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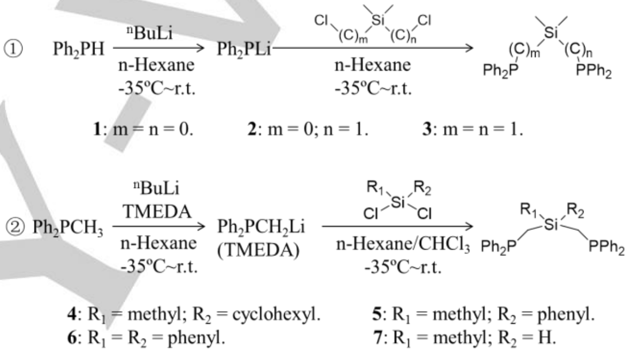
Chromium-based ethylene tetramerization catalysts supported by SBDP ligands: further combination of high activity and selectivity

Le Zhang,[a,b] Xuejiao Meng,[a] Yanhui Chen, [a] Chengang Cao, [a] Tao Jiang*[a]

Abstract: A series of silicon-bridged diphosphine (SBDP) ligands have been synthesized and characterized. The Cr pre-catalyst supported by bis(diphenylphosphinomethyl)-dimethylsilane (Ligand 3) achieved a high activity of 4.2×10^6 g/(mol Cr·h) and a high selectivity of 78.44% towards the valuable 1-octene compound using methylcyclohexane as the solvent at the ethylene pressure of 4.0 MPa and 45 °C. An intramolecular β-H transfer mechanism was proposed to explain the unequal molar proportions of cyclic C_6 byproducts. The crystal structure data of **5-Cr** and **6-Cr** complexes proved that the SBDP system with wide P-Cr-P bite angle could also exhibit a superior performance in ethylene tetramerization.

Selective ethylene oligomerization is considered to be the most effective method for producing high-purity 1-hexene and 1-octene used as preferred comonomers for linear low density polyethylene.[1] Selective ethylene trimerization has been investigated thoroughly since 1967. The activity and selectivity can reach up to 8.3×10^6 g/(mol Cr·h) and 98.1% (1-hexene) obtained from the SNS catalytic system.[2] In contrast, the first catalyst of ethylene tetramerization, the Cr-PNP catalytic system, was reported by Sasol in 2004, exhibiting an activity and selectivity to 1-octene of 1.4×10^6 g/(mol Cr·h) and 70%, respectively.[3] Since then, there have been numerous studies of the electronic and steric factors that govern the selectivity and activity,[4] as well as the backbone length and composition of the ligands in these systems.[5] Our group has also developed the binuclear[6] and trinuclear[7] PNP systems obtaining similar results. However, the combination of high activity and selectivity has not been achieved. Attempts to further enhance ethylene tetramerization performance have been largely focused on carbon-bridged diphosphines. Kim and coworkers reported a selective ethylene tetramerization catalyst system based on chiral DPPDME ligands with 77.4% selectivity for 1-octene [3.0×10^6 g/(mol Cr·h) activity].[8] Gambarotta and coworkers found that the chromium (III) complexes of [$PPh_2NR(CH_2)_4NRPPh_2$] can produce 1-octene with 88% selectivity (1.3×10^6 g/(mol Cr·h) activity).[9] Zhang and coworkers also reported that carbon-bridged diphosphine ligands can promote ethylene tetramerization with a 64.7% 1-octene selectivity [2.9×10^7 g/(mol Cr·h) activity].[10] It appears that diphosphine will be one of the most promising ligands for achieving the combination of high activity and selectivity. Therefore, we have chosen to focus our efforts on the development of a diphosphine ligand supported catalytic system. Silyl groups, as a large electropositive substituent, have a substantial effect in an complexe structrue, hence can control the stereochemistry of the reaction.[11] Herein, we describe a silicon-bridged diphosphine (SBDP) ligand system and its use in a new class of selective ethylene tetramerization catalysts, in addition to its unique C_6 products ratio and the wide bite angle in contrast to the PNP system.



Scheme 1. Synthesis of SBDP ligands **1-7**.

The target SBDP ligands **1-7** were prepared by a convenient salt metathesis of lithium phosphines and the corresponding chlorosilanes (Scheme 1). Ligand **1**/Cr(III)/MAO (methylaluminoxane) system for ethylene oligomerization in toluene has been previously reported by our group.[12] Ligands **2-7** were used in ethylene tetramerization for the first time.

All ligands were characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy. ^1H NMR data exhibit the characteristic Si-CH_3 (-0.4~0.2 ppm) and P-CH_2-Si (1.2~1.8 ppm) resonances, and the ^{31}P NMR data show a distinctive signal of P-Si (-55.86~-56.51 ppm) and P-C (-23.96~-21.42 ppm).

The ligands **1-7**, mixed with $CrCl_3(THF)_3$ in dried methylcyclohexane and stirred for at least two hours at 40 °C, proved to be active and selective catalysts for ethylene tetramerization toward 1-octene when combined with DMAO (dried MAO)/$AlEt_3$ (Table 1). The data of Entry 1-3 indicate the linker length plays an important role in selective ethylene tetramerization. An overall consideration of the data for Entry 3-7, reveal that the selectivity of 1-octene shows a strong dependence upon the ligand steric bulk with ligand 3 exhibiting better activity [3.64×10^5 g/(mol Cr·h), 1.0 MPa] and the highest selectivity (64.22%, 1.0 MPa). Ligand **7**

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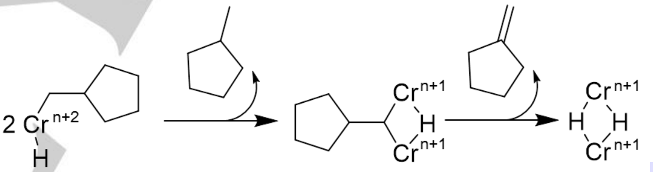
Table 1. Ethylene selective oligomerization with catalysts supported by ligands **1-7**

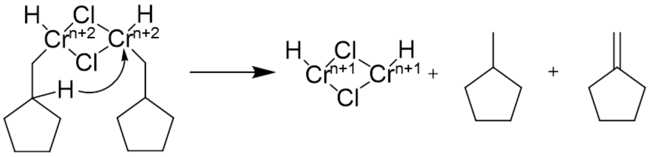
Entry	Ligand	Activity(10^5 g/(mol Cr·h))	Product selectivity(%)							
			C_4	C_6	$1\text{-}C_6^=$	$C_6'^{[a]}$	$C_6''^{[b]}$	C_8	$1\text{-}C_8^=$	$\geq 1\text{-}C_{10}^=$
1	**1**	0.17	25.21	63.65	26.81	3.66	5.87	11.13	71.41	Trace
2	**2**	1.26	6.78	40.08	64.43	2.24	2.72	53.14	93.96	Trace
3	**3**	3.64	2.27	33.51	78.32	1.86	3.28	64.43	95.03	Trace
4	**4**	4.33	1.86	40.95	80.86	2.65	5.11	57.19	>99%	Trace
5	**5**	1.60	3.34	37.72	77.92	2.67	5.65	58.94	95.18	Trace
6	**6**	1.15	3.58	41.05	82.39	2.49	4.74	55.38	95.72	Trace
7	**7**	0.76	5.31	51.93	70.23	3.79	6.63	42.76	89.34	Trace

Reaction conditions: reaction pressure:1.0 MPa; reaction time: 30 min; solvent: methylcyclohexane; Temperature: 45°C; C[Cr(THF)$_3$Cl$_3$]: 0.2 mmol•L^{-1}; nCr(III) : nLigand = 1 : 2; n(Al)/n(Cr)=500; nDMAO : nAlEt3 = 4 : 1. [a] Methylcyclopentane in all oligomerization products. [b] Methenecyclopentane in all oligomerization products.

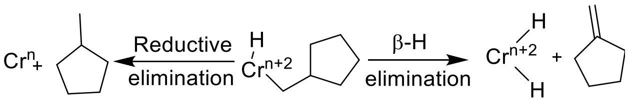
has the lowest steric bulk results in especially low activity and selectivity. The prominent performance of ligand **3** is correlated with the electronic effect and steric bulk of methylsilicane in contrast to the PCCCP ligand reported by Overett.[5a] Both linker length and steric bulk are related to the P-Cr-P bite angle as discussed below. Ligand **3** was further investigated for ethylene tetramerization under various reaction conditions such as temperature, ethylene pressure and Cr concentration (Table 2). High temperature can markedly increase the activity, but at the expense of selectivity to 1-octene. Furthermore, products with $\geq 1\text{-}C_{10}^=$ were formed when the temperature was higher than 60°C, possibly due to the formation of new active species at high temperature. A low Cr concentration can promote the activity but not the selectivity to 1-octene under high ethylene pressure. Focusing on the best example, ligand **3** exhibited a surprising/unexpected high activity of 4.2×10^6 g/(mol Cr·h), maintaining the high selectivity of 78.44% toward C_8. It is important to note the different methylenecyclopentane/methylcyclopentane ratios in all runs, shown in Table 1 and Table 2. For ligand 3, it increased with the total oligomerization activities and was approximately 1.74~1.85. Overett and coworkers reported a bimetallic disproportionation mechanism to explain the fixed ratio of 1:1 for the two C_6 cyclic byproducts (as shown in scheme 2).[13] Obviously, this mechanism is not suitable for our SBDP system. In the review by Agapie,[1b] it was reported that the PNP/Cr complex may exist as a dimer bridged by chlorine. We infer that the different ratio for the two C_6 byproducts obtained in the PNP and SBDP systems is due to the dissimilar mechanisms of β-H transfer. For the PNP system (scheme 3), the Cr cyclopentylmethyl hydride species may exist as a dimer, and the two C_6 byproducts with a ratio of 1:1 are obtained via intermolecular β-H transfer. Correspondingly, for the SBDP system (scheme 4), a mononuclear species may produce the two C_6 byproducts in unequal proportions through intramolecular β-H transfer. Additionally, the selectivities to C_6 byproducts decreased with increasing $1\text{-}C_6$ selectivity. It is shown that the active centers forming methylenecyclopentane and methylcyclopentane may be different from that for ethylene oligomerization.



Scheme 2. Bimetallic disproportionation mechanism for C_6 cyclic byproducts[13].



Scheme 3. Proposed intermolecular β-H transfer mechanism for C_6 cyclic byproducts.



Scheme 4. Proposed intramolecular β-H transfer mechanism for C_6 cyclic byproducts.

Table 2. Ethylene selective oligomerization of **3/Cr** under different reaction conditions

Entry	T(℃)	Activity(10^5 g/(mol Cr·h))	Product selectivity(%)							
			C_4	C_6	$1\text{-}C_6^=$	C_6'[d]	C_6"[e]	C_8	$1\text{-}C_8^=$	$\geq 1\text{-}C_{10}^=$
1	0	0.113	3.30	10.30	38.71	4.06	5.99	86.40	>99.00%	Trace
2	30	1.55	1.84	21.87	59.04	2.74	4.76	76.29	>99.00%	Trace
3	45	3.64	2.27	33.51	78.32	1.86	3.28	64.22	95.03	Trace
4	60	4.00	2.38	44.71	90.88	1.22	2.13	42.68	97.85	10.23
5	75	6.34	4.58	40.90	93.72	0.42	0.76	22.98	92.42	31.71
6	90	23.70	5.86	55.44	93.91	0.30	0.54	18.78	84.96	20.22
7[a]	45	1.80	3.09	26.95	75.94	2.37	4.12	69.96	83.90	Trace
8[b]	45	3.38	2.14	24.86	72.37	2.44	4.43	73.00	87.46	Trace
9[b, c]	45	42.10	1.11	20.45	58.03	3.01	5.58	78.44	97.20	Trace

Reaction conditions: reaction pressure: 1.0 MPa; reaction time: 30 min; solvent: methylcyclohexane; $C[Cr(THF)_3Cl_3]$: 0.2 mmol•L^{-1}; nCr(III):nLigand = 1:2; n(Al)/n(Cr)=500; nDMAO: nAlEt3 = 4:1. [a] reaction pressure: 2.0 MPa. [b] reaction pressure: 4.0 MPa. [C] $C[Cr(THF)_3Cl_3]$: 0.012 mmol•L^{-1}. [d] Methylcyclopentane in all oligomerization products. [e] Methenecyclopentane in all oligomerization products.

Piet and coworkers[14] considered that a wide bite angle in a metal complex can increase the effective steric bulk of the bidentate ligand and will electronically favour or disfavor certain geometries of transition metal complexes. A plausible trend was obtained that a small bite angle was beneficial for the selectivity to 1-octene.[5a, 10] However, the PNCNP system reported by Klemps[5b] and the DPPDME system reported by Kim,[8] with a wider bite angle (~80º), showed better selectivity to 1-octene than the PNP system (~65º). Therefore, the crystal structures of SBDP/Cr complexes were further investigated. Despite of the failure to obtain a single crystal of the **3-Cr** complex, single crystals of **5-Cr** and **6-Cr** were obtained. Their structures are showed in Figure 1.

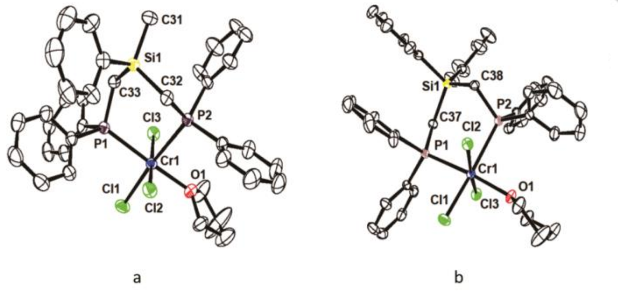


Figure 1. Molecular structures of **5-Cr** (a) and **6-Cr** (b). Selected bond distances (Å) and angles (deg): (a) O1-Cr1 = 2.090(2); Cr1-P1 = 2.492(9); Cr1-P2 = 2.577(8); P1-Cr1-P2 = 94.09(3). (b) O1-Cr1 = 2.090(1); Cr1-P1 = 2.499(1); Cr1-P2 = 2.584(1); P1-Cr1-P2 = 93.73(2).

Remarkably, the P-Cr-P bite angles (approximately 94.0º) were much larger than those found in other ethylene tetramerization systems (approximately 65.6º-83.0º). It illustrated that the catalytic system with wide P-Cr-P bite angle also can exhibit a superior performance in ethylene tetramerization. Further investigations are in progress.

In conclusion, a series of SBDP ligands were synthesized and characterized, proving to afford selective ethylene tetramerization catalysts, producing 78.44% 1-octene selectivity with activity of 4.2×10^6 g/(mol Cr·h). In this system, lower temperature is beneficial for 1-octene selectivity providing support for the extended metallocyclic mechanism. An intramolecular β-H transfer mechanism was proposed to explain the variable molar ratios of cyclic C_6 byproducts. The crystal structure of **5-Cr** and **6-Cr** complexes proved that the SBDP system with wide P-Cr-P bite angle can also exhibit a superior performance in ethylene tetramerization. Our work expanded the range of design for ethylene tetramerization catalysts and the DFT investigation of the reaction mechanism for cyclic C_6 products producing is being further investigated.

Acknowledgements

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Keywords: 1-octene • chromium • P ligands • oligomerization • tetramerization

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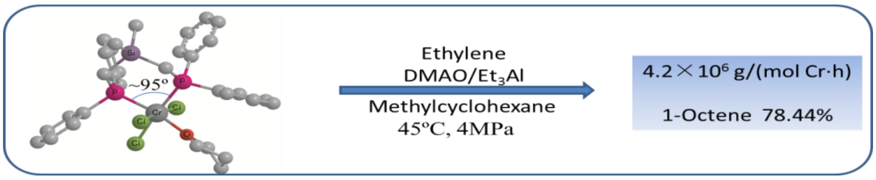

A series of silicon-bridged diphosphine (SBDP) ligands have been synthesized which presented high activity and selectivity towards the valuable 1-octene compound, combined with $CrCl_3(THF)_3$ and DMAO/Et_3Al. The crystal structure data proved that the SBDP system with wide P-Cr-P bite angle (~95°) could also exhibit a superior performance in ethylene tetramerization.

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