Supporting information

belonging to

Palladium Carbene Complexes for Selective Alkene Di- and Oligomerization

Vsevolod Khlebnikov, Angelo Meduri, Helge Mueller-Bunz, Tiziano Montini, Paolo Fornasiero, Ennio Zangrando, Barbara Milani and Martin Albrecht

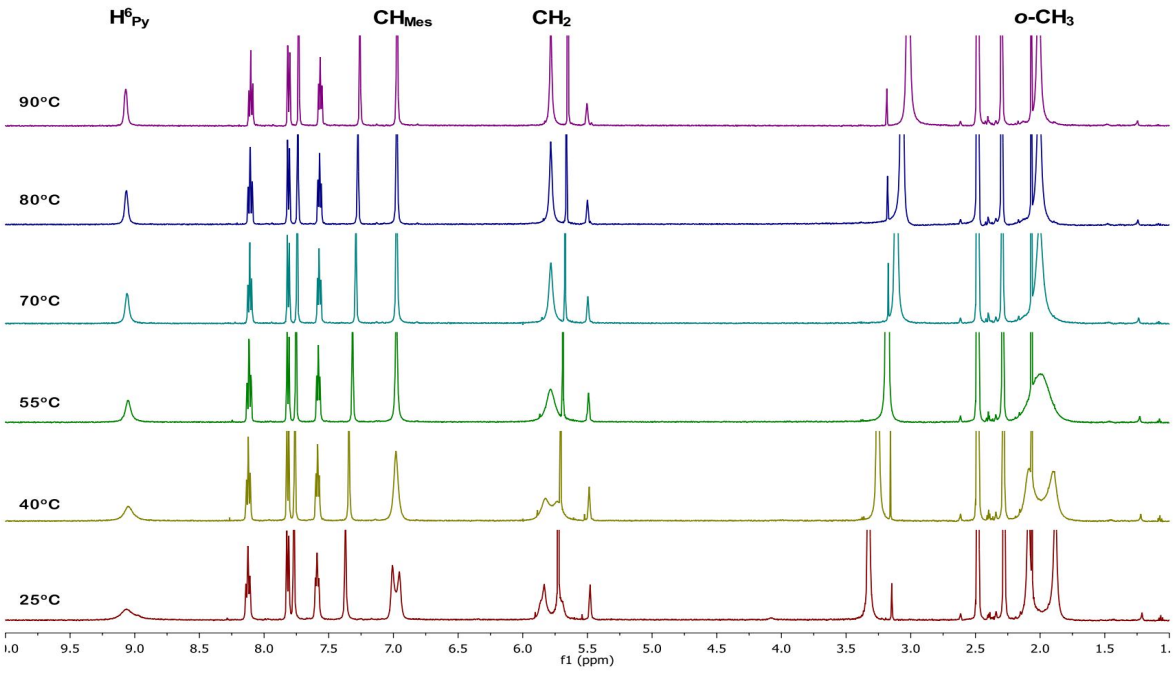

Fig S1 Variable temperature ^{1}H NMR spectra of **3a** in DMSO-d_6 solution.

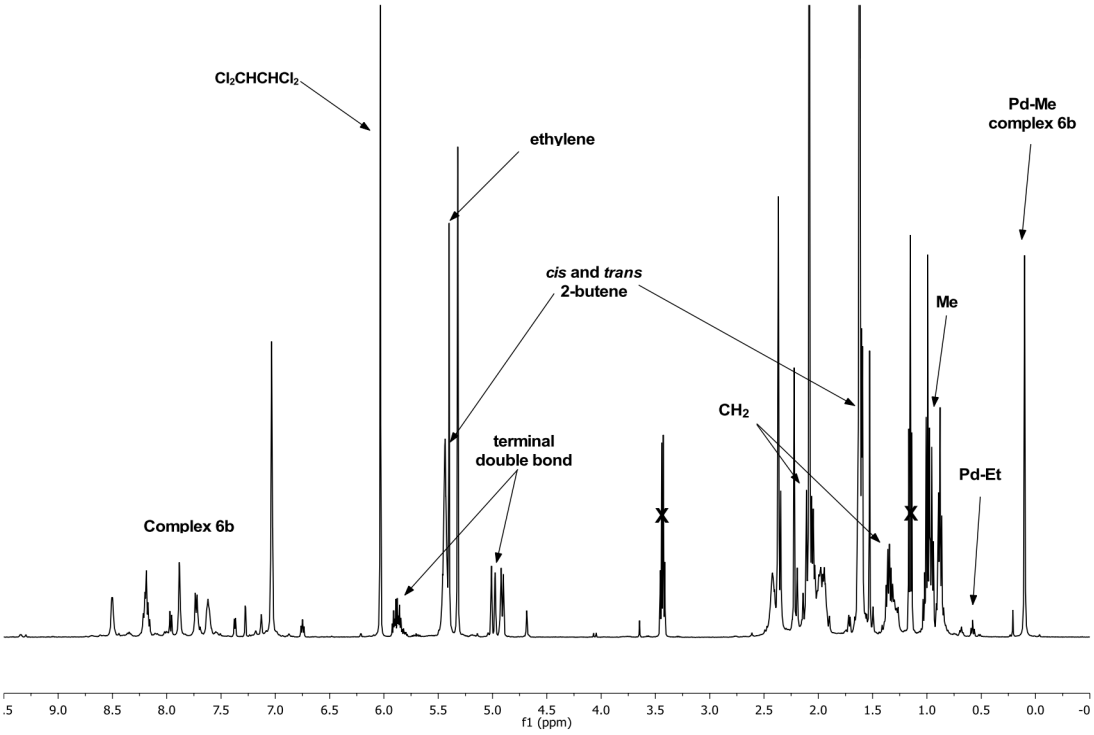

Fig S2 ^{1}H NMR spectrum of the reaction mixture of complex **6b** with ethylene after 15 h (7.5 μmol in 0.75 mL CD_2Cl_2) at room temperature, $C_2H_2Cl_4$ as internal reference.

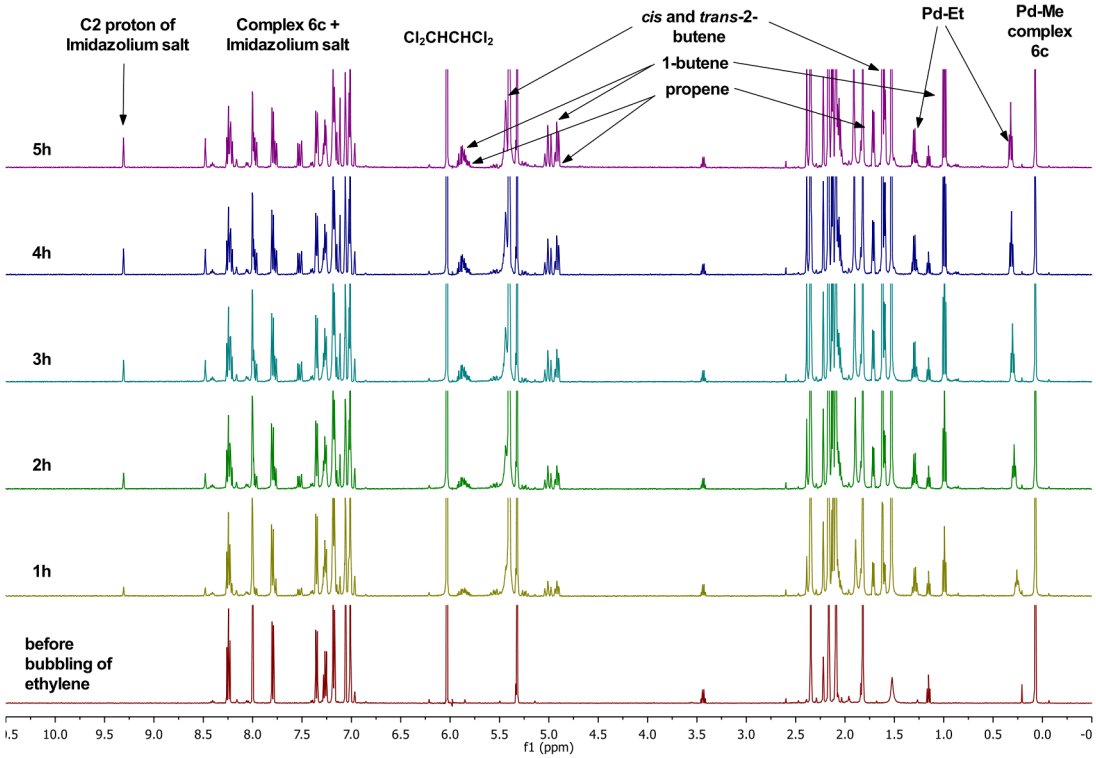

Fig S3 ^{1}H NMR spectra depicting the increase of 1- and 2-butenes from the reaction of complex **6c** with ethylene (0.75 μmol **6c** in 0.75 mL CD_2Cl_2 at room temperature, $C_2H_2Cl_4$ as internal reference). Note that the chemical shifts of the imidazolium signals are slightly different from those of **1c** because of different counterions (Br^- in **1c**, presumably PF_6^- in the product from reductive elimination) and because of the different solvents. Two-dimensional NMR spectroscopy is in full agreement with the presence of a non-coordinated pyridine unit and an imidazolium fragment.

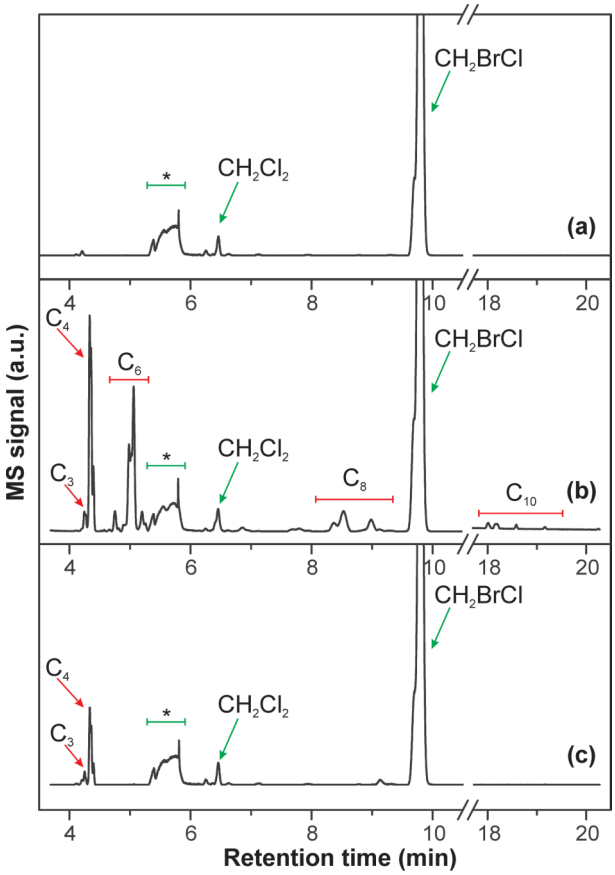

Fig. S4: GC/MS analysis of CH_2Br_2 (a) and of the reaction products of high pressure ethylene polymerization in CH_2Br_2 using complexes **6b** (b) and **6c** (c). CH_2Cl_2 and CH_2BrCl are impurities of the CH_2Br_2 solvent. * indicates impurities of MeOH used to dilute the samples for GC/MS analysis (1:5 volumetric ratio).

Table S1. Crystallographic data for complexes 3b, 4a, 5b, 6a, 6b, 6c, and 7

	3b	**4a**	**5b**
CCDC no	844760	844762	844765
crystal size /mm^{-1}	0.50 × 0.38 × 0.20	0.60 × 0.40 × 0.10	0.34 × 0.25 × 0.19
Empirical formula	$C_{21}H_{29}N_3O_2S_2Br_2Pd$	$C_{24}H_{28}N_6F_{12}P_2Pd$	$C_{19}H_{22}BrCl_2N_3Pd$
Fw	685.81	796.86	549.61
T /K	100(2)	100(2)	100(2)
crystal system	Triclinic	Triclinic	Triclinic
space group	P–1 (No. 2)	P–1 (No. 2)	P–1 (No. 2)
unit cell			
a /Å	8.2527(9)	9.4553(10)	7.7554(2)
b /Å	9.1301(10)	11.9013(12)	9.2465(3)
c /Å	17.0048(18)	14.6164(15)	15.3961(5)
α /°	92.466(2)	81.319(2)	75.065(3)
β /°	93.487(2)	81.008(2)	79.798(2)
γ /°	97.665(2)	72.485(2)	88.517(2)
Volume /Å^3	1265.8(2)	1539.8(3)	1049.67(6)
Z	2	2	2
D_{calcd} /g cm^{-3}	1.799	1.719	1.739
μ /mm^{-1}	4.078	0.806	3.050
no. total reflcns	25863	31735	21750
unique reflecns	6299	7636	6128
R_{int}	0.0221	0.0221	0.0364
Absorption correction	semi-empirical	semi-empirical	analytical
transmission range	0.327-0.496	0.767-0.924	0.533–0.716
no. parameters, restraints	287, 0	412, 0	240, 0
GOF	1.057	1.059	1.038
R_1,[a] wR_2,[b] $I > 2\sigma(I)$	0.0254, 0.0647	0.0250, 0.0642	0.0285, 0.0543
R_1,[a] wR_2,[b] all data	0.0283, 0.0660	0.0263, 0.0650	0.0378, 0.0586
largest diff. hole, peak /e Å^{-3}	–0.426 1.157	–0.325 0.664	–0.678 0.646

[a] $R_1 = \Sigma||F_O|-|F_C||/\Sigma|F_O|$; [b] $wR_2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma(w(F_O^4)]^{1/2}$

Table S1. Crystallographic data for complexes 3b, 4a, 5b, 6a, 6b, 6c, and 7 (continued)

	6a	**6b**
CCDC no.	844761	844764
crystal size /mm^{-1}	0.30 × 0.30 × 0.30	0.24 × 0.16 × 0.13
Empirical formula	$C_{22}H_{27}N_4F_6PCl_2Pd$	$C_{20}H_{23}F_6N_4PPd$
Fw	669.75	570.79
T /K	100(2)	100(2)
crystal system	Triclinic	Monoclinic
space group	P–1 (No. 2)	$P2_1/c$ (No. 14)
unit cell		
a /Å	10.6872(15)	12.6559(3)
b /Å	11.4989(15)	14.9426(3)
c /Å	11.8401(16)	12.3617(3)
α /°	112.673(2)	90
β /°	98.655(2)	105.147(3)
γ /°	98.842(2)	90
Volume /Å^3	1291.1(3)	2256.53(9)
Z	2	4
D_{calcd} /g cm^{-3}	1.723	1.680
μ /mm^{-1}	1.051	0.958
no. total reflections	26441	57565
unique reflections	6422	8057
R_{int}	0.0264	0.0376
absorption correction	semi-empirical	analytical
transmission range	0.669-0.743	0.871–0.917
no. parameters, restraints	330, 0	294, 0
GOF	1.061	1.081
R_1,[a] wR_2,[b] $I > 2\sigma(I)$	0.0261, 0.0652	0.0244, 0.0568
R_1,[a] wR_2,[b] all data	0.0291, 0.0668	0.0306, 0.0608
largest diff. hole, peak /e Å^{-3}	–0.342 0.760	–0.509 0.634

[a] $R_1 = \Sigma||F_O|-|F_C||/\Sigma|F_O|$; [b] $wR_2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma(w(F_O^4)]^{1/2}$

Table S1. Crystallographic data for complexes 3b, 4a, 5b, 6a, 6b, 6c, and 7 (continued)

	6c	**7**
CCDC no.	844763	849648
crystal size /mm^{-1}	0.20 × 0.14 × 0.10	0.35 × 0.35 × 0.30
Empirical formula	$C_{28}H_{31}F_6N_4PPd$	$C_{29}H_{27}ClN_2Pd$
Fw	674.94	545.38
T /K	100(2)	293(2)
crystal system	Monoclinic	Monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)
unit cell		
a /Å	13.2126(3)	10.491(3)
b /Å	11.4202(3)	20.997(4)
c /Å	19.3576(5)	11.263(3)
α /°	90	90
β /°	99.506(2)	90.03(3)
γ /°	90	90
Volume /Å^3	2880.77(12)	2481.0(11)
Z	4	4
D_{calcd} /g cm^{-3}	1.556	1.460
μ /mm^{-1}	0.764	0.875
no. total reflections	50061	27035
unique reflections	7495	8362
R_{int}	0.0288	0.0501
absorption correction	analytical	empirical
transmission range	0.908–0.947	0.341–0.860
no. parameters, restraints	368, 0	597, 1
GOF	1.051	0.916
R_1,[a] wR_2,[b] $I > 2\sigma(I)$	0.0231, 0.0560	0.0429, 0.0901
R_1,[a] wR_2,[b] all data	0.0272, 0.0587	0.0656, 0.0957
largest diff. hole, peak /e Å^{-3}	–0.835 0.447	–0.356 0.997

[a] $R_1 = \Sigma||F_O|-|F_C||/\Sigma|F_O|$; [b] $wR_2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma(w(F_O^4)]^{1/2}$