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Synthesis of and Ethylene Polymerization Using Iminophosphonamide Complexes of Group 4

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Summary: Efficient syntheses of iminophosphonamide $[R_2P(=NR')NHR']$ *complexes of group 4 via amine elimination reactions and the solid-state structures of* $[R_2P(NR')_2]_2ZrCl_2$ *and mixed* $Cp[R_2P(NR')_2]ZrCl_2$ *complexes are reported. These complexes are active, ethylene, polymerization catalysts* (10^6-10^7 *g PE/mol Zr × h) in the presence of MAO and provide high molecular weight poly(ethylene) with narrow molecular weight distributions.*

There is considerable current interest in the preparation of new single-site polymerization catalysts of the early transition metals not based on metallocene complexes. Numerous examples of group 4 complexes bearing heteroatom ligands have been reported, some of which are active, single-site olefin polymerization catalysts.[1]

Having said that, many of these systems are much less active than metallocene complexes for reasons that are not very obvious. In particular, (bis)amidinate or mixed amidinate(Cp) complexes of group 4 (**1** and **2**, respectively) have been prepared by a number of researchers,[2] and these complexes are either inactive in olefin polymerization[2c] or possess very low activities (ca. 10^3-10^4 g PE/mol M × h).

It had occurred to us that complexes derived from ligands analogous to amidinates in which the central atom is coordinatively saturated might prove to be useful in olefin polymerization. Iminophosphonamide (PN_2) complexes seemed particularly attractive in this regard; although complexes of these ligands have been

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(1) See, for example: (a) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 308. (b) Gibson, V. C.; Kimberley, B. S.; White, A. J. R.; Williams, D. J *J. Chem. Soc., Chem. Commun.* **1998**, 313. (c) Schrock, R. R.; Schattenmann, F.; Aizenberg, M.; Davis, W. M. *Ibid.* **1998**, 199. (d) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415. (e) Fokken, S.; Spaniol, T. P.; Okuda, J.; Serentz, F. G.; Mulhaupt, R. *Ibid.* **1997**, *16*, 4240. (f) Sarsfield, M. J.; Ewart, S. W.; Tremblay, T. L.; Roszak, A. W.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3097. (g) Tinkler, S.; Deeth, R. J.; Duncalf, D. J.; McCamley, A. *J. Chem. Soc., Chem. Commun.* **1996**, 2623. (h) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008. (i) Duchateau, R.; Cornelis, T. W.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279. (j) Black, D. G.; Swenson, D. C.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3539. (k) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 5478. (l) Cozzi, P. G.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Ibid.* **1995**, *14*, 4994. (m) Gomez, R.; Green, M. L. H.; Haggitt, J. L. *Chem. Commun.* **1994**, 2607. (n) Brand, H.; Capriotti, J. A.; Arnold, J. *Organometallics* **1994**, *13*, 4469. (o) Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 8493.

(2) (a) Schlund, R.; Lux, M.; Edelmann, F.; Reissmann, U.; Rohde, W. US Patent 5,707,913 issued to BASF AG, Jan 13, 1998. (b) Littke, A.; Sleiman, N.; Bensimon, C.; Richeson, D. S.; Yap, G. P. A.; Brown, S. J. *Organometallics* **1998**, *17*, 446−451. (c) Gomez, R.; Green, M. L. H.; Haggitt, J. L. *J. Chem. Soc., Dalton Trans.* **1996**, 939−946 and references therein. (d) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1995**, *14*, 2106−2108. (e) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Ibid.* **1995**, *14*, 1827−1833. (f) Kerskovics-Korine, D.; Eisen, M. S. *J. Organomet. Chem.* **1995**, *503*, 307−314.

(3) (a) Muller, E.; Muller, J.; Olbrich, F.; Bruser, W.; Knapp, W.; Abeln, D.; Edelmann, F. T. *Eur. J. Inorg. Chem.* **1998**, 87−91. (b) Kilimann, U.; Noltemeyer, M.; Schafer, M.; Herbst-Irmer, R.; Schmidt, H.-G.; Edelmann, F. T. *J. Organomet. Chem.* **1994**, *469*, C27−30. (c) Recknagel, A.; Steiner, A.; Noltemeyer, M.; Brooker, S.; Stalke, D.; Edelmann, F. T. *Ibid.* **1991**, *414*, 327−335. (d) Witt, M.; Roesky, H. W.; Stalke, D.; Pauer, F.; Henkel, T.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1989**, 2173−77. (e) Recknagel, A.; Witt, M.; Edelmann, F. T. *J. Organomet. Chem.* **1989**, *371*, C40−44.

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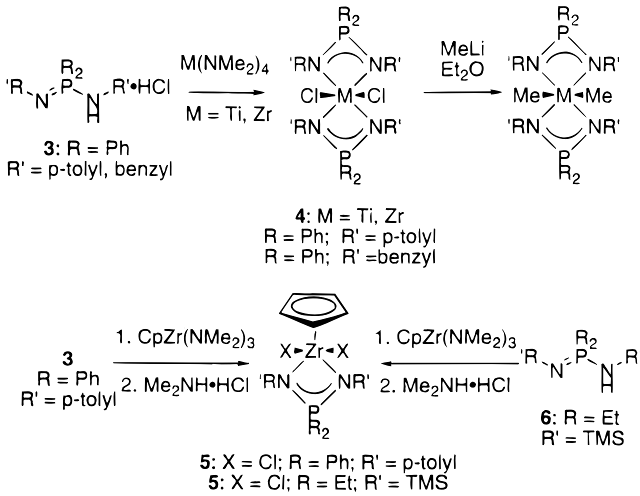
Scheme 1



reported,[3] their use in olefin polymerization has not been disclosed.[4]

A variety of these complexes were conveniently synthesized by amine elimination reactions[5] as outlined in Scheme 1. In particular, the reaction of $Zr(NMe_2)_4$ with 2 equiv of iminophosphonamidinium salts **3**[6] in toluene suspension directly furnished the bis-PN_2 dichloride complexes **4** in very high yield and purity.[7] The corresponding dimethyl complexes were accessible by reaction of **4** with MeLi or MeMgBr in ether.

Mixed cyclopentadienyl(PN_2) complexes **5** (X = Cl) were accessible by reaction of $CpZr(NMe_2)_3$ with 1 equiv of **3** [or free ligand **6** (R = Et; R′ = TMS)[8]] and in situ treatment with $Me_2NH{\cdot}HCl$. The corresponding methyl complex **5** (X= Me; R = Et; R′ = TMS) could be prepared from the dichloride complex by reaction with solid MeLi in toluene. The dichloride complexes (**4** and **5**) are stable enough in the solid state to be handled without rigorous exclusion of air and moisture, but solutions of these materials are more sensitive to adventitious hydrolysis.

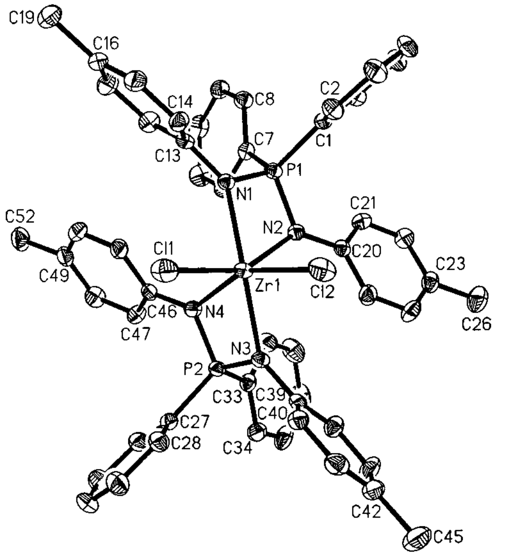


Figure 1. Molecular structure of complex **4** (M = Zr, R = Ph, R′ = *p*-tolyl) with 50% thermal ellipsoids depicted and H atoms removed for clarity.

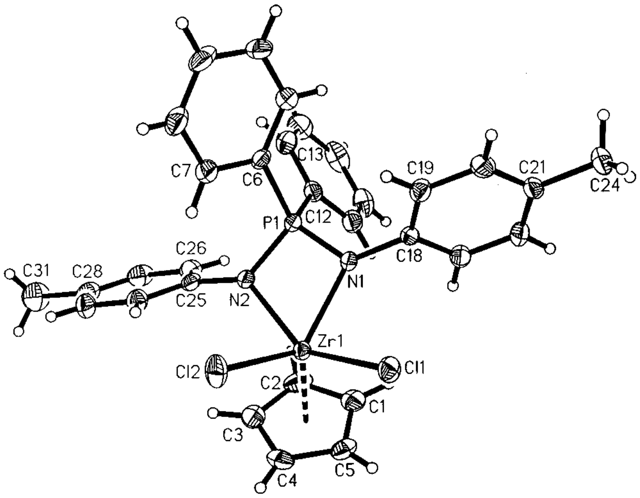


Figure 2. Molecular structure of complex **5** (M = Zr, X = Cl, R = Ph, R′ = *p*-tolyl) with 50% thermal ellipsoids depicted.

Table 1. Ethylene Polymerization Using Iminophosphonamide Complexes

entry	catalyst (MX_2)	R	R'	T (°C)	A^b	M_n(K)	M_w/M_n
1	**4** ($ZrCl_2$)	Ph	*p*-tolyl	50	7.90	144	2.07
2	**4** ($ZrCl_2$)	Ph	*p*-tolyl	70	2.50	79	3.55
3	**4** ($ZrMe_2$)	Ph	*p*-tolyl	50	6.90	190	2.68
4	**4** ($ZrMe_2$)	Ph	*p*-tolyl	70	2.90		
5	**4** ($ZrMe_2$)	Ph	benzyl	70	2.20	213	2.27
6	**4** ($ZrMe_2$)	Ph	*p*-tolyl	50	0.055	35	1.67
7	**4** ($ZrMe_2$)	Ph	benzyl	50	0.101	29	2.02
8	**4** ($ZrCl_2$)	Et	TMS	50	0.660		
9	**4** ($ZrCl_2$)	Et	TMS	70	8.90	93	2.45
10	**4** ($ZrMe_2$)	Et	TMS	50	5.30[c]	115	3.09

[a] Polymerization conditions: toluene (500 mL), metal = 10 μmol, MAO:metal = 2000:1, 75 psi C_2H_4, 1000 rpm unless otherwise noted. [b] Activity in 10^6 g PE/mol metal × h. [c] A solution of complex **5** (10 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (12 μmol) was added to a toluene solution of MAO (1.0 mmol), presaturated with ethylene.

The X-ray structures of complexes **4** (R′ = *p*-tolyl, R = Ph) and **5** (X = Cl, R′ = *p*-tolyl, R= Ph) are shown in Figures 1 and 2, respectively.[9] The structure of complex **4** (R′ = *p*-tolyl, R = Ph) reveals a cis, quasioctahedral coordination environment about the metal, having approximate C_2 symmetry, in which, predictably, the PN_2 ligands feature narrow bite angles of 65.8(1) and 65.7(1)°, respectively. However, this angle is considerably more obtuse than the bite angle in amidinate complexes (typically 58−61°). Both the Zr−N distances (average 2.221 ± 0.020 Å) and the P−N distances (average 1.626 ± 0.004 Å) within the four-membered rings are somewhat shorter than the sum of the single-bond covalent radii of Zr or P and N, suggesting partial π-electron delocalization through both P and Zr. The Zr−Cl distances and the Cl−Zr−Cl angle at 2.436(1) and 2.431(1) Å and 95.7(1)°, respectively, are quite similar to those observed in structurally characterized bis(amidinate) complexes.[2]

In the mixed complex **5**, the metrical parameters

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(4) (Collins, S.; Vollmerhaus, R.; Wang, Q. Can. WCT patent applications filed Sep 28, 1998.

(5) (a) Chandra, G.; Lappert, M. F. *J. Chem. Soc. A* **1968**, 1940. (b) Diamond, G. M.; Jordan, R. F.; Peterson, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024 and references therein.

(6) For a general synthesis of these salts, see: Cristau, H. J.; Garcia, C. *Synthesis* **1990**, 316. We note that, in our hands, this literature preparation gave mixed hydrohalide salts using R_2PCl, Br_2, and an amine, rather than pure HBr salts. Therefore, the corresponding HCl salts were synthesized from R_2PCl_3; see the Supporting Information for details.

associated with the PN_2 ligand are quite similar to those observed in **4** [i.e., P−N = 1.616(2), 1.619(2) Å, bite angle 65.9(1)°] but the bonding of the ligand to Zr is asymmetric with Zr−N(1) and Zr−N(2) being 2.186(2) and 2.215(1) Å, respectively. The PN_2Zr ring is also slightly puckered with a hinge angle of 6.9(1)° at Zr and P. The Zr−Cl distances are significantly different [2.450(1) vs 2.429(1) Å], and the Cl−Zr−Cl angle is close to 90° [91.8(1)°]. Instead of a regular, four-legged piano stool geometry being adopted about the metal, the PN_2 ligand is significantly twisted with respect to the plane defined by the centroid (Cn) of the Cp ring, Zr, and P [$\angle$N(2)P(1)Zr(1)Cn = 69.9(2)° vs an idealized value of 90°]. Similar distortions have also been observed in mixed, Cp amidinate complexes,[2c] and the reasons for these are of some interest.[10]

Ethylene polymerization using complexes **4** and **5** was investigated using MAO as a cocatalyst in toluene slurry, and the polymerization results are depicted in the Table 1. Complexes **4** (M = Zr) have polymerization activities of ca. 2−8 × 10^6 g PE/mol Zr × h with the productivity being higher at lower temperatures (entry 1 vs 2, and 3 vs 4). This result suggests that the active species may have limited thermal stability at higher temperatures.[11] The significantly broader molecular weight distribution observed at higher temperatures (entry 1 vs 2) would be consistent with this interpretation. The Ti-based complexes **4** were about 50−100 times less active than their Zr analogues under these conditions (e.g., entry 6 vs 3). Finally, complex **5** (X = Cl) shows behavior opposite to that of Zr complexes **4**, being much more active at elevated temperatures (entry 8 vs 9). This could be due to inefficient activation by MAO at lower temperatures.[12] In agreement with this hypothesis, the use of $[Ph_3C][B(C_6F_5)_4]$ as activator and **5** (X = Me) [in the presence of MAO (100:1) scrubbing agent][13] led to much higher productivity (entry 8 vs 10).

In summary, iminophosphonamide complexes of group 4 show considerable promise as a new class of single-site ethylene polymerization catalysts with activities that are comparable to metallocene catalysts. Future work will concentrate on a study of electronic and steric effects in these systems as well as fundamental reaction chemistry of the active catalytic species.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council and Nova Chemicals Ltd. of Canada for financial support of this work. We also wish to thank Nova Chemicals Ltd. for a donation of $[Ph_3C][B(C_6F_5)_4]$.

Supporting Information Available: Tables of crystallographic and refinement data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters and H-atom coordinates, and isotropic thermal parameters for **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Typical experimental procedure for complexes **4**: Compound **3** (R = Ph, R′ = *p*-tolyl; 7.00 g, 16.2 mmol) was slowly added to a solution of $Zr(NMe_2)_4$ (2.16 g, 8.08 mmol) in toluene (200 mL), and the suspension was allowed to stir for several hours at room temperature, at which time a clear solution had formed. The toluene was removed in vacuo, and the crude product was crystallized from a mixture of CH_2Cl_2 and hexane to provide **4** (R = Ph, R′ = *p*-tolyl) as a white solid (6.54 g, 85%). ^1H NMR ($CDCl_3$): δ 7.54−7.45 and 7.28−7.21 (br m, 10H) 6.89 (d, 4H, J = 8.2 Hz) 6.72 (dd, 4H, J = 8.2 Hz, $^4J_{PH}$ = 1.9 Hz) 2.28 (s, 6H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 34.8. Anal. Calcd for $C_{52}H_{48}P_2N_4ZrCl_2$: C, 65.53; H, 5.08; N, 5.88. Found: C, 65.36; H, 5.20; N, 5.74. Typical experimental procedure for complexes **5**: $CpZr(NMe_2)_3$ (2.00 g, 6.94 mmol) and compound **3** (R = Ph, R′ = *p*-tolyl; 3.00 g, 6.94 mmol) were placed in a Schlenk flask along with toluene (100 mL). The solution was allowed to stir overnight. After 12 h, $Me_2NH\cdot HCl$ (560 mg, 6.94 mmol) was added, and the solution was stirred overnight so that all of this solid had dissolved. The volume of the solution was reduced until a solid began to precipitate. The solution was reduced some more (5 mL), and hexane (100 mL) was added to precipitate all of the material. The mixture was filtered, and the solid was washed with 2 × 20 mL of hexane. The white solid was dried under vacuum (3.27 g, 77%). ^1H NMR ($CDCl_3$): δ 7.76−7.49 (br m, 10H) 6.90 (d, 4H, J = 8.2 Hz), 6.68 (s, 5H), 6.61 (dd, 4H, J = 8.2 Hz, $^4J_{HP}$ = 1.7 Hz) 2.22 (s, 6H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 31.9. Anal. Calc′d for $C_{31}H_{29}PN_2ZrCl_2$: C, 59.80; H, 4.69; N, 4.50. Found: C, 59.93; H, 4.79; N, 4.09.

(8) This compound was prepared from Et_2PH and Me_3SiN_3 according to the method reported (Paciorek, K. L.; Kratzer, R. H. *J. Org. Chem.* **1966**, *31*, 2426) for the synthesis of the $Ph_2P(NTMS)_2$ analogue; see the Supporting Information for details.

(9) Crystal data for compound $\mathbf{4}\cdot CH_2Cl_2$: monoclinic $P2_1/c$, $Z = 4$, a = 12.6325(9) Å, b = 19.0227(15) Å, c = 21.2285(15) Å, β = 102.598(4)°, V = 4978.5(9) Å^3, 6561 observed reflections with $F > 6.0\sigma(F)$, final R = 0.0323, R_w = 0.0349. Crystal data for compound **5**: monoclinic $P2_1/c$, $Z = 4$, a = 9.121(1) Å, b = 25.448(2) Å, c = 12.569(1) Å, β = 101.484(4)°, V = 2859.1(5) Å^3, 5467 observed reflections with $F > 6.0\sigma(F)$, final R = 0.0229, R_w = 0.0278.

(10) There is no obvious intramolecular steric interaction that would preclude a more symmetrical bonding mode in the solid state, although there are a number of (weak) $\pi-\pi$ stacking interactions between Ph groups on adjacent molecules within the unit cell.

(11) The magnitude of the activity difference is not entirely due to the higher ethylene concentration at 50 vs 70 °C.

(12) Methylaluminoxane seems to have less general utility as a cocatalyst for olefin polymerization for early metal complexes not based on metallocene compounds. Alkylation and ionization can often be slow and/or inefficient using MAO and a variety of complexes similar to those reported here. Vollmerhaus, R.; Rahim, M.; Xin, S.; Collins, S. Manuscript in preparation.

(13) Complex **5** (M = Zr, X = Me) is essentially inactive for ethylene polymerization at this loading of MAO at 50 °C.