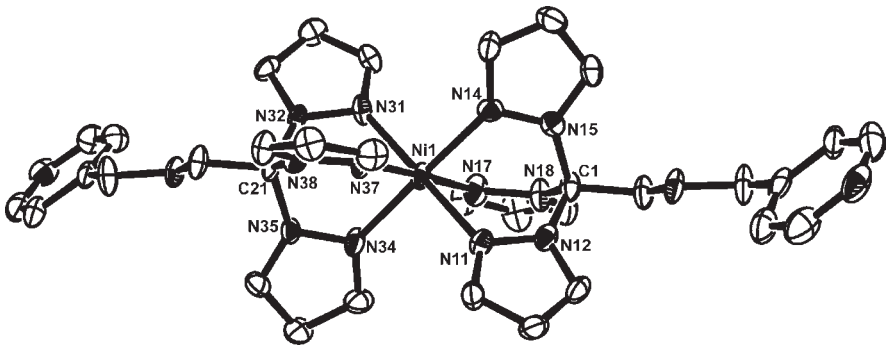


Figure 4. ORTEP plot of $[Ni(TpmPy)_2]Cl_2$ (**5**), where the ellipsoids are shown at 50% of probability and the hydrogen atoms and the two chlorides are omitted for clarity.

The tetrahedral coordination around the zinc is slightly distorted with the internal angles of 100.69(8)° for N1−Zn1−N2 and 119.77(3)° for Cl1−Zn1−Cl2, that is, the larger angle concerns the chloride ligands. The Zn−N bond lengths are identical (2.058(2) Å and 2.053(2) Å), like the Zn−Cl distances, thus showing a symmetrical elongation of the ideal tetrahedral geometry. The $O-C_{methylene}-C_{ipso}-C_{ortho}$ 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 N37−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 $[Ni(TpmPy)_2]Cl_2$ (**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 ^{1}H NMR spectrum that shows its typical paramagnetic nature (octahedral Ni^{II}, $S = 1$). Compound (**5**) is well soluble in water ($S_{25\,°C} \approx 50\,mg \cdot mL^{-1}$), 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 Ni−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., Ni−N−N−C torsion angles are within the range of 165.90°−178.04°). The disparity of the $O-C_{methylene}-C_{ipso}-C_{ortho}$ torsion angles is only of 6.5° (Table 2). The main intermolecular interactions detected in (**5**) involve $C-H\cdots\pi$ 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 H···centroid distances for these interactions are of 2.599 and 2.728 Å with C−H···centroid angles of 156.49 and 154.28°.

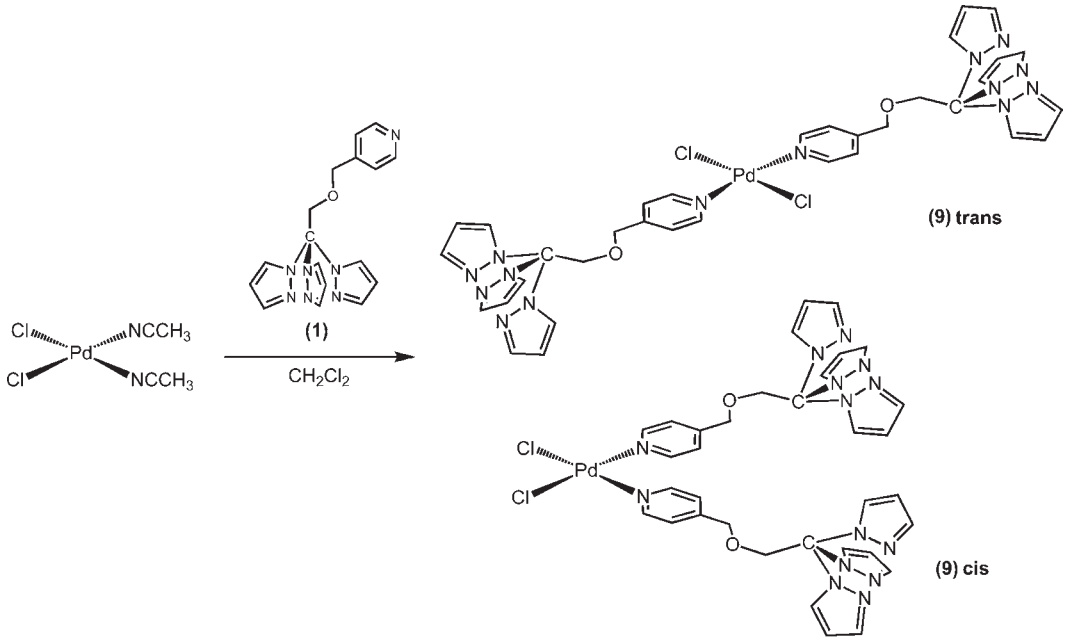
Similarly to the previous synthetic procedures, we studied the reactions of Zn^{II} and Ni^{II} chlorides with $TpmPy^{Ph}$ (**2**). The latter, being sterically hindered at the pyrazolyl-side, is expected to coordinate preferably through the pyridyl moiety. In fact, reaction of (**2**) with $ZnCl_2$ in methanol leads readily to the quantitative precipitation of $[ZnCl_2(TpmPy^{Ph})_2]$ (**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 ^{1}H 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 $[NiCl_2(TpmPy^{Ph})_2]$ (**7**) that also bears the scorpionate ligands coordinated through the pyridyl moieties. Hence, the pyrazolyl N_6-coodination 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 $[Ni(TpmPy^{Ph})Cl]^+$ and $[Zn(TpmPy^{Ph})Cl]^+$, 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 $\nu_{C=N}$ of the coordinated pyridyl moiety (see Supporting Information, Figure S.7 and Table S.1). The ^{1}H 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 $[VOCl_2(TpmPy)]$ (**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 $\nu_{C=N}$ appears at

(12) (a) Silva, T. F. S.; Luzyanin, K. V.; Guedes da Silva, M. F. C.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Adv. Synth. Catal.* **2010**, *352*, 171–187. (b) Silva, T. F. S.; Alegria, E. C. B. A.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Adv. Synth. Catal.* **2008**, *350*, 706–716. (c) Mishra, G. S.; Silva, T. F. S.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Pure Appl. Chem.* **2009**, *81*, 1217–1227.

Scheme 5. Synthesis of $[PdCl_2(TpmPy)_2]$ (**9**)



wavenumbers that are consistent with the coordinated-pyrazolyl rings (i.e., 1519−1517 cm^{-1}, see also Supporting Information, Table S.1), whereas for the pyridyl-coordinated compounds $\nu_{C=N}$ usually shifts to higher wavenumbers (i.e., in the range of 1617−1621 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 $[PdCl_2(TpmPy)_2]$ (9) and $[PdCl_2(TpmPy^{Ph})_2]$ (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[10d−g,14] 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 affinity[15] 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*-$[PdCl_2(CH_3CN)_2]$ with 2 equiv of (**1**) in dichloromethane gives the disubstituted product $[PdCl_2(TpmPy)_2]$ (**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 the coordination through the pyridyl moiety, whereas the pyrazolyl groups remain equivalent.

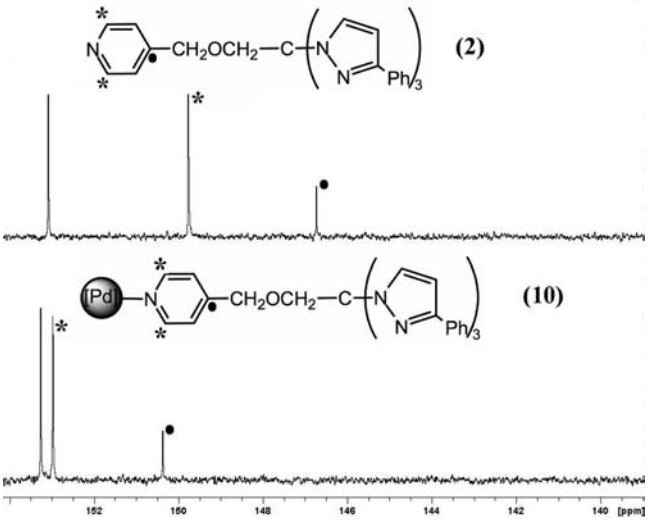


Figure 5. Shift of 2,6-C (*) and 4-C (•) pyridyl carbons resonances in ^{13}C NMR (400 MHz) spectra ($CDCl_3$) upon coordination of free (**2**) to Pd^{II} in $[PdCl_2(TpmPy^{Ph})_2]$ (**10**).

The phenyl substituted analogue, $[PdCl_2(TpmPy^{Ph})_2]$ (**10**), was prepared similarly, upon reaction of *cis*-$[PdCl_2(CH_3CN)_2]$ 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 carbons 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).

(13) (a) Tsuji, S.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1999**, *18*, 4758–4764. (b) Lee, C. K.; Ling, M. J.; Lin, I. J. B. *Dalton Trans.* **2003**, 4731–4737. (c) Qin, Z.; Jennings, M. C.; Puddephatt, R. J.; Muir, K. W. *Inorg. Chem.* **2002**, *41*, 5174–5186.

(14) (a) Sanchez-Mendez, A.; Silvestri, G. F.; de Jesus, E.; F. J. de la Mata, F. J.; Flores, J. C.; Gomez, R.; Gomez-Sal, P. *Eur. J. Inorg. Chem.* **2004**, 3287–3296. (b) Canty, A. J.; Minchin, N. J.; Engelhardt, L. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 645–650.

(15) (a) Feth, M. P.; Klein, A.; Bertagnolli, H. *Eur. J. Inorg. Chem.* **2003**, 839–852. (b) Hu, Y.-Z.; Chamchoumis, C.; Grebowicz, J. S.; Thummel, R. P. *Inorg. Chem.* **2002**, *41*, 2296–2300.

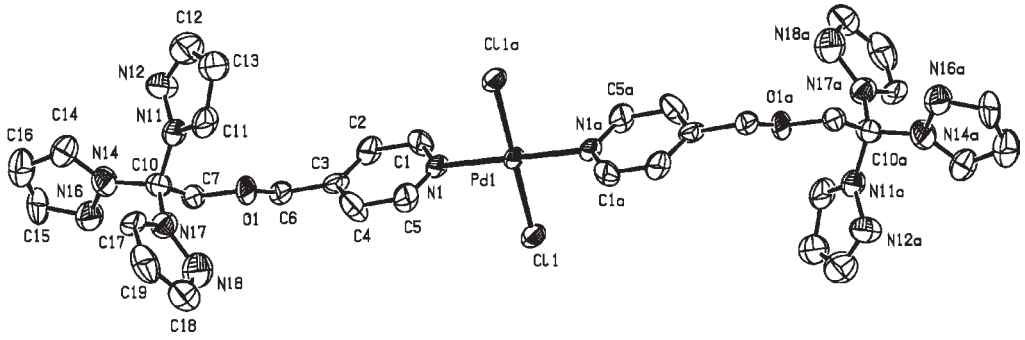
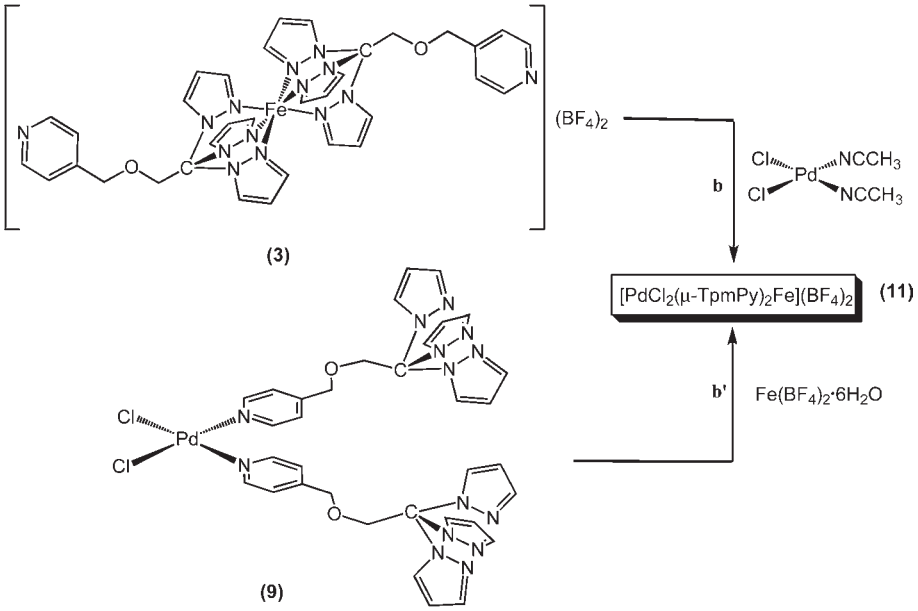


Figure 6. ORTEP plot of *trans*-$[PdCl_2(TpmPy)_2]$ (**9**), where the ellipsoids are shown at 50% of probability. Hydrogen atoms are omitted for clarity. Symmetry code to generate equivalent atoms: $2 - x, 2 - y, -z$.

Scheme 6. Synthetic Pathways for $[PdCl_2(\mu\text{-}TpmPy)_2Fe](BF_4)_2$ (**11**)



Similarly, the IR spectra of (**9**) and (**10**) show a displacement to higher wavenumbers of the $\nu_{C=N}$ 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 ν_{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*-$[PdCl_2(CH_3CN)_2]$ (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, $[PdCl_2(\mu\text{-}TpmPy)_2Fe](BF_4)_2$ (11), $[Fe(\mu\text{-}TpmPy)_2Cu(NO_3)_2](BF_4)_2$ (12), and $[PdCl_2(\mu\text{-}TpmPy^{Ph})_2Fe_2(H_2O)_6](BF_4)_4$ (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 $[Fe(TpmPy)_2](BF_4)_2$ (**3**) and *cis*-$[PdCl_2(CH_3CN)_2]$ gives $[PdCl_2(\mu\text{-}TpmPy)_2Fe](BF_4)_2$ (**11**) (Scheme 6(b)), which alternatively can be obtained upon an equimolar reaction of $[PdCl_2(TpmPy)_2]$ (**9**) with $Fe(BF_4)_2 \cdot 6H_2O$ (Scheme 6(b′)).

(16) (a) Drahos, B.; Rohlik, Z.; Kotek, J.; Cisarova, I.; Hermann, P. *Dalton Trans*. **2009**, 4942–4953. (b) Gillard, R. D.; Pilbrow, M. F. *J. Chem. Soc., Dalton Trans*. **1974**, 2320–2325. (c) Adams, D. M.; Chatt, J.; Gerratt, J.; Westland, A. D. *J. Chem. Soc*. **1964**, 734–739. (d) Goggin, P. L.; Goodfellow, R. J. *J. Chem. Soc. A* **1966**, 1462–1466. (e) Goodfellow, R. J.; Evans, J. G.; Goggin, P. L.; Duddell, D. A. *J. Chem. Soc. A* **1968**, 1604–1609. (f) Mastin, S. H. *Inorg. Chem*. **1974**, *13*, 1003–1005.

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

Similarly, reaction of $[Fe(TpmPy)_2](BF_4)_2$ (**3**) with $Cu(NO_3)_2 \cdot 2.5H_2O$ leads to the immediate precipitation of a pale violet solid of $[Fe(\mu\text{-}TpmPy)_2Cu(NO_3)_2](BF_4)_2$ (**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 ^{1}H 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 $[\{Fe(\mu\text{-}TpmPy)_2Cu_2(TpmPy)(NO_3)_3\}(BF_4)]^{+2}$ fragment, suggests the possible formation of higher nuclearity species.

In contrast with the synthesis of the full sandwich compound (**11**), the reaction of $[PdCl_2(TpmPy^{Ph})]$ (**10**) with $Fe(BF_4)_2 \cdot 6H_2O$ gives the hydrated half sandwich complex $[PdCl_2(\mu\text{-}TpmPy^{Ph})_2Fe_2(H_2O)_6](BF_4)_4$ (**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 ^{1}H 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 ^{1}H 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 $\nu_{C=N}$ 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.