Electronic supplementary information to:

Mono(NCN-Pincer Palladium)-Metalloporphyrin Catalysts: Evidence for Supramolecular Bimetallic Catalysis†

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[*Meso*-tetrakis(*p*-tolyl)porphyrinato]magnesium(II) (MgTTP)

A solution of **TTP** (102 mg, 152 μmol) in dry CH_2Cl_2 (60 mL) was treated with Et_3N (1 mL) and $MgBr_2{\cdot}OEt_2$ (500 mg, 1.94 mmol) and the mixture was stirred overnight at ambient temperature. The resulting pink solution was washed with 5% $NaHCO_3$ (3 × 100 mL) and loaded onto a column with alumina. Pure CH_2Cl_2 eluted traces of **TTP** and acetone/CH_2Cl_2 (1:9) was used to elute the product. The volatiles were evaporated and the resulting solid was stripped twice with toluene. The purple solid was then sonicated with hexanes (60 mL) for 30 min, and the mixture was cooled at –30 ºC overnight to give the **MgTTP** as purple crystals, which were isolated by centrifugation and dried *in vacuo*. Yield: 104 mg (98%). ^{1}H NMR ($CDCl_3$/1% pyridine-d_5): δ = 8.88 (s, 8H, *β-H*), 8.09 (d, $^3J_{HH}$ = 8.0 Hz, 8H, Ar*H*), 7.51 (d, $^3J_{HH}$ = 8.0 Hz, 8H, Ar*H*), 2.69 (s, 12H, ArC*H*$_3$) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$/1% pyridine-d_5): δ = 150.1, 141.0, 136.6, 134.7, 131.8, 127.0, 121.6, 21.6 ppm; UV/Vis [λ_{max} (log ε), CH_2Cl_2]: 426 (5.70), 565 (4.36), 605 (4.18) nm; LDI-TOF MS: *m*/*z* 1404.67 ([2M+H_2O]$^+$), calcd. for $C_{96}H_{74}Mg_2N_8O$: 1404.57; 708.88 ([M+O]$^+$), calcd. for $C_{48}H_{36}MgN_4O$: 708.27; 691.83 ([M]$^+$), calcd. for $C_{48}H_{36}MgN_4$: 692.28;

[*Meso*-tetrakis(*p*-tolyl)porphyrinato]nickel(II) (NiTTP)

TTP (120 mg, 179 μmol) and $Ni(acac)_2$ (1.18 g, 4.59 mmol) were suspended in dry toluene and the mixture was heated to reflux for 4 h. All volatiles were subsequently evaporated *in vacuo* and the remaining orange solid was dissolved in CH_2Cl_2 (70 mL) and washed with 5% K_2CO_3 (4 × 40 mL). The organic layer was isolated, dried ($MgSO_4$) and filtered over silicagel with CH_2Cl_2. The orange band was concentrated to 3 mL, MeOH (50 mL) was added and the orange mixture was concentrated to 20 mL. After 1 h, the orange crystals were isolated by centrifugation and dried *in vacuo*. Yield: 120 mg (92%). MALDI-TOF MS (NA): *m*/*z* 726.12 ([M]$^+$), calcd. for $C_{48}H_{36}N_4Ni$: 726.23; all other analysis data were identical to those reported in the literature.[1]

[*Meso*-tetrakis(*p*-tolyl)porphyrinato]zinc(II) (ZnTTP)

TTP (60 mg, 90 μmol) was dissolved in dry CH_2Cl_2 (60 mL), stirred at room temperature and shielded from ambient light with Al foil. Subsequently, a saturated solution of $Zn(OAc)_2{\cdot}2\ H_2O$ in degassed MeOH (4 mL, excess) was added and

stirring was continued. After 2 h, H_2O (40 mL), CH_2Cl_2 (20 mL), and K_2CO_3 (6 M, 2 mL) were added and the phases were separated. The organic layer was washed with brine (30 mL), dried ($MgSO_4$), filtered and loaded onto a silicagel column and eluted with CH_2Cl_2. The pink band was evaporated *in vacuo* and the purple residue was re-dissolved in CH_2Cl_2 (20 mL), hexanes (60 mL) were added and the solution was concentrated to 20 mL. The precipitated red crystals was collected by centrifugation and dried *in vacuo* to give the title compound. Yield: 63 mg (96%). LDI-TOF MS: *m*/*z* 731.61 ($[M]^+$), calcd. for $C_{48}H_{36}N_4Zn$: 732.23; all other analysis data were identical to those reported in literature.[2]

References

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2. G. Lipiner, I. Willner and Z. Aizenshtat, *Nouv. J. Chim.*, 1986, **10**, 91–92.