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Catalytic Copolymerization of CO and Ethylene with a Charge Neutral Palladium(II) Zwitterion

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Received September 6, 2001

Late transition-metal polymerization catalysts currently enjoy widespread scrutiny in academia and industry,[1] partly because their low oxophilicity relative to early metal systems is desirable for polar comonomer incorporation.[2] The cationic polymerization systems are frequently generated by methide or halide abstraction with an activator such as a Lewis acidic borane.[3] We are pursuing an alternate approach whereby charge-neutral zwitterions incorporating a borate counteranion might themselves serve as polymerization catalysts.[4,5] Aside from eliminating the need for a cocatalyst, one might anticipate significant differences between zwitterionic and traditionally cationic systems due to (i) differences in their relative electrophilicities, (ii) differences in donor ligand lability, and (iii) reduced or completely eliminated ion-pairing effects in the zwitterionic systems. To begin to understand the utility of zwitterionic systems in polymerization catalysis, well-defined comparative model studies are required.[6]

In this communication, we describe a zwitterionic palladium(II) alkyl complex supported by the anionic ligand $[Ph_2B(CH_2PPh_2)_2]^-$ (abbreviated as $[Ph_2BP_2]$).[7] This system serves as a charge neutral relative to the highly active class of cationic, phosphine-supported palladium CO/ethylene copolymerization catalysts such as $[(dppp)Pd(Me)(solv)]^+$ (dppp = bis-diphenyl(phosphino)propane)).[8,9] We specifically address whether a related zwitterionic palladium system is active for CO and ethylene copolymerization by comparing its reactivity to that of cationic systems supported by structurally similar bidentate phosphines (Figure 1). Notably, neutral group 10 systems supported by anionic LX-type ligands are generally regarded as poor catalysts for CO/ethylene copolymerization.[8b,10]

Preparation of the target palladium alkyl complex proceeds first by reaction of an acetonitrile solution of the bis(phosphino)borate ligand, $[ASN][Ph_2BP_2]$ (ASN = 5-azonia-spiro[4.4]nonane),[7] with a benzene solution of $(tmeda)PdMe_2$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). The resulting product, $[ASN][(Ph_2BP_2)PdMe_2]$ (**1**), is then protonated by the ammonium salt $[HN^iPr_2Et][BPh_4]$ to cleanly generate the target zwitterion, $[Ph_2BP_2]PdMe(THF)$ (**2**), as a light-peach solid (Scheme 1).

With the solvento adduct **2** in hand, we examined the scope of its reactivity under CO and ethylene gas. A light yellow solution results when a dilute THF solution (ca. 10 μM) of **2** is exposed to a CO atmosphere. The unstable product, $[Ph_2BP_2]Pd(C(O)Me)(CO)$ (**3**), is related to a cationic derivative, $[(dppp)Pd(C(O)Me)(CO)][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$, recently reported by Brookhart and coworkers.[11] On the basis of their relative carbonyl stretching frequencies, it is clear that the palladium center of the zwitterion is more electron-rich than in the cationic derivative.[12] At 30 psi of CO and 30 psi of ethylene, strictly alternating polyketone material rapidly precipitates from solution (established by ^{13}C NMR and MALDI-TOF). The activity of catalyst **2** was examined at higher pressures (200 psi, vide infra), and calculated TON values (kg polymer mol^{-1} catalyst h^{-1}) establish that it is a very active catalyst for polyketone production at room temperature (Table 1).

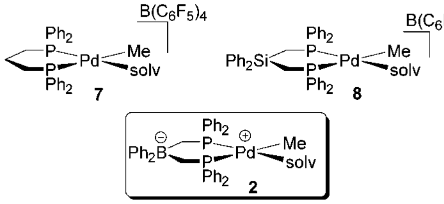

Figure 1. Comparing a neutral palladium zwitterion with its prototypical cationic relatives.

Scheme 1

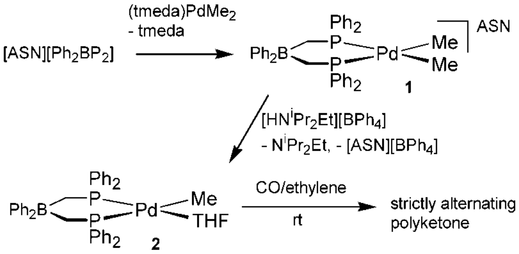

Table 1. Copolymerization Results for Catalysts **2**, **7**, and **8**[a]

cat.	activity (TON)[b]	yield (g polymer)[c]	M_w (10^3)[d]	M_n (10^3)[d]	M_w/M_n
2	39 ± 1	0.36 ± 0.01	138 ± 1	112 ± 3	1.3
7	35 ± 2	0.32 ± 0.02	130 ± 1	99 ± 2	1.3
8	45 ± 1	0.42 ± 0.01	190 ± 1	130 ± 5	1.5

[a] Conditions: 9.3×10^{-6} mol Pd catalyst in 10 mL THF; 100 psi CO; 100 psi ethylene; 23 °C; 1 h. [b] TON values are expressed as kg of polymer per mol catalyst per h. [c] Average mass of polymer obtained from eight independent runs. [d] Determined by GPC using polystyrene standards for calibration (1,3-cresol; 1 mL/min; 120 °C; duplicate runs).

Interestingly, the reactivity of catalyst **2** with CO gas, in the absence of ethylene, is concentration-dependent. At high concentrations of **2** (ca. 20 mM), exposure to an atmosphere of CO produces an orange solution (^{31}P NMR, singlet at 22 ppm),[13] which turns red (two doublets at 11 and 30 ppm) upon replacing the CO atmosphere with dinitrogen. The final red product is accessible by other routes (vide infra), and its crystallographic characterization establishes it to be the dimeric Pd(I) complex, $\{[Ph_2BP_2]Pd\}_2$ (**4**),[14,15] shown in Scheme 2. An alternative method for cleanly generating dimeric **4** results from exposure of **2** to ethylene gas in the absence of CO. In this case, the color change to red is rapid. Monitoring this transformation under ethylene at low temperature (from −78 to −10 °C) establishes one observable intermediate, assigned as an insertion product, $[Ph_2BP_2]Pd(C_2H_5)(H_2C{=}CH_2)$ (**5**). A related cationic species, $[(dppp)Pd(C_2H_5)(H_2C{=}CH_2)][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$, has also been reported by Brookhart and coworkers.[11] Storage of intermediate **5** at −10 °C under excess

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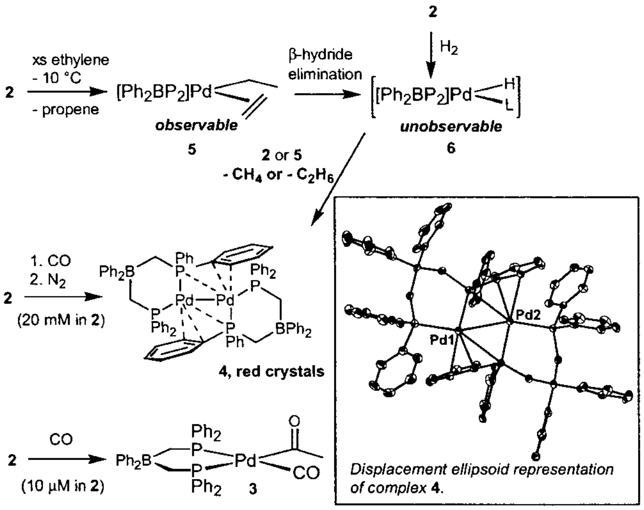
10.1021/ja017011s CCC: $22.00

Scheme 2



ethylene effects the catalytic production of butenes. On warming, the only new species detectable by ^{31}P NMR is the red dimer **4**. The expected product of β-hydride elimination, [Ph$_2$BP$_2$]Pd(H)(L) (**6**) (L = THF or ethylene), was not observed. Furthermore, an independent attempt to generate the hydride **6** by addition of H_2 to **2**, while generating dimeric **4** quantitatively, offered no evidence for a detectable hydride intermediate. Considered collectively, the data suggests that the conversion of **2** to **4** under ethylene may occur as follows (Scheme 2): initial ethylene insertion and rapid β-hydride elimination, followed by a second ethylene insertion to give the observable intermediate **5**. Intermediate **5** undergoes further chemistry with ethylene to generate butenes catalytically. At higher temperatures, a bimolecular path competes in which the unobservable hydride **6**, generated by β-hydride elimination, reacts with a palladium alkyl, such as **5**, to produce alkane and the dimeric palladium(I) species **4**. Notably, gas analysis of a reaction mixture from the conversion of **2** to **4** under ethylene showed no evidence for hydrogen production. Bimolecular loss of H_2 from a hydride intermediate such as **6** does not occur.

Having established some of the comparative reaction chemistry between charge neutral **2** and its cationic dppp counterpart, [(dppp)Pd(Me)(solv)][B(C$_6$F$_5$)$_4$], we sought to compare their activities for CO/ethylene copolymerization. The THF adduct complex, [(dppp)Pd(Me)(THF)][B(C$_6$F$_5$)$_4$] (**7**), was thus prepared, and its copolymerization activity was measured (Table 1). To our surprise, under analogous conditions, zwitterionic **2** proved to be a slightly better copolymerization catalyst (Table 1). To examine whether the slightly increased activity and higher-weight polymers of the [Ph$_2$BP$_2$] system were perhaps due to the difference in relative charge between the palladium centers in **2** and **7**, we sought a second comparison. A cationic complex that is structurally similar to neutral **2**, [(Ph$_2$SiP$_2$)Pd(Me)(THF)][B(C$_6$F$_5$)$_4$] (**8**), was prepared using the neutral phosphine chelate Ph$_2$Si(CH$_2$PPh$_2$)$_2$ (abbreviated as (Ph$_2$SiP$_2$)).[16] Under analogous conditions, cationic **8** proved to be a slightly better catalyst than zwitterionic **2** (Table 1), indicating that the phenyl substituents incorporated within the ligand backbones of **2** and **8** may also contribute to slight differences in reactivity by comparison to the dppp system **7**. Likewise, others have observed significant increases in activity for CO copolymerization with ethylene and propene by incorporating methyl groups onto the central carbon of bis(phosphino)propane ligands.[17,18]

In summary, the zwitterionic Pd(II) complex **2** is a very active catalyst for the copolymerization of CO and ethylene at ambient temperature. Most significant is that a more electron-rich, zwitterionic [Ph$_2$BP$_2$] system is essentially as active as the conventional dppp and (Ph$_2$SiP$_2$) systems that are based upon cationic palladium. Ongoing work includes comparative kinetic studies of the elementary insertion processes relevant to polymerization for both cationic and zwitterionic palladium systems.[19]

Acknowledgment. We thank the NSF (CHE-0132216) and the Dreyfus Foundation for funding. Dr. Michael Day and Lawrence Henling are acknowledged for crystallographic assistance, Mona Shahgholi for MALDI-TOF, and Rapra Technology Limited for GPC analyses of polyketone.

Supporting Information Available: Experimental protocols; crystallographic data for complex **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Complex **3** shows two very intense bands at 1694 cm^{-1} {ν(C(*O*)Me} and 2108 cm^{-1} {ν(CO)} in CH$_2$Cl$_2$. The stretches reported for [(dppp)Pd(C(O)Me)(CO)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] in CH$_2$Cl$_2$ are 1715 cm^{-1} {ν(C(*O*)Me} and 2130 cm^{-1} {ν(CO)} (ref 11a).

(13) We suspect the orange species initially produced to be the dimeric palladium(I) species {[Ph$_2$BP$_2$]Pd(μ-CO)}$_2$.

(14) X-ray data for (**4**·3CH$_2$Cl$_2$), MW = 1594.38, red plate, collection temp = 98 K, monoclinic, space group = $P2_1/c$, a = 22.389(3) Å, b = 20.690(2) Å, c = 16.3816(18) Å, β = 104.361(5)°, V = 7265.2(14) Å^3, Z = 4, R_1 = 0.0606 [$I > 2\sigma(I)$], GOF = 2.522 (see Supporting Information).

(15) A related, dicationic species, [{(dppp)Pd}$_2$][OTf]$_2$, has been previously obtained by hydrogenation of (dppp)Pd(OTf)$_2$. See Budzelaar, P. H. M.; van Leeuwen, W. N. M.; Roobeek, C. F.; Orpen, G. A. *Organometallics* **1992**, *11*, 23−25.

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(18) According to ref 17c, exchanging the central CMe$_2$ unit for SiMe$_2$ in the bis(phosphino)propane ligand backbone does not significantly alter the copolymerization rate or the polymer molecular weight.

(19) For example, low-temperature measurement of the ethylene insertion rate for neutral [Ph$_2$BP$_2$]Pd(CH$_3$)(CH$_2$=CH$_2$) ($k_{obs} \approx 1.2 \times 10^{-4}$; −45.8 °C in CH$_2Cl_2$) is surprisingly similar to that reported for [(dppp)Pd(C(O)Me)(CO)][B(3,5-(CF$_3$)$_2$−C$_6$H$_3$)$_4$] (ref 11a) under analogous conditions ($k_{obs} \approx 4.9 \times 10^{-4}$; −45.6 °C).

JA017011S