Supporting information

Synthesis

Owing to high stability of fully oxidized ligands and lanthanide salts all manipulations can be performed without strictly anhydrous conditions. Nevertheless, all solvents used (methanol, dichloromethane) were dried and distilled prior to use.[1] Preparation of $Ph_2P(O)$-C_5H_3N-$P(O)Ph_2.H_2O_2$ was reported previously,[2] and $Ph_2P(O)$-CH_2CH_2-$P(O)Ph_2$ was obtained by oxidation of Ph_2P-CH_2CH_2-PPh_2 with hydrogen peroxide in tetrahydrofuran.

Preparation of $Pr[Ph_2P(O)$-C_5H_3N-$P(O)Ph_2]_2(NO_3)_3$ (1)

$Ph_2P(O)$-C_5H_3N-$P(O)Ph_2.H_2O_2$ (250 mg, 0.487 mmol) was dissolved in dichloromethane (10ml) and the suspension of $Pr(NO_3)_3.6H_2O$ (85 mg, 0.195 mmol) in dichloromethane (10 ml) was added. After the mixture was stirred overnight, the dichloromethane was allowed to evaporate slowly over approximately 10 days. Pale green solid was then isolated and washed with methanol. The product consists of crystals suitable for single crystal X-ray diffraction (characterized as $Pr[Ph_2P(O)$-C_5H_3N-$P(O)Ph_2]_2(NO_3)_3.2CH_2Cl_2$) and the powder (microcrystalline) fraction (characterized by elemental analysis as $Pr[Ph_2P(O)$-C_5H_3N-$P(O)Ph_2]_2(NO_3)_3$). Yield 100 mg (39.8 %, calc. for $Pr[Ph_2P(O)$-C_5H_3N-$P(O)Ph_2]_2(NO_3)_3$). M.p. > 280 °C. IR: 3062w, 1590w, 1567w, 1539vw, 1438vs, 1306vs, 1205m, 1170s, 1150vs, 1123s, 1091s, 1029m, 997w, 988w, 817w, 751s, 745s, 727m, 709m, 693s, 555vs, 537s, 528vs, 509w. Microanalyses (microcrystalline phase): C 54.2, H 3.6, N 5.4 calc., C 54.5, H 3.5, N 5.2 found.

Preparation of $Pr[Ph_2P(O)$-CH_2CH_2-$P(O)Ph_2]_{1.5}(NO_3)_3$ (2)

A mixture of $Ph_2P(O)$-CH_2CH_2-$P(O)Ph_2$ (250 mg, 0.581 mmol) and $Pr(NO_3)_3.6H_2O$ (126 mg, 0.290 mmol) in methanol (30 ml) was sealed in a 250-ml stainless-steel reactor with a Teflon liner, heated to 140 °C for 2 days, and then slowly cooled to room temperature. After 2 days pale green crystals were collected and washed with methanol. Yield 219 mg (77.7 %). M.p. > 280 °C. IR: 3056w, 1590vw, 1437vs, 1406m, 1398m, 1309vs, 1274s, 1201m, 1186m, 1170s, 1146vs, 1124s, 1090vs, 1036m, 1027m, 998w, 935w, 872vw, 817w, 810vw, 785vw, 769m, 750s, 728s, 703m, 694m, 653vw, 563vw, 552vw, 533vs, 511s. Microanalyses: C 48.2, H 3.7, N 4.3 calc., C 48.3, H 3.7, N 4.5 found.

Thermogravimetric analysis

The samples were heated in static air at 5 °/min to 1000 °C on a MOM Derivatograph C instrument.

Infrared spectroscopy

IR spectra (4000 – 400 cm^{-1}) were collected on an EQUINOX 55/S/NIR FTIR spectrometer. Samples were prepared as nujol mulls.

Elemental analysis

Microanalyses were performed using a Fisons EA 1108 instrument.

X-ray powder diffraction

A Stoe-Cie transmission diffractometer STADI P was used to acquire the diffraction data.

Crystallography

Diffraction data were collected on a KUMA KM-4 κ-axis diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) equipped with CCD detector and low-

temperature device (120 K). Both structures were solved by direct methods and refined by full-matrix least-squares techniques using anisotropic thermal parameters for the non-hydrogen atoms. The software packages used were: Xcalibur CCD system for the data collection/reduction,[3] and ShelXTL for the structure solution, refinement, and drawing preparation (thermal ellipsoids are drawn at the 50% probability level).[4] Details of the data collection, cell determination, and structure refinement are listed in Table 1.

References

(1) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, Pergamon Press, **1988**.

(2) Sevcik, R.; Necas, M.; Novosad, J. *Polyhedron* **2003**, *22*, 1585-1593.

(3) Oxford Diffraction Ltd., Xcalibur CCD System, CrysAlis Software System, Version 1.170. Oxford, England, **2003**.

(4) Bruker, SHELXTL. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA, **1997**.

Table 1. Crystal data and refinement parameters.

	1	**2**
Empirical formula	$C_{60}H_{50}Cl_4N_5O_{13}P_4Pr$	$C_{39}H_{36}N_3O_{12}P_3Pr$
Formula weight	1455.64	972.53
Temperature [K]	120 (2)	120 (2)
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$P2_1/n$
a [Å]	15.20 (1)	13.022 (2)
b [Å]	16.44 (1)	19.989 (4)
c [Å]	24.33 (2)	16.747 (4)
α [°]	90	90
β [°]	90	108.38 (2)
γ [°]	90	90
Volume [$Å^3$]	6077 (9)	4137 (1)
Z	4	4
Calc. density	1.591	1.562
μ [mm^{-1}]	1.151	1.359
Crystal size [mm]	0.30 x 0.20 x 0.20	0.50 x 0.40 x 0.40
υ range [°]	3.11 to 24.99	3.28 to 25.00
No. of refections	37297	19663
Independent data	10645	6531
Final R indices	0.0428, 0.0923	0.0330, 0.0871
$\Delta\rho_{max}/\Delta\rho_{min}$ [e. $Å^{-3}$]	1.445 and –0.848	1.174 and –0.833