

C_2 -Symmetrical Diazabutadiene Complexes of Platinum(II) and the Promotion of Cationic Polymerization

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Received May 24, 1999

Summary: The synthesis, characterization, and reaction chemistry of a cationic Pt(II) solvato complex (**2**) are described. The complex demonstrates the unprecedented ability to promote polymerization of the electron-rich olefins ethyl vinyl ether (EVE), *N*-vinylcarbazole (NVC), and 2,3-dihydrofuran (DHF) via cationic initiation and subsequent propagation of the carbocation.

During the past decade, interest in the use of palladium and other late-transition-metal complexes as catalysts for α -olefin and CO/olefin polymerization has grown considerably.^{1–11} A corresponding interest in analogous Pt(II) complexes has also increased.^{12–20} While these Pt(II) complexes bind the same olefinic substrates readily, they are relatively inactive in catalyzing polymerization reactions, leading to the view that they constitute excellent structural models for catalytically important species in the Pd systems. Additionally, interest in these and related Pt(II) complexes has been stimulated by electrophilic C–H bond activation,^{21–30}

which they have been found to promote. The Pd catalysts for α -olefin polymerization described by Brookhart and Johnson contain substituted diaryldiazabutadiene (Ar₂DAB) ligands, and Pt analogues of these systems have been reported by several groups.^{12–16,30} Our initial reports^{17,18} have focused on derivatives of Ar₂DAB leading to potentially C_2 -symmetric metal–diimine chelate rings and characterization of their complexes. Herein we describe the synthesis, characterization, and reaction chemistry of a new cationic Pt(II) Ar₂DAB solvato complex, including an unprecedented ability among Pt(II) complexes to promote the polymerization of various α -olefins through a cationic polymerization mechanism.^{31,32}

The precursor to the unsymmetrical cationic complex is synthesized by a three-step procedure starting from commercially available 2-amino-3-methylbenzyl alcohol. Protection of the alcohol with a triisopropylsilyl (TIPS) group is followed by Schiff base condensation with glyoxal to form the desired ligand as a yellow microcrystalline solid in ca. 70% yield. Subsequent reaction of the ligand with *trans*-Pt(SMe₂)₂MeCl in refluxing dichloromethane results in formation of the purple chloromethyl complex (Ar₂DAB)Pt(Me)Cl (**1**) in ca. 90% yield. Complex **1** may then be reacted with AgBF₄ in acetonitrile to generate the cationic solvato complex **2** (eq 1). X-ray-quality crystals³³ of **2** were obtained by slow evaporation of an acetonitrile/benzene solution. The ORTEP diagram of **2** is shown in Figure 1 with the crystallographic parameters, bond distances, and bond angles summarized in the Supporting Information. The diffraction study shows that **2** exists as a distorted square-planar complex in which the silyl-ether groups

- (1) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663–681.
- (2) Drent, E.; van Broekhoven, J. A. M.; Budzelaar, P. H. M. *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 263–270.
- (3) Lai, T.-W.; Sen, A. *Organometallics* **1984**, *3*, 866–870.
- (4) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303–310.
- (5) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143–7144.
- (6) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049–4050.
- (7) Brookhart, M.; Rix, F. C.; DeSimone, J. M.; Barborak, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 5894–5895.
- (8) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415.
- (9) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664–11665.
- (10) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888–899.
- (11) Vrieze, K.; Groen, J. H.; Delis, J. G. P.; Elsevier, C. J.; van Leeuwen, P. W. N. M. *New J. Chem.* **1997**, *21*, 807–813.
- (12) van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706–720.
- (13) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1994**, *33*, 1521–1531.
- (14) van Asselt, R.; Elsevier, C. J.; Amatore, C.; Jutand, A. *Organometallics* **1997**, *16*, 317–328.
- (15) Baar, C. R.; Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 4329–4331.
- (16) Baar, C. R.; Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 32–40.
- (17) Yang, K.; Lachicotte, R. J.; Eisenberg, R. *Organometallics* **1997**, *16*, 5234–5243.
- (18) Yang, K.; Lachicotte, R. J.; Eisenberg, R. *Organometallics* **1998**, *17*, 5102–5113.
- (19) Fusto, M.; Giordano, F.; Orabona, I.; Ruffo, F. *Organometallics* **1997**, *16*, 5981–5987.
- (20) Ganis, P.; Orabona, I.; Ruffo, F.; Vitagliano, A. *Organometallics* **1998**, *17*, 2646–2650.
- (21) Labinger, J. A.; Herring, A. M.; Lyon, D. K.; Luinstra, G. A.; Bercaw, J. E. *Organometallics* **1993**, *12*, 895–905.
- (22) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **1994**, *13*, 755–756.

- (23) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *504*, 75–91.
- (24) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961–5976.
- (25) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848–849.
- (26) Holtcamp, M. W.; Neling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1998**, *270*, 467–478.
- (27) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235–10236.
- (28) Kushch, K. A.; Lavrushko, V. V.; Misharin, Y. S.; Moravsky, A. P.; Shilov, A. E. *New J. Chem.* **1983**, *7*, 729.
- (29) Goldshleger, N. F.; Eskova, V. V.; Shilov, A. E.; Shteinmann, A. A. *Zh. Fiz. Khim.* **1972**, *46*, 1353.
- (30) Johansson, L.; Olav, B. R.; Tilset, M. *J. Am. Chem. Soc.* **1999**, *121*, 1974–1975.
- (31) Wang, Q.; Baird, M. C. *Macromolecules* **1995**, *28*, 8021–8027.
- (32) Quyoun, R.; Wang, Q.; Tudoret, M.-J.; Baird, M. C.; Gillis, D. J. *J. Am. Chem. Soc.* **1994**, *116*, 6435–6436.
- (33) Crystal data for **2**: orange crystal with dimensions 0.40 × 0.30 × 0.18 mm, monoclinic, space group $P2_1/c$, $a = 10.4784(2)$ Å, $b = 22.2394(3)$ Å, $c = 19.5738(3)$ Å, $\beta = 90.42^\circ$, temperature -80°C , $Z = 4$, $R_1(F_o)_{\text{obsd}} = 4.18\%$, GOF = 1.063.

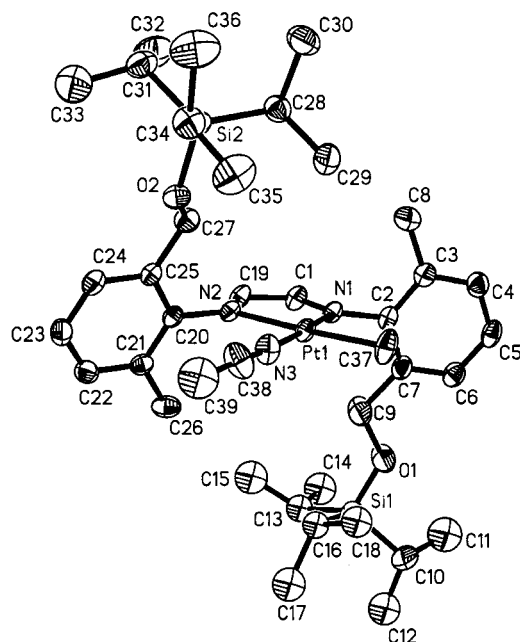
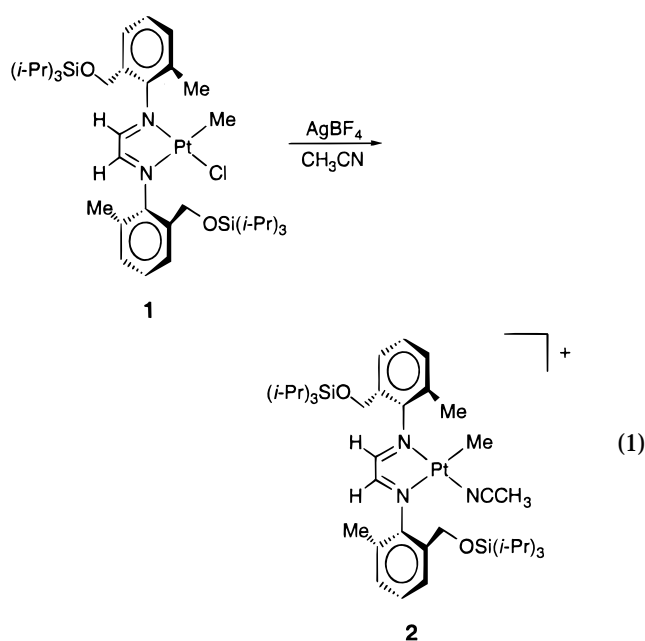


Figure 1. ORTEP diagram of complex **2**. Thermal ellipsoids are shown at 30% probability. The BF_4^- anion and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pt(1)–N(1) = 1.985(4); Pt(1)–N(2) = 2.098(3); Pt(1)–N(3) = 1.955(4); Pt(1)–C(37) = 2.043(5).



are oriented on opposite sides (anti) of the coordination plane. Due to the bite constraints of the DAB ligand, the N(1)–Pt–N(2) angle is 78.20(14)°. The chelate ring is essentially planar, with the imine aryl rings oriented nearly perpendicular to the coordination plane due to steric interactions between the chelate ring and the ortho aryl substituents. The bond distances and angles are similar to those of other reported square-planar platinum diimine complexes.^{17,18,34}

The lability of the coordinated acetonitrile in **2** has been examined by a series of exchange reactions. Ethylene, acrylonitrile,³⁵ benzonitrile, carbon monoxide,

(34) van der Poel, H.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1980**, *19*, 1145.

Table 1. Results of Ethyl Vinyl Ether Polymerizations Promoted by Complex **2 at 29 °C in Various Solvents over the Period of 3 days in the Absence of Light.**

solvent	triads obsd (%)			dyads obsd (%)		dyads calcd (%) ^a		M_w^b	M_n^b
	rr	mr	mm	m	r	m	r		
CD_3NO_2	27	45	28	50	50	51	49	3000	2.0
CDCl_3	13	52	35	61	39	61	39	8900	1.7
CD_2Cl_2	15	53	32	60	40	59	41	10500	1.4
$\text{C}_6\text{D}_5\text{Br}$	13	52	35	61	39	61	39	6000	1.9
$\text{CDCl}_3/\text{C}_6\text{D}_5\text{CD}_3^c$	12	47	41	64	36	65	35	5000	1.9

^a Calculated dyad values were determined by using the following equations: $(r) = (rr) + 1/2(mr)$; $(m) = (mm) + 1/2(mr)$. ^b Values determined by GPC relative to polystyrene calibration. ^c Solution was 1:8 v/v.

and dimethyl sulfide all displace acetonitrile. Additionally, a kinetics study of acetonitrile exchange using benzonitrile shows that exchange occurs via an *associative* pathway despite the steric influence of the ortho (triisopropylsilyloxy)methyl substituents that appear to hinder access to the Pt(II) center above and below the coordination plane. A detailed report of this study will be forthcoming,³⁶ while kinetic plots of the exchange reaction of **2** with benzonitrile are given in the Supporting Information.

The reaction³⁷ of complex **2** with ethyl vinyl ether (EVE) in CDCl_3 gave an unexpected result. New resonances were seen to grow in slowly at δ 3.62, 3.49, 1.98 (free acetonitrile), 1.60–1.80, and 1.20. When an excess of EVE was employed in the reaction system, the intensities of the new resonances continued to increase while the olefin was eventually consumed. During the course of the reaction, no new vinyl resonances corresponding to Pt coordinated olefin were observed. From the reaction mixture, an oily residue was isolated, the ^1H NMR spectrum of which was virtually identical with that of a polyEVE standard obtained from Aldrich. Additionally, a GPC of the oil from a reaction done at 29 °C in CDCl_3 demonstrated a M_w value of ca. 8900 with a polydispersity of 1.7. A $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the product oil allowed for the determination of polymer tacticity based on the method described by Matsuzaki et al.³⁸ Examination of the α -CHO and β - CH_2 multiplets gave a triad distribution—i.e., *mm*, *mr*, and *rr*—of 35, 52, and 13%, respectively (see Table 1), leading to the conclusion that the polyEVE made under these reaction conditions is a random polymer with slight isotactic character. The absence of major stereoregularity suggested that **2** was serving as the initiator of polymerization and not as the site of chain propagation.

Further experiments to probe the efficacy and mechanism of **2** as a catalyst or promoter of polymerization were carried out using related substrates. Two isomers

(35) Coordination of acrylonitrile is most likely occurring through nitrogen, vs being olefin bound, as is indicated by the ca. 70 cm^{-1} shift of the ν_{CN} stretch seen in the IR. Similarly, the corresponding complex from ref 18 most likely demonstrates this manner of coordination.

(36) Albietz, P. J.; Yang, K.; Lachicotte, R. J.; Eisenberg, R. Unpublished results.

(37) All of the monomer was consumed when reactions with EVE were examined. For 2,3-DHF and NVC, some of the unreacted monomer remained. Control experiments were conducted in the absence of **2** for all of the polymerizations. In those experiments, no polymer was observed.

(38) Matsuzaki, K.; Ito, H.; Kawamura, T.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *11*, 971–987.

of dihydrofuran (DHF), 2,3 and 2,5, serve as excellent probes of the polymerization mechanism. If the mechanism is one of cationic initiation by **2** followed by carbocation propagation on the polymer chain, then one would expect polymerization only for 2,3-DHF, where the propagating cation can be stabilized by the furan oxygen. Indeed, this was found to be the case. When complex **2** was allowed to react with either of the two DHF isomers, oligomer³⁷ was observed only for 2,3-DHF. The isolated oil had an M_w value of ca. 300 and a polydispersity of 1.1. From the ¹H NMR spectrum, it was evident that most of the formed oligomer was due to head-to-tail addition of the olefinic carbons. However, weak resonances were present in the range of δ 4.8–5.5, indicating the occurrence of a small degree of ring-opening oligomerization.³⁹

Polymerization of the electron-rich olefin *N*-vinylcarbazole was also examined. Its polymerization typically proceeds via cationic or free radical initiation and not by coordination/insertion processes. The reaction of **2** with 300 equiv of NVC at room temperature in CDCl₃ with the rigorous exclusion of light results in the formation of polyNVC.³⁷ After workup, the polymer product is a white solid that demonstrates relatively low solubility. Molecular weight determinations showed that the polyNVC had an M_w value of ca. 23 000 with an $M_w/M_n = 3.1$. Additionally, determination of the T_g value (220 °C) from a DSC analysis indicated that 62% of the dyads within the polymer were syndiotactic.^{40,41}

Another probe of polymerization mechanism is solvent effects. For cationic polymerizations, solvation of the propagating charge and the influence of solvent on charge-stabilizing structures and conformations can be substantial.^{41,42} Table 1 summarizes the results of tacticity analyses and M_w and polydispersity determinations obtained in different solvents for polyEVE using **2**. The tacticity analysis for the product obtained in CD₃-NO₂ reveals a 1:2:1 distribution of triads and a 1:1 distribution of dyads consistent with completely atactic polymer, as would be expected from a system in which the propagating carbocation is well-solvated. The polymer products from reactions run in CDCl₃, CD₂Cl₂, and C₆D₅Br are similar to each other and exhibit an increase

in isotactic character. Finally, for a reaction run in CDCl₃/C₆H₅CD₃ (1:8 v/v), the amount of isotactic character increases again. These results can be understood as arising from the greater importance of a charge-stabilizing conformation in less polar media during the polymerization process.⁴³

It has been reported by Loontjens et al.⁴⁴ that cationic polymerizations quenched with methanol followed by a water extraction show resonances near 9 ppm due to aldehydic end groups. An end group analysis of the polyEVE samples that were prepared using **2** and were worked up in this manner exhibited a weak resonance at ca. δ 9.8. This observation is thus consistent with a carbocation mechanism for the reaction. While the mechanism cannot be unambiguously proven, the results of the experiments discussed above are clearly consistent with cationic polymerization.

In summary, a new diaryldiazabutadiene ligand and a cationic Pt(II) methyl complex containing it (**2**) have been prepared. Complex **2** has been characterized crystallographically and shown to possess a *C*₂-symmetric metal–Ar₂DAB chelate structure. The complex undergoes exchange reactions that, despite the bulk of ortho aryl substituents, proceed in an associative manner. Complex **2** functions as a promoter for polymerization of vinyl ethers and *N*-vinylcarbazole that proceeds by a cationic mechanism. The ability to initiate this type of reaction using a Pt(II) complex has not been described previously and indicates an interesting electrophilic chemistry for cationic Pt(Ar₂DAB) systems. Recent results by Tilset on C–H activation by a cationic Pt(Ar₂DAB) complex further support this notion.³⁰

Acknowledgment. We thank the National Science Foundation (Grant CHE 97-29311) for support of this work. We also wish to acknowledge Dr. Rene J. Lachicotte for help in the crystal structure determination.

Supporting Information Available: Text giving experimental details, including all of the pertinent crystallographic information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM9903947

(39) Nuyken, O.; Aechtner, S. *Polym. Bull.* **1992**, *28*, 117–122.

(40) According to $(T_g - 399)(1 - X_2) + (T_g - 549) \times X_2 = 0$.

(41) Terrell, D.; Evers, F. *J. Polym. Sci.* **1982**, *20*, 2529–2543.

(42) Deffieux, A.; Subira, F.; Stannett, V. T. *Polymer* **1984**, *25*, 1131–1135.

(43) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley-Interscience: New York, Chichester, Brisbane, Toronto, and Singapore, 1991.

(44) Loontjens, T.; Derks, F.; Kleuskens, E. *Polym. Bull.* **1992**, *27*, 519–526.