Efficient Bulky Phosphines for the Selective Telomerization of 1,3-Butadiene with Methanol

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Supporting information:

I. Catalytic test and kinetics:

Phosphine 2:

Bd conversion		MeOH/Bd		
		2	2,6	5
Temp	60	38,64		
	75			
	90	50,19		
	100			

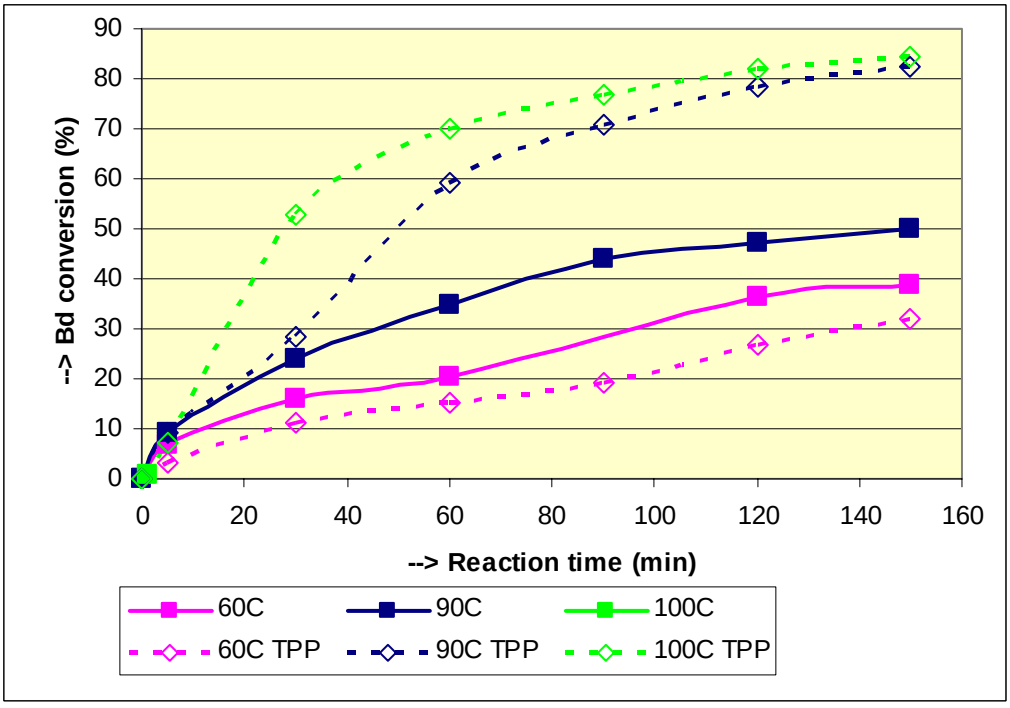
1-MOD selectivity		MeOH/Bd		
		2	2,6	5
Temp	60	85,30		
	75			
	90	69,76		

	100			

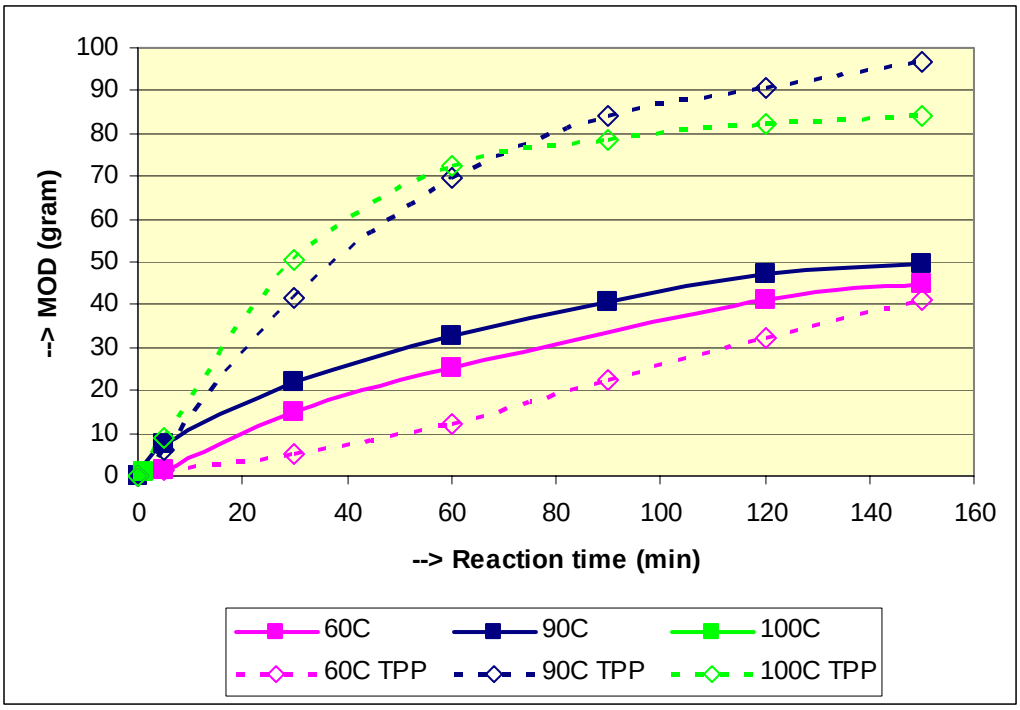
Pd precipitation		MeOH/Bd		
		2	2,6	5
Temp	60	-5,27		
	75			
	90	34,61		
	100			

Variable temperature at MeOH/Bd weight ratio = 2.

Bd conv. vs time:



1-MOD formation vs time:



Phosphine 4:

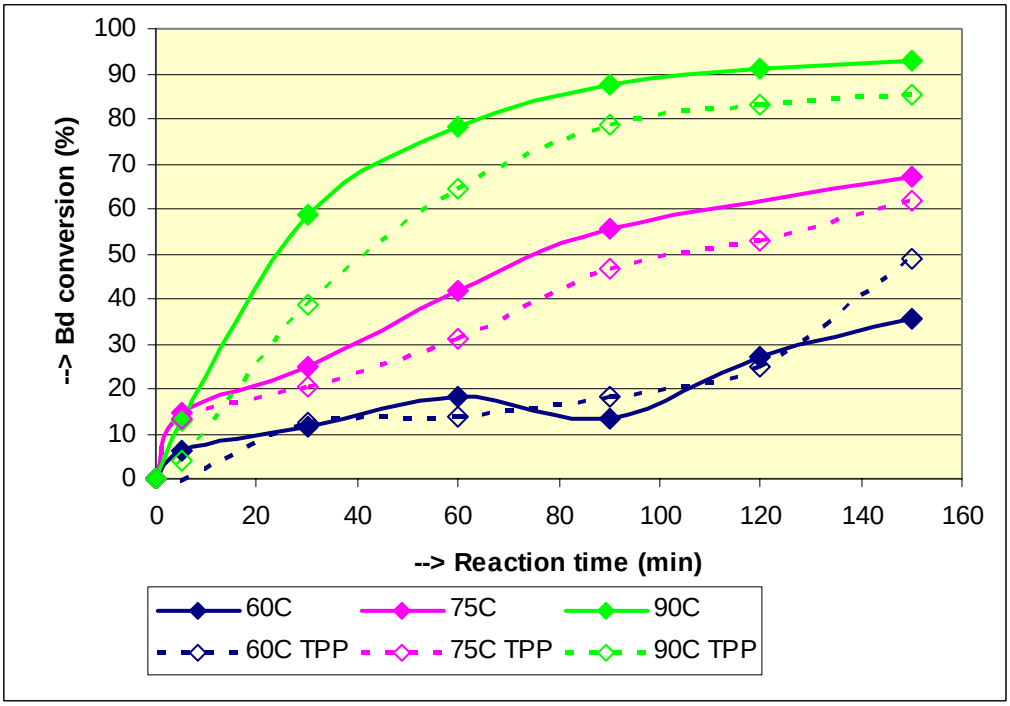
Bd conversion		MeOH/Bd		
		2	2,6	5
Temp	60	40	36	33
	75		67	
	90	89	93	
	100	91		
	110	90		
	120	88		

1-MOD selectivity		MeOH/Bd		
		2	2,6	5
Temp	60	94	94	94
	75		93	
	90	88	89	
	100	84		
	110	81		
	120	78		

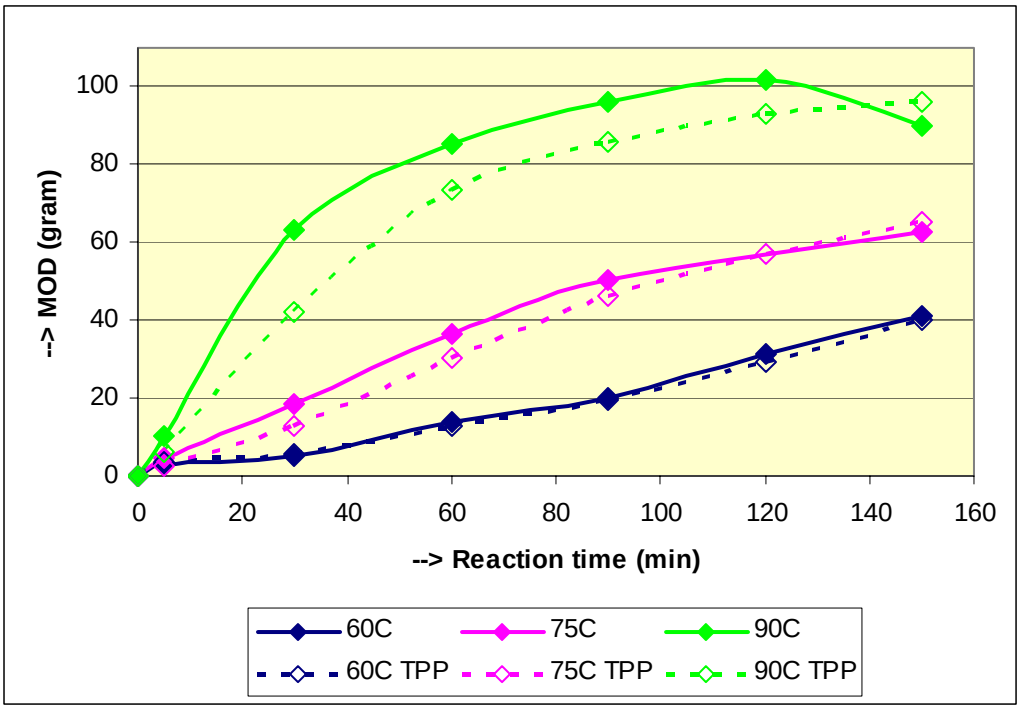
Pd precipitation		MeOH/Bd		
		2	2,6	5
Temp	60	-2	2	-4
	75		12	
	90	2	6	
	100	2		
	110	6		
	120	37		

Variable temperatures at MeOH/bd (w/w) 2.7.

Bd conversion vs time:

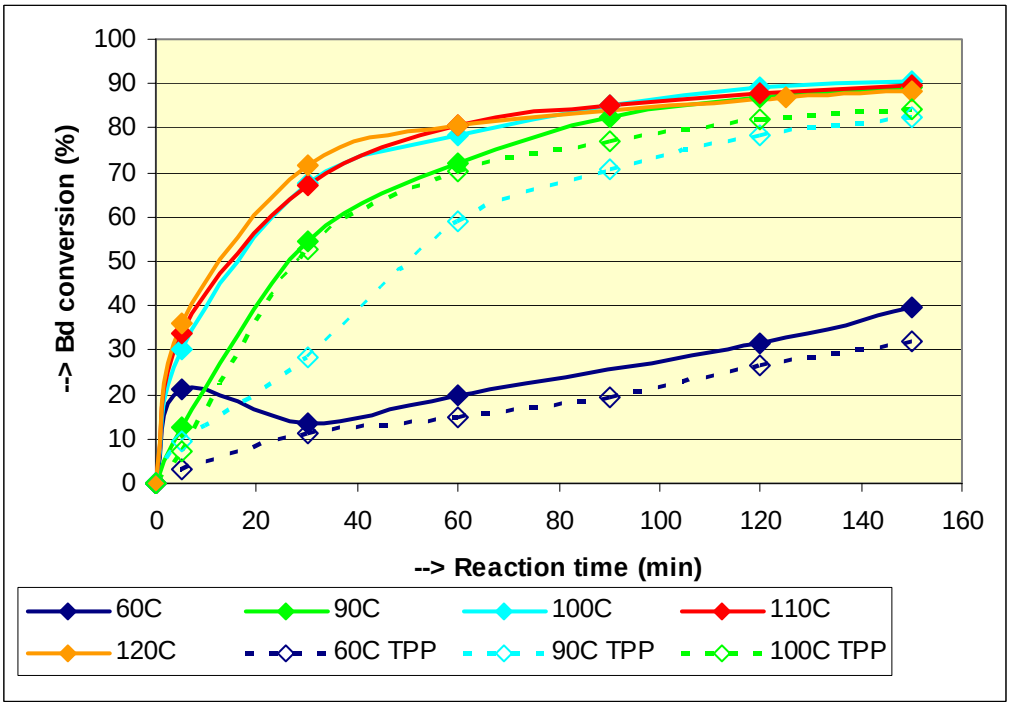


1-MOD formation vs time:

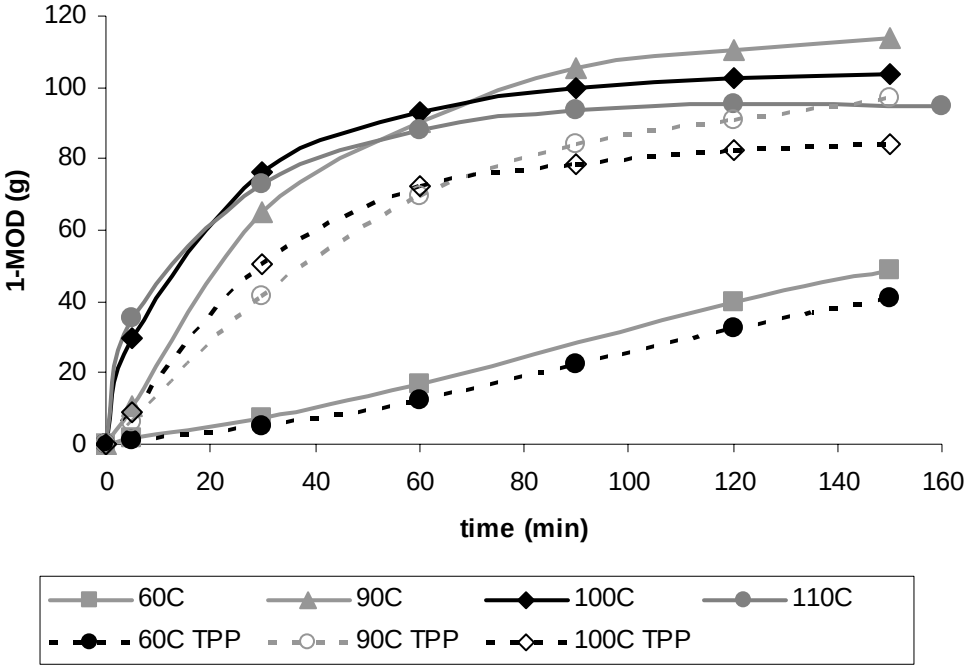


Variable temperatures at MeOH/bd (w/w) = 2.

Bd conversion vs time:

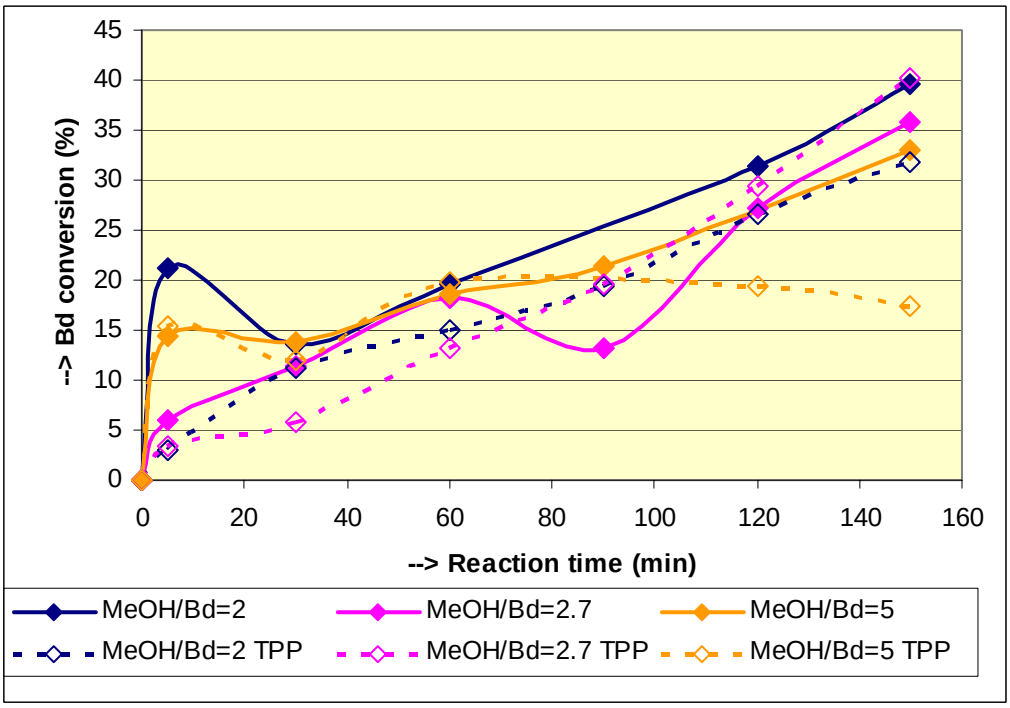


1-MOD formation vs time:

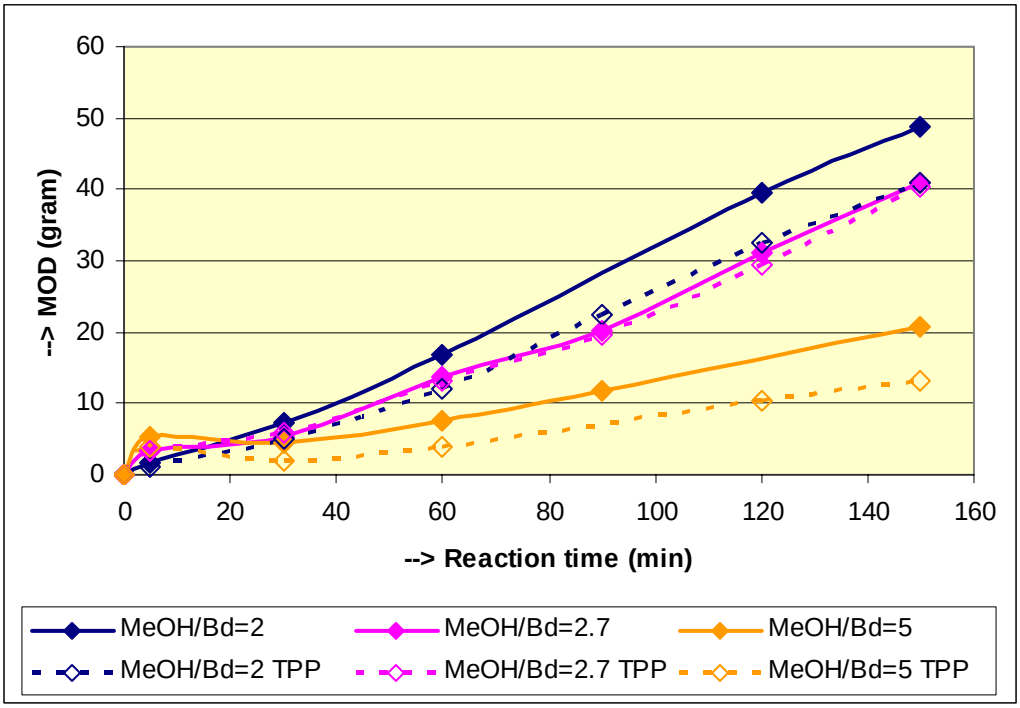


Variable MeOH/Bd weight ratio at 60°C:

Bd conversion vs time:

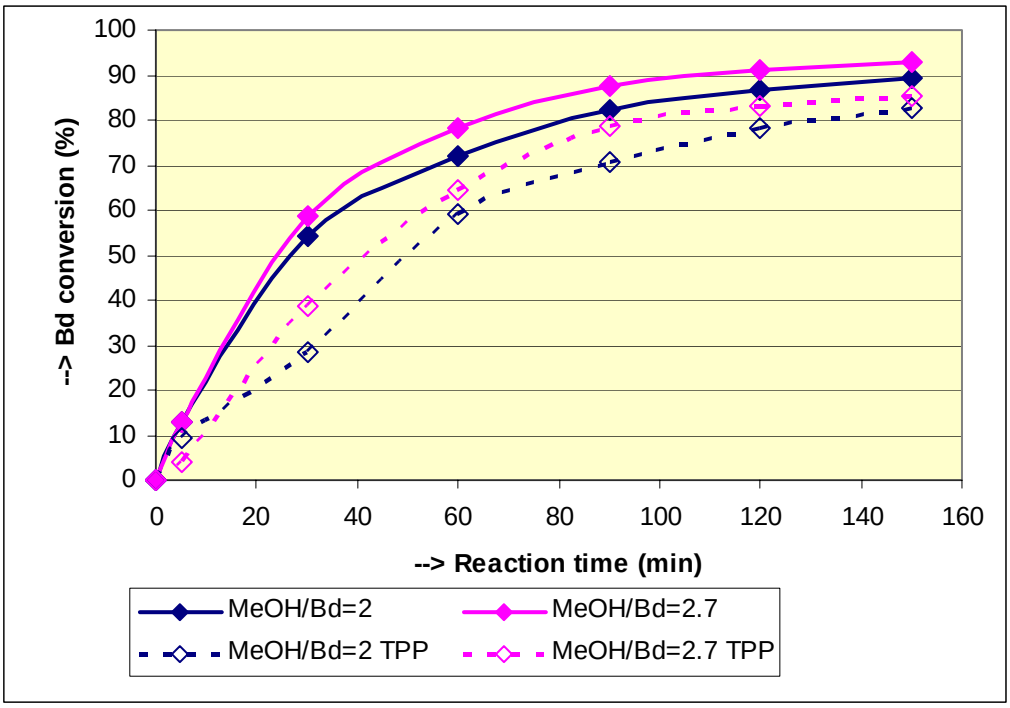


1-MOD formation vs time:

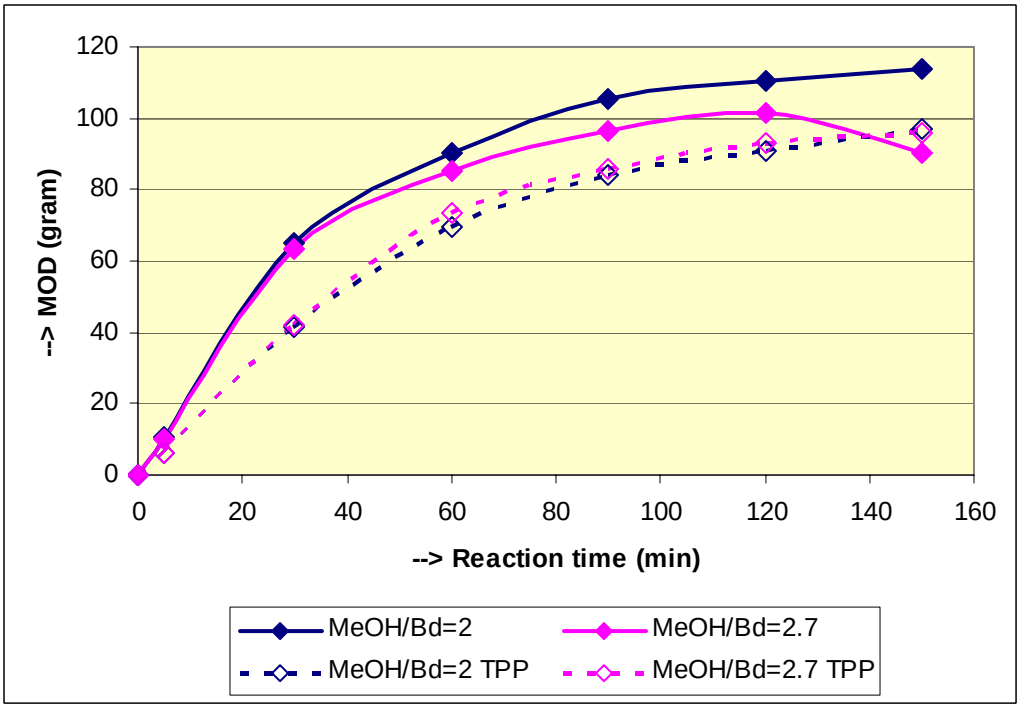


Variable MeOH/Bd weight ratio at 90°C:

Bd conversion vs time:



1-MOD formation vs time:



Phosphine 5:

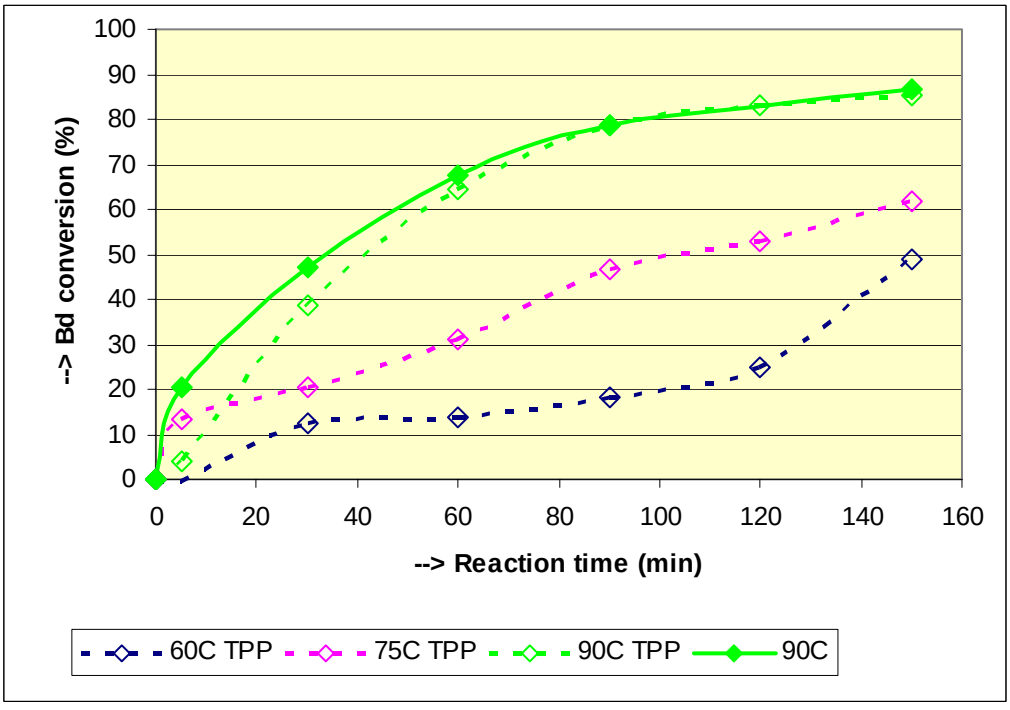
Bd conversion		MeOH/Bd		
		2	2,6	5
Temp	60			

	75			
	90		86,71	
	100			

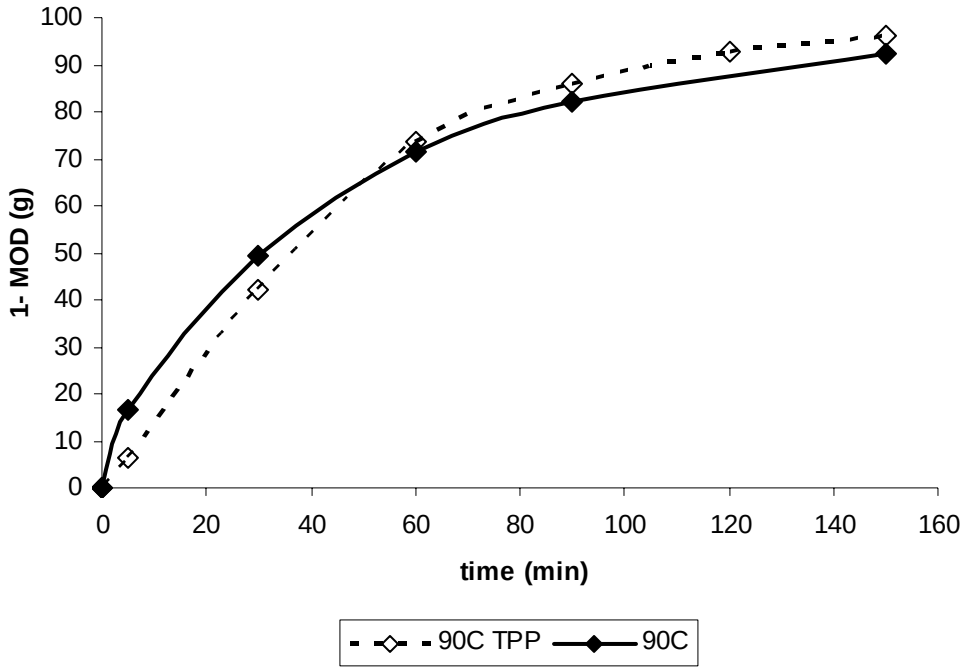
MOD selectivity		MeOH/Bd		
		2	2,6	5
Temp	60			
	75			
	90		82,51	
	100			

Pd precipitation	MeOH/Bd		
	2	2,6	5
60			
75			
90		30,01	
100			

Butadiene conversion vs time at 90 ºC with a MeOH/Bd ratio of 2.7:



1-MOD formation vs time at 90 ºC with a MeOH/Bd ratio of 2.7:



Phosphine 9:

	% conv	Molar selectivity						norm	Yield
		MOD-1	MOD-3	VCH	OT	Heavies	cycl MOD	(%)MOD1/MOD tot	MOD
9: 90 deg C ; MeOH-Bd = 2.67 wt/wt ratio	52.99	89.15	3.93	0.00	4.34	0.408	0.030	95.774	47.245
9: 90 deg C ; MeOH-Bd = 0.61 wt/wt ratio	82.11	92.06	4.47	0.17	2.98	0.154	0.030	95.371	75.591
9: 70 deg C ; MeOH-Bd = 2.64 wt/wt ratio	38.91	92.15	3.19	0.74	2.65	0.297	0.027	96.658	35.860
9: 70 deg C ; MeOH-Bd = 0.6 wt/wt ratio	57.47	95.17	3.47	0.14	1.06	0.083	0.005	96.479	54.700

Phosphine 11:

Bd conversion		MeOH/Bd		
		2	2,6	5
Temp	60	10,03	9,93	
	75			
	90	30,38		
	100	29,07		

200 eq Na		MeOH/Bd		
		2	2,6	5
Temp	60			
	75			
	90	48,57		
	100			

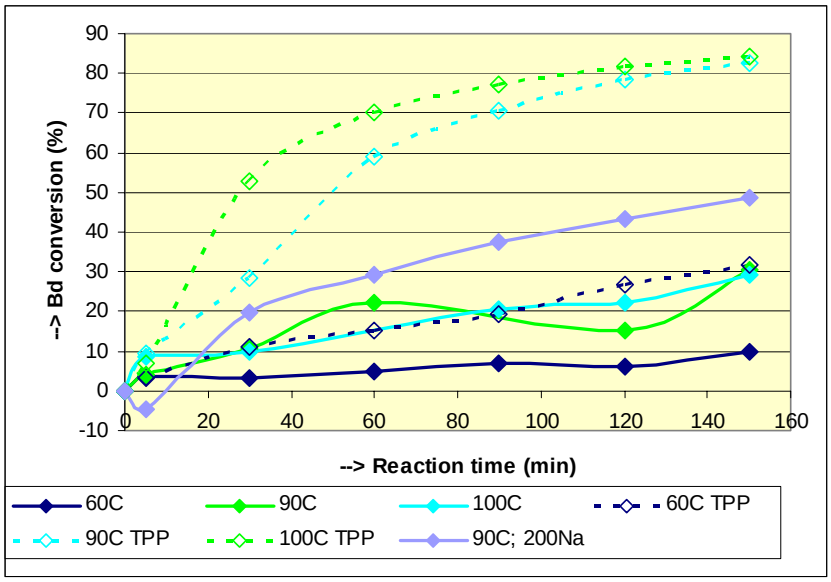
MOD selectivity	MeOH/Bd		
	2	2,6	5
60	74,90	61,13	
75			
90	76,36		
100	71,24		

200 eq Na	MeOH/Bd		
	2	2,6	5
60			
75			
90	77,54		
100			

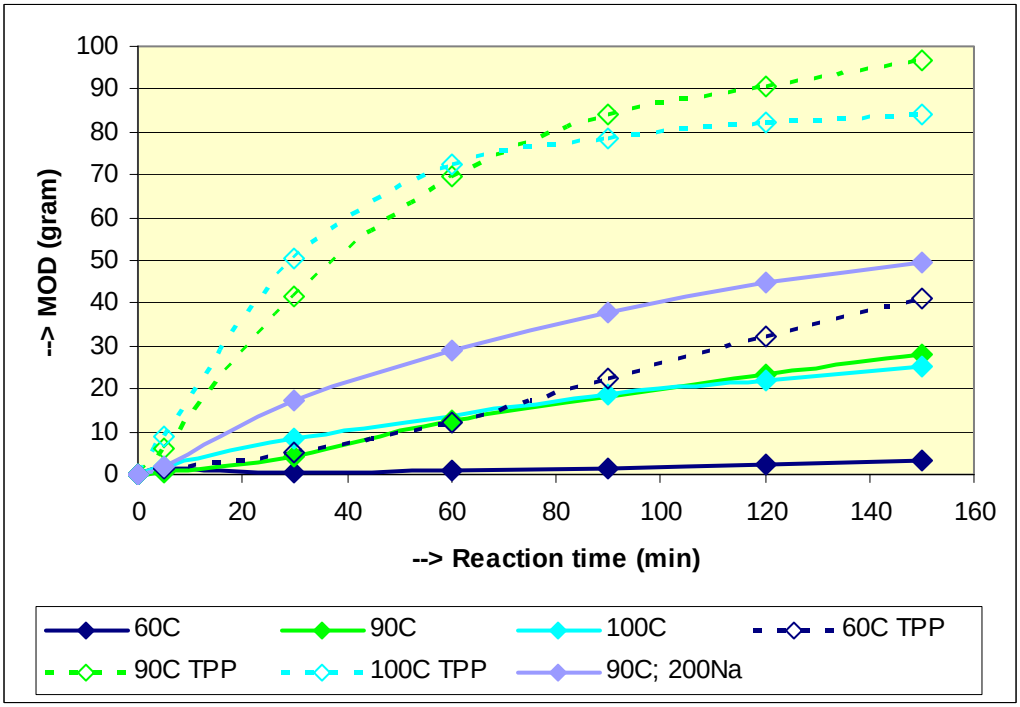
Pd precipitation		MeOH/Bd		
		2	2,6	5
Temp	60	-9,62	4,00	
	75			
	90	31,52	51,00	
	100	52,66		

200 eq Na		MeOH/Bd		
		2	2,6	5
Temp	60			
	75			
	90	54,77		
	100			

Bd formation vs time.

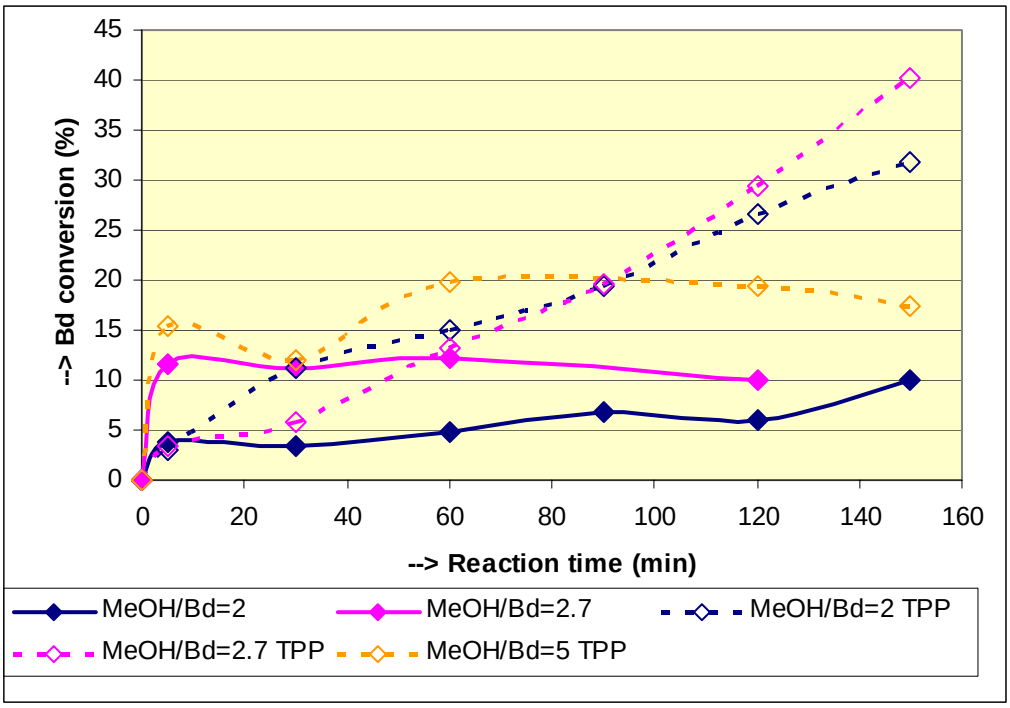


1-MOD formation vs time.

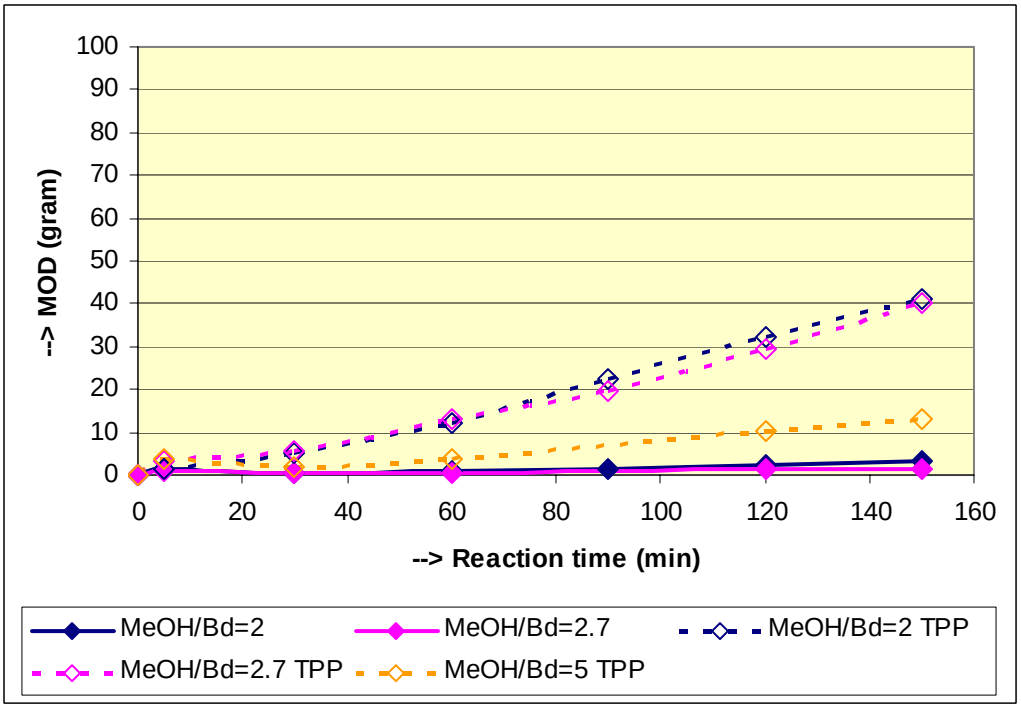


Variable MeOH/Bd weight ratio at 60°C.

Bd conv. vs time:

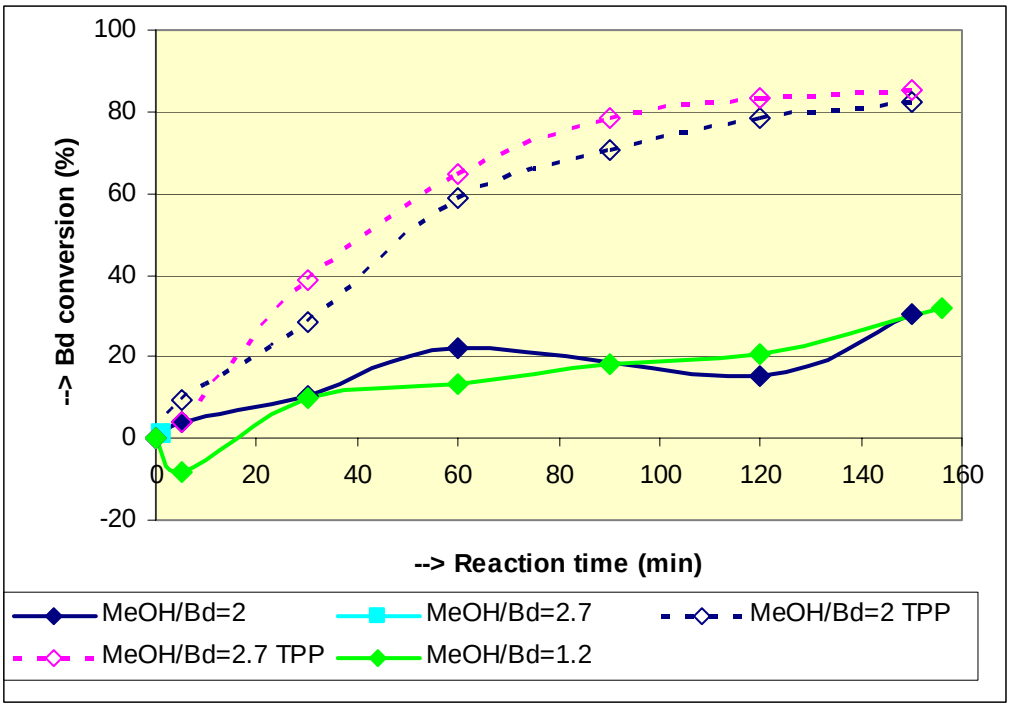


1-MOD formation vs time:

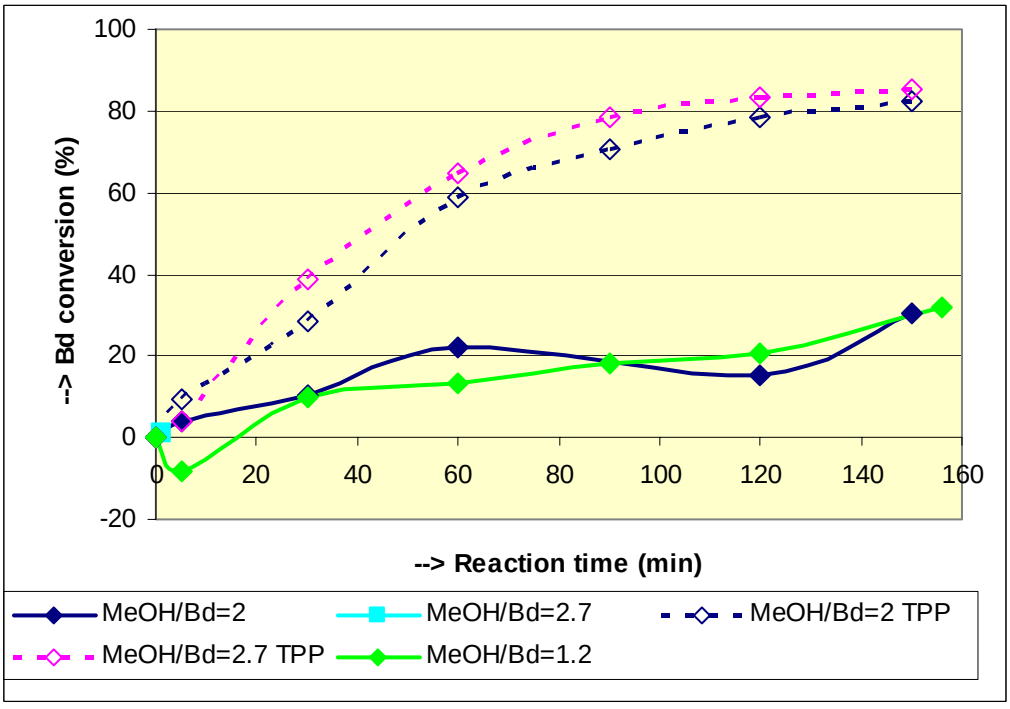


Variable MeOH/Bd weight ratio at 90°C.

Bd conv. vs time:



1-MOD formation vs time:



II. X-ray Structure Determination:

Crystals of **1a**, **2a** and **3a** were obtained by slow evaporation of a concentrated solution of the complex in ether. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data Collection. Measurements were made on a Bruker-Nonius diffractometer equipped with a APPEX 2 4K CCD area detector, a FR591 rotating anode with $Mo_{K\alpha}$ radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = –173 ^{o}C). Full-sphere data collection was used with ω and φ scans.

Programs used: Data collection Apex2 V 1.0–22 (Bruker-Nonius 2004), data reduction Saint+ V 6.22 (Bruker-Nonius 2001) and absorption correction SADABS V. 2.10 (2003).

Structure Solution and Refinement. SHELXTL Version 6.10 (Sheldrick, 2000) was used.

Table 5: Crystal data for compounds **1a**, **2a** and **3a**.

Compound	**1a**	**2a**	**3a**
Formula	$C_{32}H_{37}O_1P_1Pd_1Si_2$	$C_{34}H_{41}O_3P_1Pd_1Si_2$	$C_{31}H_{37}O_1P_1Pd_1Si_2$
Formula weight	631.17	691.22	619.16
Crystal size (mm^3)	0.40 x 0.40 x 0.20	0.30 x 0.20 x 0.20	0.50 x 0.35 x 0.20
Crystal color	brown	yellow	white
Temp (K)	100	100	100
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$C2/c$	$P\bar{1}$
A (Å)	12.243(2)	20.0915(17)	10.2083(3)
B (Å)	8.8775(18)	17.3002(17)	12.3688(4)
C (Å)	27.705(6)	18.7964(18)	12.3907(4)
α (deg)	90	90	90.612(2)
β (deg)	98.35(3)	94.156(4)°	94.8070(10)
γ (deg)	90	90	110.8610(10)
V (Å^3)	2979.3(10)	6516.2(11)	1455.42(8)
Z	4	8	2
ρ (g/cm^3)	1.407	1.409	1.413
μ (mm^{-1})	0.781	0.725	0.797
θ_{max} (°)	40.01	36.30	39.53
Reflec. measured	43752	57788	32852
Unique reflections	15060 [R_{int}=0.0258]	12955 [R_{int}=0.0583]	13395 [R_{int}=0.0286]
Absorpt. correct.	SADABS (Bruker)	SADABS (Bruker)	SADABS (Bruker)
Trans. min/max	0.8672/1.0000	0.9347/1.0000	0.8068/1.0000
Parameters	354	376	346
R1/wR2 [I>2σ(I)]	0.0294/0.0734	0.0587/0.0671	0.0349/0.0407
R1/wR2 [all data]	0.0734/0.0753	0.1527/0.1659	0.0889/0.0935

Goodness-of-fit (F^2)	1.064	1.029	1.054
Peak/hole (e/Å^3)	1.885/–1.011	5.059/–5.637	2.546/–1.116