Supplementary Material (ESI) for Dalton Transactions

Synthesis and coordination chemistry of arene soluble 4-alkyl-2,6-bis[(diphenyl-phosphino) methyl] pyridine N,P,P′-trioxide ligands

X.M. Gan[a], R. T. Paine[*,a], E.N. Duesler[a] and H. Nöth[b]

[a]Department of Chemistry, University of New Mexico, Albuquerque, NM 87131, U.S.A.

e-mail: rtpaine@unm.edu

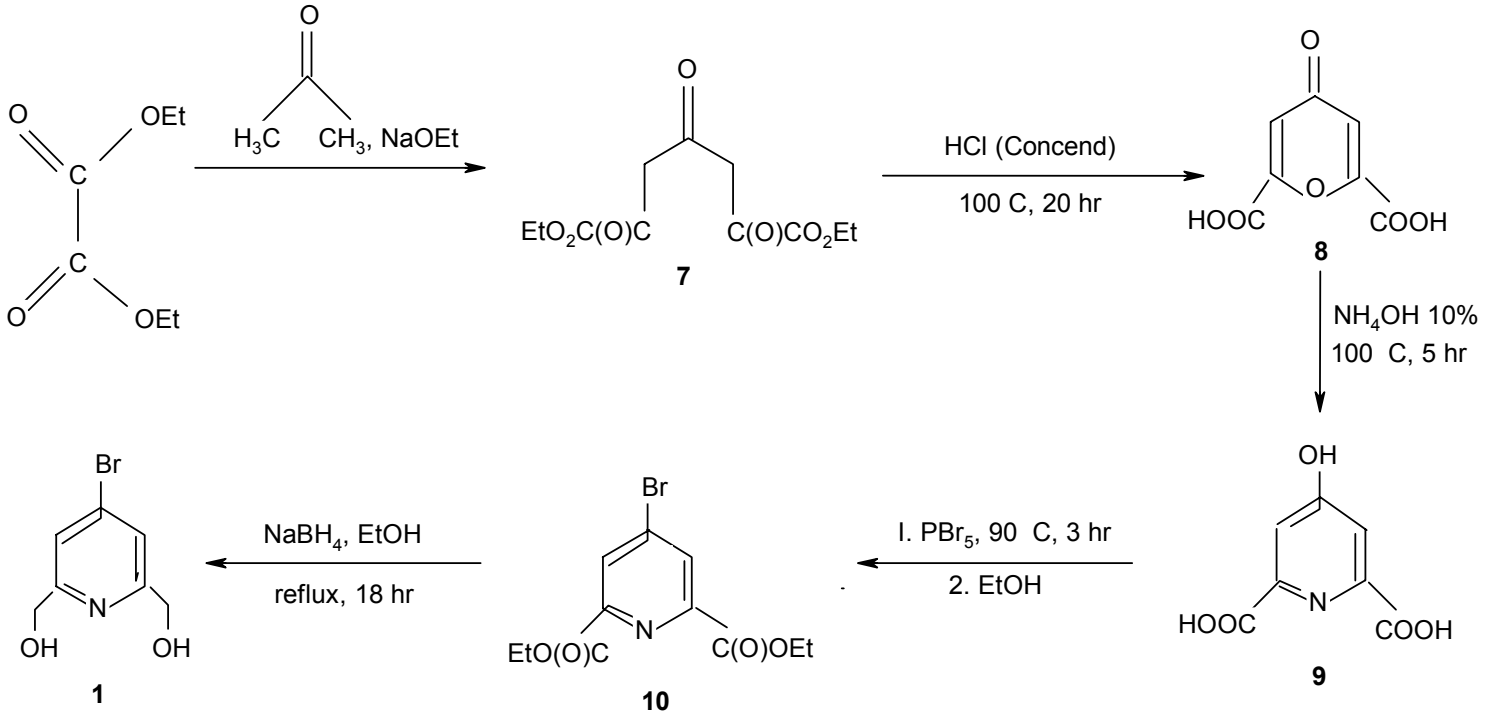
[b]Department of Chemie, University of Munich, Butenandtstr. 5-13, Haus D, D-81377, Munich, Germany

e-mail: Hnoeth@lrz.uni-muenchen.de

Contents

Supplementary Material (ESI) for Dalton Transactions

Table S-1 Synthesis Scheme for Starting Materials.



Supplementary Material (ESI) for Dalton Transactions

Section S-2. Preparative Description for Starting Materials

The starting material **1** is not commercially available and it must be prepared via a five step procedure from diethyloxalate. Each step has been described in the literature[1-4] although some details are sparse, and the step following **9** is described only in Chinese language literature.[2] Therefore, full details and ^{1}H and ^{13}C NMR data are provided here in order to simplify the effort of others wishing to obtain **1** or the subsequent compounds **2 - 6**.

Starting Material Syntheses

The first step is described by Riegel and Zwilgmeyer.[1] A three necked flask fitted with a reflux condensor, solids addition tube and nitrogen inlet tube was used for the preparation of **7**. The top of the reflux condensor was capped with a gas bubbler. The flask was swept with nitrogen gas and Na (16.2 g, 0.7 mol) was added in portions to dry ethanol (EtOH) (200 ml) in the flask. Toward the end of the reaction the mixture was heated until all of the Na disappeared. About half of the NaOEt solution was transferred under nitrogen to a second flask containing diethyloxalate (50 g, 0.34 mol). This mixture was kept warm with a heating mantle while the remaining portion of NaOEt solution was combined with a mixture of acetone (19.7 g, 0.34 mol) and diethyloxalate (50 g, 0.34 mol) while stirring the NaOEt solution. After this addition is complete, the second portion containing NaOEt/diethyloxalate is added. The fully combined mixture was stirred at 25 ºC (1 h). Excess EtOH was distilled from the mixture at 100 ºC and ambient pressure and the solid residue was dried under vacuum. The solid was then added to a mixture of concentrated HCl (100 ml) and ice (350 g) with stirring. The resulting yellow paste was filtered, the solid collected and dried *in vacuo* over $CaCl_2$ (12 h). Compound **7**, diethylacetonedioxalic ester, was obtained as a light yellow solid (85 g, 97%); ^{1}H NMR ($CDCl_3$)

δ 1.39 (t, = 7.1 Hz), 4.37 (q, = 7.1 Hz), 6.38; $^{13}C\{^{1}H\}$NMR ($CDCl_3$) δ 13.9, 62.6, 103.9, 161.4, 161.9, 196.3.

A suspension of **7** (85 g, 0.33 mol) in conc. HCl (100 ml) was stirred at 100 ˚C (20 h), cooled to 23 ˚C and ice (100 g) was added with stirring. The resulting solid was collected by filtration, washed with cold water (3 x 30 ml) and dried *in vacuo* over $CaCl_2$ (12 h). The solid product, chelidonic acid[1] **8** was isolated (50.3 g, 83%); ^{1}H NMR (DMSO=d_6) δ 5.71, 6.89; $^{13}C\{^{1}H\}$NMR (DMSO-d_6) δ 118.5, 155.2, 161.2, 180.

The conversion of chelidonic acid **8** to chelidamic acid **9** is described by Huang et al.[2] Compound **8** (50.2 g, 0.27 mol) was combined with aqueous NH_4OH solution (10%, 270 ml) with stirring and heated to 100 ˚C (5 h). During the reaction period, additional NH_4OH solution (28%, 15 ml) was added each hour. Following the reaction the volatiles were removed *in vacuo* at 30˚ - 40 ˚C. The residue was dissolved in water (200 ml) and conc. HCl (60 ml) was added at 0 ˚C. The resulting solid was collected by filtration, washed with cold water (3 x 30 ml) and dried *in vacuo* over $CaCl_2$. Chelidamic acid **9** was obtained as an off-white solid (48.1 g, 96%); ^{1}H NMR (DMSO-d_6) δ 7.50, 8.25; $^{13}C\{^{1}H\}$NMR (DMSO-d_6) δ 115.1, 149.1, 165.5, 167.1.

PBr_5 was prepared under nitrogen by slow addition of PBr_3 (230 g, 0.85 mol) in pet. ether (bp 35˚ - 60 ˚C) (100 ml) to a solution of Br_2 (135 g, 0.84 mol) in pet ether (300 ml). The resulting yellow solid was washed with pet. ether (4 x 100 ml) and dried *in vacuo* leaving PBr_5 (305 g, 0.71 mol, 84%). A sample of PBr_5 (270 g, 0.63 mol) was mixed with **9** (38.3 g, 0.21 mol) and the solid mixture heated (90 ˚C, 2.5 h), then cooled to 23 ˚C. The residue was extracted with $CHCl_3$ (210 ml) and the red-purple solution filtered under nitrogen. Absolute EtOH (700 ml) was added slowly to the filtrate cooled to ice temperature and the resulting orange solution was evaporated to dryness *in vacuo* at 30 ˚C. The residue was dissolved in CH_2Cl_2 (200 ml) and the solution extracted with aqueous $Na_2CO/NaHCO_3$ solution (150 ml). The phases were separated

and the aqueous phase (pH 7-8) was washed with CH_2Cl_2 (3 x 100 ml). The combined organic phases were dried with Na_2SO_4, filtered and the filtrate evaporated to dryness. The residue was dried *in vacuo* at 50 ˚C (4 h) leaving a light orange solid diethyl 4-bromo-2,6-pyridinedicarboxylate[3] **10** (52.2 g, 83%); ^{1}H NMR ($CDCl_3$) δ 1.41 (t, = 7.1 Hz), 4.45 (q, = 7.1 Hz), 8.38; $^{13}C\{^1H\}$NMR ($CDCl_3$) δ 14.1, 62.6, 131.0, 134.8, 149.5, 163.5.

A solution of **10** (45 g, 0.15 mol) in absolute EtOH (1400 ml) was combined with $NaBH_4$ (25.3 g, 0.67 mol) in portions at 23 ˚C. The mixture was stirred at 23 ˚C (2.5 h) and then refluxed (18 h). The solvent was removed *in vacuo* at 45 ˚C and the solid residue added to saturated aqueous $NaHCO_3$ solution (240 ml). This mixture was briefly boiled (120 ˚C oil bath, 1 min), water (340 ml) added with stirring and the resulting mixture allowed to stand at 0 ˚C (12 h). The mixture was filtered and the solid collected and dried *in vacuo* over $CaCl_2$. The solid was extracted with acetone (5 x 800 ml) and the combined acetone layers vacuum evaporated leaving **1** as a white solid[4] (27.5 g, 85%); ^{1}H NMR (DMSO-d_6) δ 4.51 (d, = 5.7 Hz), 5.52 (t, = 5.9 Hz), 7.50; $^{13}C\{^1H\}$NMR (DMSO-d_6) δ 63.7, 121.1, 133.2, 163.2.

References

1. E.R. Riegel and F. Zwilgmeyer *Org. Synth. Coll.* 1944, **2**, 126.
2. L. Huang, K. Wu, J. Meng, M. Zhang, J. Chen, J. Yang and L. Li *Huaxue Shiji* 1982, **4**, 193.
3. H. Takalo and J. Kankare *Acta Chem. Scand.* 1987, B41, 219.
4. H. Takalo, P. Pasanen and J. Kankare *ibid.* 1988, **B42**, 373.

Supplementary Material (ESI) for Dalton Transactions

Section S-2. Variations in the Synthesis of 6-Oct

As stated in the full paper, the synthesis of **6-Oct** compares closely with that described for **6-Et**. The following represent variations.

1. The synthesis of **3-Oct** was carried out on a smaller scale using **6** (3.8 g 15.4 mmol) and OctMgBr (9.5 ml, 2M in Et_2O, 19 mmol). The amounts of reagents used in the work-up were similarily scaled back. Following the evaporation of THF, water (60 ml) was added to the residue and the resulting mixture was treated with pentane (4 x 80 ml) instead of Et_2O. The combined pentane fraction was washed with saturated aqueous $NaHCO_3$ (50 ml) and dried over Na_2SO_4. Subsequent evaporation of the pentane gave **3-Oct** (2.9 g, 67%) as an orange oil; ^{1}H NMR ($CDCl_3$) δ 0.81 (t, = 6.7 Hz), 1.20 (m), 1.57 (m), 2.54 (t, = 7.7 Hz), 3.39 4.47, 7.09; ^{13}C{^{1}H}NMR ($CDCl_3$) δ 13.7, 22.3, 28.8, 28.9, 29.0, 30.0, 31.5, 35.2, 58.3, 75.2, 119.6, 152.9, 157.3.
2. The conversion of **3-Oct** to **4-Oct** was conducted in a fashion like the Et derivative except the reaction was done on half the scale and the work up steps employed pentane as the extraction solvent instead of Et_2O. **4-Oct** was obtained as an orange oil (2.81 g, 87%); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, = 6.8 Hz), 1.25 (m), 1.61 (m), 2.58 (t, = 7.7 Hz) 4.48, 7.16; ^{13}C{^{1}H}NMR ($CDCl_3$) δ 14.0, 22.5, 29.0, 29.2, 30.0, 31.7, 33.6, 35.0, 122.9, 154.2, 156.4.
3. The Grignard reaction of **4-Oct** to give **5-Oct** proceeds as described for **5-Et**. The product **5-Oct** is obtained as a white solid (2.95 g, 72%) mp 46 - 48 °C; ν_{PO} 1195 cm^{-1} (KBr); ^{31}P NMR ($CDCl_3$) δ 30.9; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, = 6.8 Hz, 3H), 1.15 - 1.33 (m; 12 H), 2.32 (t, = 7.7 Hz, 2H), 3.77 (d, J(PH) = 14.6 Hz), 6.89 (1H), 7.37 - 7.47 (12

H), 7.66 - 7.74 (8H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 14.0, 22.6, 29.1, 29.2, 30.0, 31.8, 34.9, 40.5 (d, J(CP) 64.9 Hz), 123.1, 128.3, (d, J(CP) = 12.0 Hz), 131.2 (d, J(CP) = 9.6 Hz), 131.6, 132.5 (d, J(CP) = 100.3 Hz), 151.8 (d, J(CP) = 7.2 Hz), 152.6.

The N-oxidation of **5-Oct** was performed as described for **5-Et**. Following removal of the CH_2Cl_2 and $CHCl_3$ by vacuum evaporation, the residue was redissolved in a minimum of acetone and cooled to -20 ˚C whereupon crystals of **6-Oct** formed and were recovered (1.07 g, 95%); mp 127 - 128 ˚C, (Found: C, 73.35, H, 7.15; N, 2.10%. $C_{39}H_{43}NO_3P_2$ requires C, 73.68; H, 6.82; N, 2.20. M^+ 635.2697, $C_{39}H_{43}NO_3P_2$ requires M 635.2718; υ_{NO} 1236 cm^{-1}, υ_{PO} 1197 cm^{-1} (KBr); ^{31}P NMR ($CDCl_3$) δ 31.6; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, = 6.7 Hz, 3H), 1.08 - 1.36 (12 H), 2.33 (t, = 7.6 Hz, 2H), 4.09 (d, = 13.9 Hz, 4H), 7.29 - 7.44 (13 H), 7.70 - 7.78 (8 H); $^{13}C\{^{1}H\}$NMR ($CDCl_3$) δ 14.0, 22.5, 28.8, 29.0, 29.1, 30.0, 31.5 (d, J(CP) = 67.1 Hz), 31.7, 34.2, 125.6, 128.4 (d, J(CP) = 1.6 Hz), 132.1 (d, J(CP) = 101.6 Hz), 140.6, 142.8 (d, J(CP) = 3.8 Hz). Solubility: soluble in $CHCl_3$, C_6H_6 (3 x 10^{-1} M), toluene (1 x 10^{-1} M), o-xylene (5 x 10^{-2} M), decane (3 x 10^{-4} M).

Section S-3. Synthesis of [Nd(6-Oct)$_2$(NO$_3$)] (NO$_3$)$_2$ • H$_2$O

$Nd(NO_3)_3 \bullet 6\ H_2O$ (44 mg, 0.1 mmol) and **6-Oct** (127 mg, 0.2 mmol) were dissolved in MeOH (10 mL) and stirred at 23 ºC (10 min). Ethyl acetate was added to the mixture and the solution filtered. Slow evaporation (10 d) gave purple-blue crystals [Nd(**6-Oct**)$_2$(NO$_3$)] (NO$_3$)$_2$ • H$_2$O (Found: C, 56.93; H, 5.97; N, 4.13 %. $C_{78}H_{88}N_5NdO_{16}P_4$ requires C, 57.84; H, 5.48; N, 4.32%). IR (KBr, cm^{-1}): ν_{NO} 1155, ν_{PO} 1128.

A crystal (0.36 x 0.25 x 0.14 mm) was selected from the sample described above and it was placed in a glass capillary and flame sealed for single crystal x-ray analysis.