SUPPORTING INFORMATION FOR:

A coordination polymer of (Ph₃P)AuCl prepared by post-synthetic modification and its application in alkene/alkane separation

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Contents

Figure S1 – XRPD patterns for PCM-10 and Au-PCM-10	2
Figure S2 – ³¹ P-MAS-NMR for PCM-10 and Au-PCM-10	3
Figure S3 – TGA data	4
Figure S4–XPS data for as-synthesized Au-PCM-10	5
Figure S5 – CO ₂ isotherms for PCM-10 and Au-PCM-10	6
Figure S6 – In situ FT-IR spectra	7
Experimental Section	9
Single Crystal X-ray data for PCM-10	11



Figure S1.XRPD (bottom to top): PCM-10 simulated (black); PCM-10 as-synthesized observed (orange); PCM-10 CHCl₃ exchanged and evacuated(green); Au-PCM-10 simulated using PCM-10 single crystal data with 'dummy' AuCl added using idealized coordinates from ref. 10 (red); Au-PCM-10 observed post CHCl₃ wash (blue); arrows indicate positions of most notable additional peaks in the AuCl post-modified sample. Data were recorded at 298 K on dry crystalline solids in borosilicate capillaries using a Rigaku R-Axis Spider diffractometer operating with Cu K α radiation (1.5418 Å).



Figure S2. ³¹P-MAS-NMR: PCM-10 as-synthesized (black); Au-PCM-10 obtained by reaction with (Me₂S)AuCl (red); control sample stirred in DCM under identical conditions as for Au-PCM-10 synthesis but in the absence of (Me₂S)AuCl (blue). Literature values: $R_3P(=O) = 31-33 \text{ ppm}^{7,a}$; R_3P -AuCl = 30 ppm.^b

a. Humphrey, S. M.; Oungoulian, S. E.; Yoon, J. W.; Hwang, Y. K.; Wise, E. R.; Chang, J.-S., *Chem. Commun.* **2008**, 2891.

b. Bowmaker, G. A.; Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Pakawatchai, C.; White, A. H., J. Chem. Soc. Dalton Trans. 1987, 1089.



Figure S3.TGA profiles: PCM-10 as-synthesized (blue, broken); PCM-10 post CHCl₃ exchange and evacuated (green, broken); Au-PCM-10 as-synthesized (red); Au-PCM-10 post CHCl₃ wash and evacuated (purple). All data recorded on a TA Instruments Q50 under He carrier flow.



Figure S4. Additional XPS data for freshly prepared Au-PCM-10: (A) C 1s; (B) P 2p; (C) Cl 2p.



Figure S5. CO₂ isotherms at 196 K; all samples were pre-evacuated for 12 h at 373 K.



Figure S6A. In situ FT-IR. Top: C–H bending region during *n*-hexane adsorption and desorption in Au-PCM-10. Bottom: 1-hexene adsorption and subsequent desorption at 303 K showing retention of the alkene under vacuum.



Figure S6B. In situ FT-IR. Top: C–H stretching region during *n*-hexane adsorption and desorption in Au-PCM-10. Bottom: 1-hexene adsorption and subsequent desorption in the same spectral region.

Experimental Section

General: The ligand $P(C_6H_4-CO_2H)_3$ was synthesized according to the literature method;^c 1,2dibromobenzene was purchased from alfa aesar and used as received; *n*-butyllithium (1.6M in hexanes) was obtained from Acros; metal salts were purchased from Aldrich; all solvents were purified using a purification system (Innovative Technologies) and stored on molecular sieves prior to use. FT-IR data were recorded using a Thermo Nicolet Avatar 330. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q50 with ultra-high purity N₂ carrier gas in the range of 25-800 °C. Solid-state NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at a proton frequency of 399.9 MHz, equipped with a 4mm double resonance magic-angle spinning probe (spinning rate 15 kHz). Single crystal X-ray diffraction of PCM-10 was performed using a crystal mounted on a thin glass fiber using perfluoropolyether oil, which was frozen *in situ* by a nitrogen gas Cryostream flow. Data was collected on an Enraf Nonius Kappa CCD diffractometer using monochromated MoKa radiation (0.71073 Å). Cell refinement and data reduction was performed using the HKL SCALEPACK and DENZO^d and COLLECT^e utilities. Absorption corrections were made based on y- and w-scans using the SORTAV^f program. Structures were solved using direct methods and refined on F2 using the program SIR-92^g and then refined using SHELXTL-97^h software. All non-hydrogen atoms were refined anisotropically, except for uncoordinated and disordered solvent molecules, which were refined with isotropic displacement parameters. X-ray Powder Diffraction (XRPD) experiments of the crystalline powders were collected in borosilicate capillaries in a Rigaku R-Axis Spider difractometer using CuKα radiation (1.54 Å) with data collected in the range 5.0-40.0° 2θ using multiple scans that were averaged. The simulated XRPD patters were generated using the single crystal reflection data via the SimPowPatt facility in PLATON.¹

Synthesis of PCM 10: The phosphine ligand $P(C_6H_4-CO_2H)_3$ (39 mg, 0.10mmol) was dissolved in DMF/H₂O/EtOH (1:1:1, 2.5 cm³). To this was added a second solution of Ca(OH)₂ (13 mg, 0.175 mmol) dissolved in 2.5 cm³ of the same solvent. NaOH(0.10 cm³, 1.0 M) was added to the resulting slurry and the solution was sonicated(10-15 sec). The reaction was heated in a scintillation vial using a graphite thermal bath at 70 °C for 4-5 days. The resulting colorless crystals of PCM-10 were isolated by consecutive washes with EtOH and decanting away any impurities. The solid was then suspended in CHCl₃ (10 cm³) overnight, after which the solvent was decanted off and fresh CHCl₃ was added. This process was repeated 3 times before the crystals were finally evacuated to dryness on a schlenk line. Yield: 15%. ³¹P-NMR (solid, 161.9 MHz) $\delta = -6.7$ (R₃*P*); 29.9 (R₃*P*(=O)); v_{max} (KBr/cm-1): 3630s, 3369 br s, 2930 m, 1944 s, 1664 s, 1590 m, 1535 m, 1495 s, 1402 m, 1304 s, 1275 m, 1183 s, 1144 m, 1104 s, 1016 s, 856m, 777 s, 725 m, 703 s, 671 s, 634 m, 580 m, 544 m, 485 m.

Post-synthetic modification procedure for Au-PCM-10: 100 mg of PCM-10 from above was suspended in 5 cm³ of degassed CH₂Cl₂, to which a solution of (PPh₃)AuCl (50 mg, 0.17 mmol) dissolved in the same solvent (5.0 cm³) was slowly added drop-wise under a N₂ atmosphere in the dark. The reaction was stirred in the dark for 4 h at room temp. The solvent and other volatiles were then removed *in vaccuo* and the composite was then treated with CH₂Cl₂ (5 cm³), allowed to settle for a few minutes (10-15 min) and the solvent was removed. The solid was filtered and washed with more degassed CH₂Cl₂. The resulting off-white crystalline solid was dried under reduced pressure, and transferred to a vial and stored under N₂. ³¹P-NMR (solid, 161.9 MHz) $\delta = 31.3$ (R₃PAuCl).

- c. R. Amengual, E. Genin, V. Michelet, M. Savignac and J.-P. Gen^{et}, *Adv. Synth. Catal.*, 2002, 344, 393.
- d. Z. Otwinowski, W. Minor, *HKL SCLAEPACK, Methods in Enzymology Volume 276, Macromolecular Crystallography, Part A*, ed. C. W. Carter, Jr. and R. M. Sweet, New York Academic Press, 1997, 307.
- e. Nonius COLLECT, Nonius BV, Delft, The Neterlands.
- f. R. H. Blessing, SORTAV, Acta Crystallogr., Sect. A: Found. Crystallogr., 1994, 51, 33.
- g. A. Altamore, M. C. Burla, G. Camalli, G. Cascarano, C. Giacovazzo, A. Gualiardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
- h. G. M. Sheldrick, SHELXTL Version 6.10, Bruker AXS Inc., Madison, Wisconsin, 1997.
- i. A. L. Spek, PLATON Version 07, J. Appl. Crystallogr., 2003, 36, 7.

Crystal data and structure refinement for PCM-10

Identification code	sh0804	
Empirical formula	C48 H37 Ca3 N2 O15 P2	
Formula weight	1063.98	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pcca	
Unit cell dimensions	$a = 23.476(5) \text{ Å}$ $\alpha = 90^{\circ}.$	
	$b = 9.5054(19) \text{ Å} \qquad \beta = 90^{\circ}.$	
	$c = 27.629(6) \text{ Å} \qquad \gamma = 90^{\circ}.$	
Volume	6165(2) Å ³	
Ζ	4	
Density (calculated)	1.146 Mg/m ³	
Absorption coefficient	0.376 mm ⁻¹	
F(000)	2196	
Crystal size	0.12 x 0.07 x 0.02 mm ³	
Theta range for data collection	3.54 to 23.99°.	
Index ranges	-26<=h<=26, -8<=k<=8, -31<=l<=3	
Reflections collected	19685	
Independent reflections	4327 [R(int) = 0.1269]	
Completeness to theta = 23.99°	89.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.996 and 0.541	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4327 / 6 / 321	
Goodness-of-fit on F ²	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0810, $wR2 = 0.2172$	
R indices (all data)	R1 = 0.1178, $wR2 = 0.2360$	
Largest diff. peak and hole	1.431 and -0.361 e.Å ⁻³	