New Imine−Phosphine Palladium Complexes Catalyze Copolymerization of CO−Ethylene and CO−Norbornylene and Provide Well-Characterized Stepwise Insertion Intermediates of Various Unsaturated Substrates

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Received March 30, 1999

Summary: New imine−phosphine palladium complexes [Pd(P−N)(CH$_3$)(CH$_3$CN)](BF$_4$) (P−N = o-(diphenylphosphino)-N-benzaldimine derivatives) are synthesized and are found to be active for copolymerization of CO−ethylene and CO−norbornylene, respectively. Stepwise addition of carbon monoxide and various olefins into the new complexes is investigated.

Insertion of unsaturated molecules into a metal−carbon bond is a fundamental step in palladium(II)-catalyzed copolymerization of carbon monoxide and olefins.[1,2] Among the studied systems, catalysts are confined to either bidentate phosphine[3] and imine[4] or monodentate phosphine.[5] Although the soft and hard donor natures of phosphorus and nitrogen are known to bind Pd in a unique way, the imine−phosphine ligands, in which imine acts as a weak π-acceptor and phosphine as a good σ-donor, have not been well explored. The importance of these ligands in Pd-based catalysis, however, is evident with some recent observation in copolymerization,[6] ethylene oligomerization,[7] and cross-coupling reactions.[8]

From a mechanistic viewpoint, although the basic mechanism for chain propagation of CO/olefin copolymerization at the *cis* site of Pd(II) species has been established,[9] only the inserted intermediates with bulky and strained alkenes have been isolated.[10] The availability of β-hydrogen in simple alkenes which leads to decomposition is generally believed to be responsible for difficulty in isolating inserted intermediates. However, the success of ethylene[11] and propene[12] insertion into the Pd−acyl bond demonstrates that the steric requirement is not the sole factor for the stability of inserted products but the electronic factors governed by the auxiliary ligands also play an important role. We report in this communication that new imine−phosphine palladium complexes exhibit catalytic activity in copolymerization of ethylene−carbon monoxide (E−CO) and norbornylene−CO. Still, the controlled reactions of such imine−phosphine Pd(II) complexes uniquely provide the well-characterized intermediates of sequential insertion of CO with ethylene as well as functionalized olefins and alkynes.

Using the new imine−phosphine complex [Pd(P−N)(CH$_3$)(CH$_3$CN)](BF$_4$) (P−N = *o*-(diphenylphosphino)-*N*-benzaldimine (**1a**))[13] as catalyst, copolymerization of E−CO can be carried out under mild conditions. In one of the typical reactions, **1a** (22.0 mg, 0.03 mmol) with CO and ethylene (40 psi for each in a 200 mL autoclave) in 75 mL of CH$_2$Cl$_2$ at 75−80 °C produces 0.5 g of polyketone after 48 h.[14] Complex **1a** also affords the copolymerization of norbornylene−CO, but the fluori-

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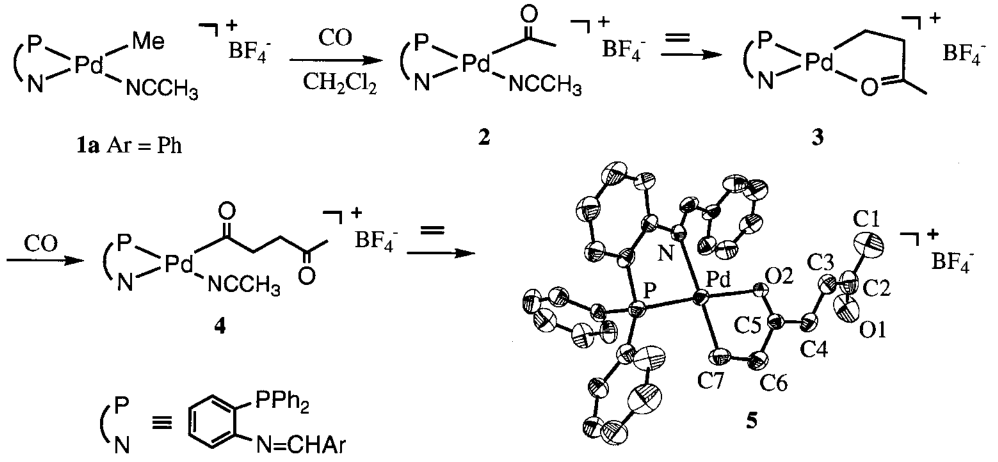
[13] Spectroscopic data for complex **1a**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.57 (d, $^3J_{\mathrm{P-H}}$ = 1.6 Hz, 3 H, PdC**H**$_3$), 1.81 (s, 3 H, Pd−NCC**H**$_3$), 7.09−7.57 (m, 16 H), 8.03 (m, 1 H), 8.23 (d, J = 7 Hz, 2 H), 9.26 (s, 1 H); ^{13}C NMR δ −2.1 (Pd-**C**H$_3$), 1.81 (NC**C**H$_3$); ^{31}P NMR δ 38.6.

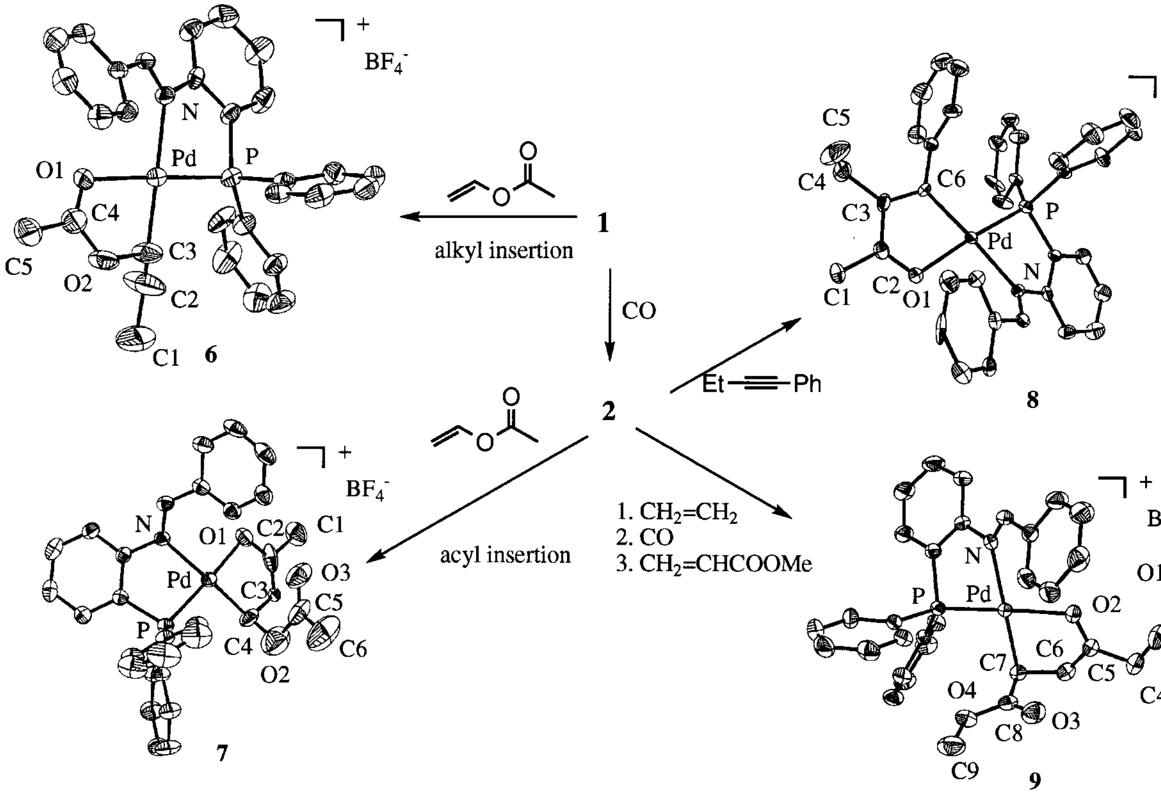
10.1021/om990222+ CCC: $18.00

Scheme 1. Stepwise CO/Ethylene Insertion into the Pd−C Bond[a]



[a] Numbering of aromatic carbons in ORTEP plot of cation **5** omitted for clarity. Selected bond distances (Å): Pd−C7 = 2.003(9), C5−O2 = 1.20(1), C2−O1 = 1.18(1).

Scheme 2. Results of Insertion Studies with Various Unsaturated Carbon−Carbon Substrates[a]



[a] Selected bond distances (Å): Pd−O1 = 2.088(8), Pd−C3 = 2.00(1), C4−O1 = 1.21(2) for **6**; Pd−O1 = 2.104(4), Pd−C4 = 2.000(6), C2−O1 = 1.283(9) for **7**; Pd−O1 = 2.080(4), Pd−C6 = 1.986(5), C2−O1 = 1.238(7), C3−C6 = 1.352(8) for **8**; Pd−O2 = 2.148(3), Pd−C7 = 2.058(4), C5−O2 = 1.245(5) for **9**.

nated-benzaldimine−phosphine derivative **1b** (Ar = p-$FC_6H_4^-$) provides a better yield. The resulting material is a white solid and is soluble in most organic solvents. The molecular weight was determined by GPC analysis ($M_n = 2500$, $M_w/M_n = 1.26$).[15]

At 25 °C, consecutive bubbling of CO and ethylene into the dichloromethane solution of **1a** uniquely resulted in the formation of **2**−**5** (Scheme 1).[16] Intermediates **3** and **5**, which have been isolated in the solid state, are stable. In contrast, acyl complexes **2** and **4** decompose slowly in solution as well as in the solid state. Appearance of a single ^{31}P signal for **2**−**5** at 18.4, 36.7, 19.9, and 36.8 ppm, respectively, suggests the quantitative formation of only one product in each step. The infrared spectrum of compound **5** shows two C=O stretching bands at 1712 and 1629 cm^{-1} corresponding to free and coordinated carbonyl groups, respectively.

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(14) CO/ethylene copolymer: IR(KBr) ν_{CO} 1691 cm^{-1}; ^{13}C NMR δ-($CDCl_3$ + CF_3COOH) 36.2, 213.8.

(15) In a 100 mL autoclave was placed **1b** (30 mg), norbornylene (350 mg), CH_2Cl_2 (20 mL), CH_3CN (50 mL), and CO (60 psi). When the mixture was heated at 50−60 °C for 24 h, the polymer was precipitated, which was washed with aqueous hydrochloric acid and hexane and dried (150 mg): ^1H NMR ($CDCl_3$) δ 3.30−1.90 (br, 4 H), 1.85−0.85 (br, 6 H); ^{13}C NMR δ 211.2−209 (br), 57.9−49.0 (Br), 40.8−36.4 (br), 30.9−27.0 (br); IR(KBr) ν_{CO} 1720 cm^{-1}.

Coordination of the C=O moiety to the palladium is well-documented via the formation of a five-membered chelate.[10] The possibility of six-membered chelation in compound **4** is ruled out on the basis of the ^{13}C NMR spectrum, which shows two peaks at 223.1 and 206.6 ppm corresponding to metal-bound acyl and free carbonyl groups, respectively. No shift in the latter peak is observed upon ethylene insertion leading to the formation of **5**. The chelated carbonyl carbon in **5**, however, is shifted downfield and appears at 231.3 ppm.

The X-ray single-crystal structure of **5** reveals its composition in detail. The coordinating alkyl group is *cis* to the phosphine, which is in agreement with the crystal structure data available for the Pd−imine−phosphine complex[7] and is considered to be the thermodynamically favored form.[17] However, the other isomer in which alkyl group is *trans* to phosphine, reported by Shirakawa and co-workers for the Pd complex,[8a] is not observed in our studies. In viewing the retention of stereochemistry through all insertion steps in **1a**, the new imine−phosphine ligands appear to stabilize the alkyl and acyl species in a selective manner. Complex **5** is stable at room temperature even in air without any decomposition for several days, indicating that the β-elimination process is suppressed. In fact, the similar intermediates for the copolymerization of norbornylene and carbon monoxide can be isolated.

To understand the relative migratory insertion rates for the present system, 0.013 mmol each of **1a** and **3** are dissolved in 0.5 mL of $CDCl_3$ (with 5% CD_3CN) under a CO atmosphere. The relative intensity of CO-inserted products (**2** and **4**) in the ^{31}P NMR spectrum suggests that the first insertion is 1.6 times faster than the second insertion. Similarly, under an ethylene atmosphere the relative consumption (disappearance) of intensity of ^{31}P signals corresponding to **2** and **4** shows that the first and second ethylene insertion rates are basically the same. The absence of any CO insertion for **3** in $CDCl_3$ suggests that releasing the chelation via the dissociation of the coordinated carbonyl moiety should be a prerequisite for CO insertion. Further evidence is that addition of the limited amount of CH_3CN facilitates CO insertion. Presumably acetonitrile, even a stronger ligand than CO, significantly stabilizes the CO-insertion intermediates. This also explains the slightly faster carbonylation in **1a**, where there is no such chelation.

Besides ethylene, other substituted olefins and alkynes undergo similar insertion reactions with such new imine−phosphine complexes, which are summarized in Scheme 2.[18] Vinyl acetate is found to undergo alkyl migration with **1a** and acyl migration with **2** to yield the insertion products **6** and **7**, respectively. In both cases, the insertion takes place at the terminal carbon of the olefin. Insertion of ethylphenylacetylene into the metal−acyl bond proceeds regioselectively at room temperature in dichloromethane solution to produce **8**. Although the insertion of the alkyne into a Pd−acyl bond is well-documented,[19] the intermolecular insertion of substituted acetylene into a Pd−acyl bond with exclusive regioselectivity is unprecedented. Even a consecutive insertion of ethylene, carbon monoxide, and methyl acrylate is accomplished under mild conditions to give **9** as the exclusive product. When the reactions are monitored by ^{31}P NMR, all are shown to proceed cleanly to yield a single product without the formation of the other possible stereoisomeric metal complexes in each instance, revealing again the unique features of these imine−phosphine complexes. All products in Scheme 2 have been characterized spectroscopically and further confirmed by X-ray single-crystal analyses.

In conclusion, the present results show that by using imine−phosphine ligands it is possible to stabilize the CO- and alkene- or alkyne-inserted products, which may thus serve as a catalyst for copolymerization with functionalized olefins and/or alkynes. The imine−phosphine complex also demonstrates its versatility toward different olefins in the insertion reaction. Subsequent insertion of various olefinic substrates into the M−C bond and their synthetic application are currently under investigation.

Acknowledgment. We thank the National Science Council (Grant No. NSC88-2113-M002-32) for financial support.

Supporting Information Available: Text giving experimental procedures and complete descriptions of the X-ray crystallographic structure determinations of **5**−**9**, including figures showing ORTEP plots and tables of crystal data, atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Spectroscopic data for complex **2**: IR (KBr) ν_{CO} 1707 cm^{-1}; ^{1}H NMR (500 MHz, −50 °C, $CDCl_3$) δ 1.76 (s, 3 H, $\mathrm{Pd{-}NCC}\mathbf{H}_3$), 1.99 (s, 3 H, $\mathrm{PdCOC}\mathbf{H}_3$), 7.20−7.69 (m, 16 H), 7.97 (m, 1 H), 8.28 (m, 2 H), 9.11 (s, 1 H); ^{13}C NMR δ 2.0 ($\mathrm{NC}\mathbf{C}\mathrm{H}_3$), 37.3 ($\mathrm{CO}\mathbf{C}\mathrm{H}_3$), 226.9 ($\mathrm{Pd}\mathbf{C}\mathrm{OCH}_3$); ^{31}P NMR δ 18.4. Complex **3**: IR (KBr) ν_{CO} 1636 cm^{-1} (coordinated); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.86 (t, $J = 7$ Hz, 2 H, $\mathrm{Pd{-}CH}_2$), 2.18 (s, 3 H, $\mathrm{COC}\mathbf{H}_3$), 3.10 (t, $J = 7$ Hz, 2 H), 7.23−7.69 (m, 17 H), 8.29 (m, 2 H), 9.15 (s, 1 H); ^{13}C NMR δ 21.6 ($\mathrm{Pd}\mathbf{C}\mathrm{H}_2$), 27.5 ($\mathrm{CO}\mathbf{C}\mathrm{H}_3$), 50.4 ($\mathrm{Pd}\mathbf{C}\mathrm{H}_2$), 232.9 ($\mathbf{C}\mathrm{OCH}_3$); ^{31}P NMR δ 36.7. Complex **4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77 (s, 3 H, $\mathrm{PdNCC}\mathbf{H}_3$), 1.94 (s, 3 H, $\mathrm{COC}\mathbf{H}_3$), 2.26 (br, 2 H, $\mathrm{PdCOC}\mathbf{H}_2$), 2.72 (br, 2 H), 7.19−7.69 (m, 16 H), 7.89 (1 H), 8.26 (2 H), 9.07 (s, 1 H); ^{13}C NMR δ 29.3 ($\mathrm{CO}\mathbf{C}\mathrm{H}_3$), 37.4 ($\mathrm{CO}\mathbf{C}\mathrm{H}_2$), 44.5 ($\mathrm{PdCO}\mathbf{C}\mathrm{H}_2$), 206.6 ($\mathbf{C}\mathrm{OCH}_3$), 223.1 ($\mathrm{Pd}\mathbf{C}\mathrm{O}$); ^{31}P NMR δ 19.9. Complex **5**: IR (KBr) ν_{CO} 1712 (free), 1629 (coordinated) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.89 (m, 5 H, $\mathrm{COC}\mathbf{H}_3 + \mathrm{PdCOC}\mathbf{H}_2$), 2.32 (t, $J = 7$ Hz, 2 H), 2.77 (t, $J = 7$ Hz, 2 H), 3.03 (t, $J = 7$ Hz, 2 H), 7.18−7.95 (m, 17 H), 8.30 (m, 2 H), 9.20 (s, 1 H); ^{13}C NMR δ 20.7 ($\mathrm{Pd}\mathbf{C}\mathrm{H}_2$), 29.1 ($\mathrm{CO}\mathbf{C}\mathrm{H}_3$), 33.7 ($\mathrm{CO}\mathbf{C}\mathrm{H}_2$), 36.7 ($\mathrm{CO}\mathbf{C}\mathrm{H}_3$), 48.9 ($\mathrm{Pd}\mathbf{C}\mathrm{H}_2\mathrm{CH}_3$), 206.3 ($\mathbf{C}\mathrm{OCH}_3$), 231.3 ($\mathrm{CH}_2\mathbf{C}\mathrm{OCH}_2$); ^{31}P NMR δ 36.8.

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[18] Selective spectral data for **6**−**9** are as follows. Complex **6**: IR (KBr) ν_{CO} 1612 cm^{-1}; ^{1}H NMR δ 1.04 (s, 3 H, $-\mathrm{C}\mathbf{H}_3$), 1.59 (m, 2 H, $-\mathrm{C}\mathbf{H}_2-$), 2.0 (s, 3H, $\mathrm{COC}\mathbf{H}_3$), 5.27 (m, 1 H, $\mathrm{PdC}\mathbf{H}-$); ^{31}P NMR δ 34.7. Complex **7**: IR (KBr) ν_{CO} 1713, 1610 cm^{-1}; ^{1}H NMR δ 1.92 (s, 3 H), 2.12 (s, 3 H), 2.78 (m, 2 H), 5.12 (m, 1 H, $\mathrm{PdC}\mathbf{H}-$); ^{31}P NMR δ 35.67. Complex **8**: IR (KBr) ν_{CO} 1607 cm^{-1}; ^{1}H NMR δ 0.77 (t, $J = 7$ Hz, 3 H, $-\mathrm{C}\mathbf{H}_3$), 1.80 (q, $J = 7$ Hz, 2 H, $-\mathrm{C}\mathbf{H}_2-$), 2.08 (s, 3 H, $\mathrm{COC}\mathbf{H}_3$); ^{31}P NMR δ 38.9. Complex **9**: IR (KBr) ν_{CO} 1723, 1696, 1623 cm^{-1}; ^{1}H NMR δ 1.85 (s, 3 H, $\mathrm{COC}\mathbf{H}_3$), 2.22 (m, 2 H, $-\mathrm{C}\mathbf{H}_2\mathrm{CHPd}$), 2.87 (m, 4 H, $-\mathrm{C}\mathbf{H}_2\mathrm{C}\mathbf{H}_2-$), 3.5 (m, 1 H, $\mathrm{PdC}\mathbf{H}-$); ^{31}P NMR δ 37.7.

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