Synthesis, Structures, and Reactions of Methylplatinum(II) and -palladium(II) Complexes Bearing Diphosphinidenecyclobutene Ligands (DPCB-Y)

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Dimethylplatinum(II) complexes coordinated with 1,2-diaryl-3,4-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobutenes (DPCB-Y; aryl = 4-methoxyphenyl, phenyl, 4-trifluoromethylphenyl, 3,5-bis(trifluoromethyl)phenyl] are prepared by ligand displacement of $Pt_2Me_4(\mu\text{-}SMe_2)_2$ with corresponding DPCB-Y, which is a novel class of ligands having sp^2-hybridized phosphorus as coordination atoms. Comparison of the NMR data with those of diimine- and diphosphine-coordinated analogues indicates intermediate magnitude of trans-influence of DPCB-Y ligands. This observation is supported by X-ray structural analysis. On the other hand, structural deviations of the coordinated DPCB-Y from free DPCB-Y suggest the occurrence of strong π-back-donation from the platinum to the ligands. Reflecting the strong π-back-donation, the ethylene protons in $[PtMe(\eta^2\text{-}C_2H_4)(DPCB\text{-}Y)]OTf$ appear at δ 5.22−5.02 in the ^1H NMR spectra, the chemical shifts of which are significantly lower than those so far reported for platinum(II) complexes (ca. δ 4.0) and comparable to that of free ethylene (δ 5.30). Ethylene polymerization using methylpalladium catalysts bearing DPCB-Y ligands is also reported.

Introduction

The coordination chemistry of phosphaalkenes has attracted a great deal of recent interest because of the unique electronic structures of C═P bonds.[1] Figure 1 compares frontier orbitals of carbon monoxide, imine, phosphaethene, and phosphine.[2] The π^* orbital level of the C═P bond is much lower than those of C≡O and C═N bonds. On the other hand, the nonbonding orbital including lone pair electrons on the phosphorus is situated at a high energy level, close to that of phosphine. Therefore, phosphaalkenes may effectively combine with transition metals by the σ-donation and π-back-donation interactions. Especially, reflecting the markedly low-lying π^* orbital, the π-back-donation should be remarkable, leading to rather unique structures and reactivities of phosphaalkene complexes.

In this context, we recently synthesized several palladium and platinum complexes bearing 1,2-diaryl-3,4-diphosphinidenecyclobutene ligands (DPCB-Y, Chart 1) and examined their chemical properties in catalytic systems.[3,4] It has been found that DPCB-Y-coordinated (π-ally)palladium complexes efficiently catalyze hydroamination of dienes and direct conversion of allylic alcohols to *N*- and *C*-allylation products.[3a,b] Methylpalladium complexes serve as ethylene-polymerization catalysts with high thermal stability.[3c] Furthermore, methylplatinum triflates having DPCB-Y ligands catalyze dehydrosilylation of a variety of ketones in almost

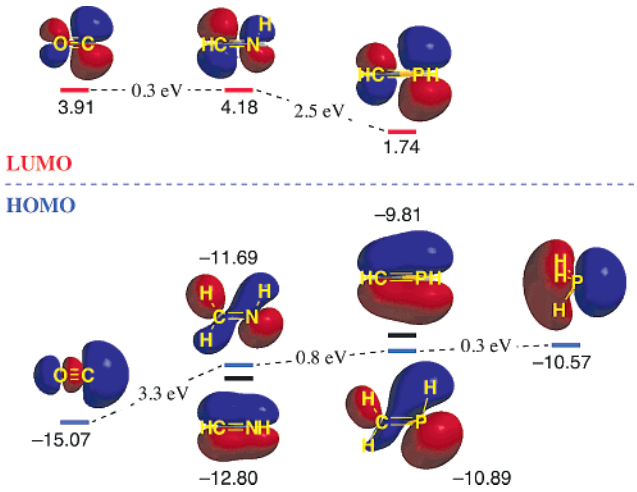

Figure 1. Schematic diagrams for the frontier orbitals of C≡O, H_2C═NH, H_2C═PH, and PH_3. The orbital levels were estimated by ab initio MO calculations (HF/6-311G(d)).

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(1) (a) Mathey, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1578. (b) Mathey, F. *J. Organomet. Chem.* **2002**, *646*, 15. (c) Yoshifuji, M. *Phosphorus Sulfur* **2002**, *177*, 1827. (d) Le Floch, P.; Mathey, F. *Coord. Chem. Rev.* **1998**, *179*−*180*, 771. (e) Yoshifuji, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3343.

(2) The ab initio calculations were carried out by Prof. S. Sakaki, Kyoto University, using the Gaussian 98 program and 6-311G(d) basis sets. The data for phosphaethene were consistent with those previously estimated by experimental and theoretical studies: Lacombe, S.; Gonbeau, D.; Cabioch, J.-L.; Pellerin, B.; Denis, J.-M.; Pfister-Guillouzo, G. *J. Am. Chem. Soc.* **1988**, *110*, 6964.

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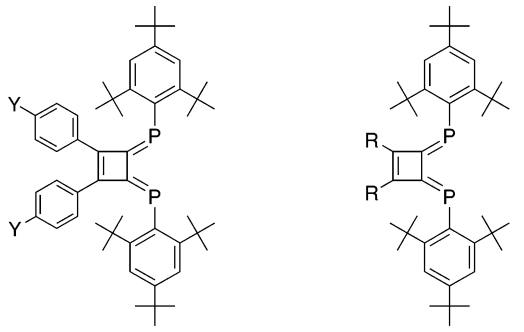
Chart 1



1a: Y = OMe [DPCB-OMe]
1b: Y = H [DPCB]
1c: Y = CF_3 [DPCB-CF_3]
1d: R = 3,5-$(CF_3)_2C_6H_3$ [DPCB-$(CF_3)_2$]
1e: R = H
1f: R = $SiMe_3$

perfect selectivities.[3d] In these catalyses, DPCB-Y complexes exhibit much higher reactivities than the corresponding diphosphine and diimine complexes with analogous structures.

There are two characteristic points commonly observed for DPCB-Y catalysts. First, the presence of phenyl groups at the 1- and 2-positions of the cyclobutene ring is of particular importance to gain high catalytic activities. Thus, the complexes without phenyl groups (i.e., those having **1e** and **1f** in Chart 1) are much less reactive and less stable in catalytic systems. Secondary, the catalytic activities are highly sensitive to the electronic nature of substituents Y on the phenyl groups, despite their rather remote positions from the metal center.

To clarify the origin of these unique features, detailed information about the electronic and geometrical structures of DPCB-Y complexes is desirable. We therefore prepared in this study a series of dimethyl- and monomethylplatinum complexes and examined them by NMR and/or X-ray diffraction analysis. The ^{195}Pt-coupling in NMR spectroscopy is a widely accepted probe for the nature of platinum−element bonds.[5] Syntheses and catalytic properties of related methylpalladium complexes in ethylene polymerization are also reported.[6]

Results and Discussion

Dimethylplatinum Complexes. The platinum complexes bearing four kinds of DPCB-Y ligands (**2a**−**d**) were prepared by ligand displacement of $[PtMe_2(\mu\text{-}SMe_2)]_2$[7] with **1a**−**d** in Et_2O at room temperature, respectively (Scheme 1). The use of Et_2O as a solvent was of particular importance for synthesizing the complexes in high yields. Thus, the synthetic reactions

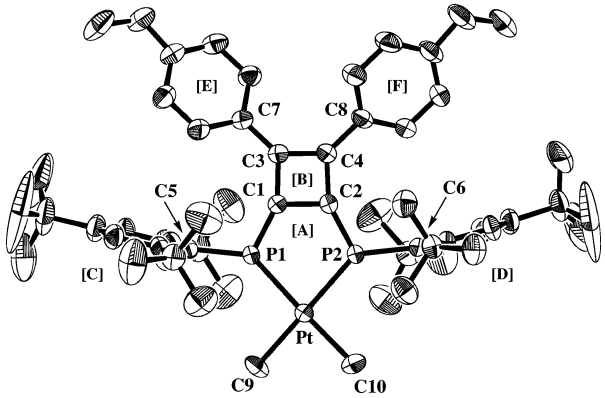
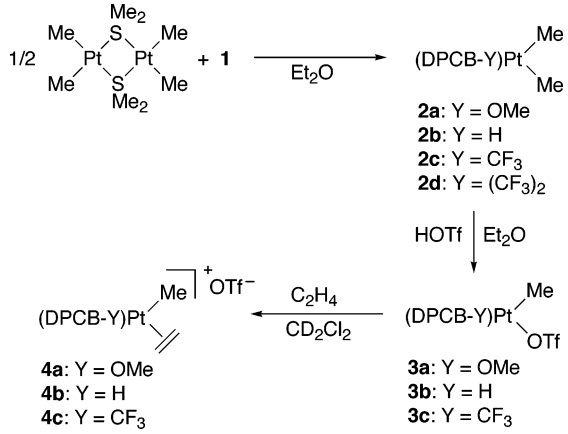


Figure 2. X-ray structure of **2a**. Hydrogen atoms are omitted for clarity.

Scheme 1



proceeded heterogeneously in Et_2O, and this condition was profitable to minimize undesirable side reactions leading to degradation of DPCB-Y ligands. The complexes were isolated as orange crystalline solids and identified by NMR spectroscopy and elemental analysis. Complexes **2a** and **2b** were further characterized by X-ray diffraction studies.[6]

Figure 2 illustrates an ORTEP diagram of **2a**, which adopts a square-planar configuration around the platinum. The coordination plane A is coplanar to the cyclobutene ring B but almost perpendicular to the aryl rings C and D on the phosphorus atoms.

Table 1 compares structural parameters of DPCB-Y ligands in **1a**, **2a**, and **2b**. The values given in square brackets show deviations from free DPCB (**1a**).[8] It is seen that C1−P1−C5 and C2−P2−C6 angles are expanded, whereas P1−C1−C2 and P2−C2−C1 angles are narrowed by the coordination. These changes may be attributed to directing effects associated with chelate formation. Notable variations are also found for C1−C2 and C3−C4 bonds of the cyclobutene ring. Thus, although the distances in free **1a** are roughly assignable to single and double bonds, respectively, the former is clearly shortened while the latter is elongated in the complexes. Furthermore, dihedral angles between cyclobutene ring B and phenyl rings E and F are significantly reduced by the coordination.

Figure 3 shows π^* orbitals of DPCB, which correspond to two LUMOs of the ligand.[9] The structural variations

(3) (a) Minami, T.; Okamoto, H.; Ikeda, S.; Tanaka, R.; Ozawa, F.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4501. (b) Ozawa, F.; Okamoto, H.; Kawagishi, S.; Yamamoto, S.; Minami, T.; Yoshifuji, M. *J. Am. Chem. Soc.* **2002**, *124*, 10968. (c) Ikeda, S.; Ohhata, F.; Miyoshi, M.; Tanaka, R.; Minami, T.; Ozawa, F.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4512. (d) Ozawa, F.; Yamamoto, S.; Kawagishi, S.; Hiraoka, M.; Ikeda, S.; Minami, T.; Ito, S.; Yoshifuji, M. *Chem. Lett.* **2001**, 972. (e) Toyota, K.; Masaki, K.; Abe, T.; Yoshifuji, M. *Chem. Lett.* **1995**, 221.

(4) Catalytic applications of sp^2-hybridized phosphorus compounds have been reviewed: Weber, L. *Angew. Chem., Int. Ed.* **2002**, *41*, 563.

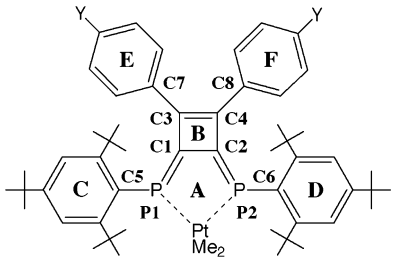
(5) Appleton, T. G.; Bennett, M. A. *J. Am. Chem. Soc.* **1978**, *17*, 738, and references therein.

(6) A portion of this study including the X-ray structure of **2b** (CCDC-147540) has been communicated.[3c]

(7) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.

(8) Appel, R.; Winkhause, V.; Knoch, F. *Chem. Ber.* **1987**, *120*, 243.

Table 1. Comparison of Bond Distances (Å) and Angles (deg) for DPCB-Y Ligands



description	DPCB (**1a**)	$PtMe_2$(DPCB-OMe) (**2a**)		$PtMe_2$(DPCB) (**2b**)	
C1−C2	1.535(8)	1.500(4)	[−2.3%]	1.498(5)	[−2.4%]
C3−C4	1.380(9)	1.406(4)	[+1.9%]	1.410(6)	[+2.2%]
C1−C3	1.467(10)	1.473(4)	[+0.4%]	1.480(4)	[+0.9%]
C2−C4	1.462	1.478(4)	[+1.1%]	1.480(4)	[+1.2%]
C3−C7	1.472(8)	1.451(4)	[−1.4%]	1.449(4)	[−1.6%]
C4−C8	1.487	1.456(4)	[−2.1%]	1.449(4)	[−2.6%]
P1−C1	1.690(8)	1.671(3)	[−1.1%]	1.669(3)	[−1.2%]
P2−C2	1.679	1.670(3)	[−0.5%]	1.669(3)	[−0.6%]
P1−C5	1.861(6)	1.832(3)	[−1.6%]	1.829(3)	[−1.7%]
P2−C6	1.871	1.834(3)	[−2.0%]	1.829(3)	[−2.2%]
C1−P1−C5	105.5(3)	111.3(1)	[+5.5%]	111.8(1)	[+6.0%]
C2−P2−C6	104.7	111.7(1)	[+6.7%]	111.8(1)	[+6.8%]
P1−C1−C2	124.8(4)	117.5(2)	[−5.8%]	117.3(1)	[−6.0%]
P2−C2−C1	125.0	117.6(2)	[−5.9%]	117.3(1)	[−6.2%]
C3−C4−C8	130.7	136.4(3)	[+4.2%]	136.7(2)	[+4.6%]
C4−C3−C7	133.7(7)	136.0(3)	[+1.7%]	136.7(2)	[+2.2%]
A−B	6.0	0.8(1)		1.4(1)	
A−C	99.8	95.71(8)		92.5(1)	
A−D	94.7	90.93(8)		92.5(1)	
B−E	40.0	25.2(2)		23.2(1)	
B−F	42.6	25.7(2)		23.2(1)	

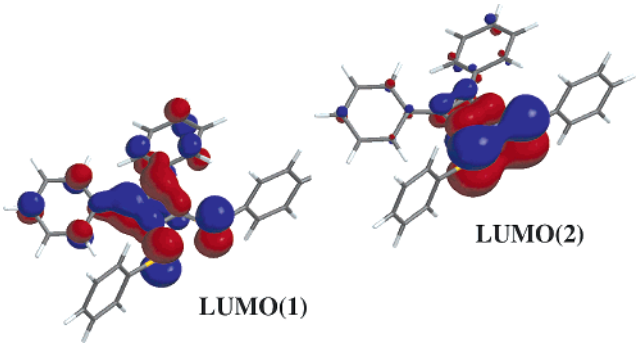


Figure 3. The π^* orbitals of DPCB.

described above are rationalized by assuming π-back-donation from platinum to these orbitals. Thus, the LUMO(1) with b_2 symmetry, which is distributed over the molecule including the diphosphinidenecyclobutene skeleton and the two phenyl groups on the cyclobutene ring, has an antibonding character between C3 and C4 atoms. On the other hand, the LUMO(2) with a_1 symmetry contains a bonding orbital between C1 and C2 atoms. Therefore, the π-back-donation causes elongation of the C3−C4 bond and shortening of the C1−C2 bond. Furthermore, the phenyl groups should adopt parallel orientations against the coordination plane to extend the π-conjugation system.

Table 2 compares structural parameters around the platinum for **2a**, **2b**, and related complexes.[10] The Me−Pt−Me angles of **2a** and **2b** are comparable to those of

Table 2. Comparison of Bond Distances (Å) and Angles (deg) for Dimethylplatinum(II) Complexes

compound	Pt−Me	Pt−L	Me−Pt−Me	L−Pt−L
[DPCB-Y complex]				
$PtMe_2$(DPCB-OMe) (**2a**)	2.088(4)	2.2945(7)	86.0(2)	83.33(3)
	2.073(3)	2.2878(8)		
$PtMe_2$(DPCB) (**2b**)	2.093(3)	2.2909(8)	85.1(2)	82.85(4)
[diimine complex]				
$PtMe_2$(Ani-DABD)[a]	2.061(4)	2.138(4)	85.6(2)	77.1(2)
	2.046(5)	2.113(4)		
$PtMe_2$(Ar*-DABD)[b]	2.059(3)	2.093(2)	86.9(1)	77.04(9)
	2.079(3)	2.112(2)		
[diphosphine complex]				
$PtMe_2$(DPPV)[c]	2.108(7)	2.246(2)	86.6(3)	86.01(7)
	2.112(6)	2.254(2)		

[a] Ani-DABD = 1,4-bis(4-methoxyphenyl)-1,4-diazabutadiene: ref 10a. [b] Ar*-DABD = 1,4-bis(2-methoxymethyl-4,6-di-*tert*-butylphenyl)-1,4-diazabutadiene: ref 10b. [c] DPPV = 1,2-bis(diphenylphosphino)ethylene: ref 10c.

the other complexes. On the other hand, the bite angles (L−Pt−L) are slightly smaller than that of the diphosphine complex but much larger than those of diimine complexes. The platinum−methyl carbon distances (Pt−Me) are intermediate between those of the diimine and diphosphine complexes. Thus, it is considered that the DPCB-Y ligands possess medium magnitude of trans-influence. In other words, DPCB-Y ligands are intermediate σ-donors between diimine and diphosphine ligands, and this observation is consistent with the orbital level of lone pair electrons of phosphaethene, which is between those of imine and phosphine (Figure 1).

(9) The orbital diagrams were generated by semiempirical MO calculations (PM3) using the Spartan program package (Wavefunction, Irvine, CA). The geometrical parameters for the DPCB skeleton were taken from the X-ray structure of **2b**, while the *t*-Bu groups on the PPh groups were omitted for simplicity.

(10) (a) Johansson, L.; Ryan, O. B.; Rømming, C.; Tilset, M. *Organometallics* **1998**, *17*, 3957. (b) Yang, K.; Lachicotte, R. J.; Eisenberg, R. *Organometallics* **1998**, *17*, 5102. (c) Smith, D. C., Jr.; Haar, C. M.; Stevens, E. D.; Nolan, S. P.; Marshall, W. J.; Moloy, K. G. *Organometallics* **2000**, *19*, 1427.

Table 3. Comparison of NMR Data for Dimethylplatinum(II) Complexes

compound	^{1}H NMR δ_{PtMe} ($^2J_{PtH}$)	^{13}C{^{1}H} NMR δ_{PtMe} ($^1J_{PtC}$)	^{31}P{^{1}H} NMR δ_P ($^1J_{PtP}$)	^{195}Pt{^{1}H} NMR δ_{Pt}[d]
[DPCB-Y complex]				
$PtMe_2$(DPCB-OMe) (**2a**)[a]	1.05 (80.2)	−2.0 (722)	164.7 (1594)	−3887[b]
$PtMe_2$(DPCB) (**2b**)[a]	1.06 (80.3)	−1.9 (723)	171.6 (1590)	−3847[b]
$PtMe_2$(DPCB-CF_3) (**2c**)[a]	1.13 (80.0)	−1.1 (721)	181.8 (1558)	−3774[b]
$PtMe_2$[DPCB-$(CF_3)_2$] (**2d**)[a]	1.02 (81.9)	−1.7 (711)	193.7 (1605)	*k*
[diimine complex]				
$PtMe_2$(Xyl-DABD)[b,e]	1.44 (87)	−13.9 (802)		−1452
$PtMe_2$(Dip-DABD)[b,f]	1.52 (86)	−13.7 (805)		−1344
$PtMe_2$(Tol-BIAN)[a,g]	1.47 (87.8)	−14.4 (808)		*k*
[diphosphine complex]				
$PtMe_2$(dppe)[a,h]	1.08 (71)[c]	1.0 (610)	54.0 (1783)	−4611
$PtMe_2$(dppp)[a,i]	0.57 (69)	5.0 (600)	3.2 (1767)	−4634
$PtMe_2$(dppv)[b,j]	0.67 (71)	*k*	56.8 (1779)	*k*
[DPCB-Y ligand]				
DPCB-OMe (**1a**)[a]			162.6	
DPCB (**1b**)[a]			169.5	
DPCB-CF_3 (**1c**)[a]			180.7	
DPCB-$(CF_3)_2$ (**1d**)[a]			192.4	

[a] In $CDCl_3$. [b] In CD_2Cl_2. [c] In C_6D_6. [d] Relative to K_2PtCl_4. [e] Xyl-DABD = 1,4-bis(2,6-dimethylphenyl)-1,4-diazabutadiene: ref 11a. [f] Dip-DABD = 1,4-bis(2,6-diisopropylphenyl)-1,4-diazabutadiene: ref 11a. [g] Tol-BIAN = bis(4-methylphenylimino)acenaphthene: ref 11b. [h] dppe = 1,2-bis(diphenylphosphino)ethane: refs 11c,d. [i] dppe = 1,2-bis(diphenylphosphino)ethane: refs 11c,d. [j] dppv = 1,2-bis(diphenylphosphino)ethylene: ref 10c. [k] Not measured or not reported.

Table 4. Comparison of NMR Data for Monomethylplatinum(II) Complexes

complex	^{1}H NMR δ_{PtMe} ($^2J_{PtH}$)	^{1}H NMR δ_{C2H4} ($^1J_{PtC}$)	^{13}C{^{1}H} NMR δ_{PtMe} ($^1J_{PtC}$)	^{13}C{^{1}H} NMR δ_{C2H4} ($^1J_{PtC}$)	^{31}P{^{1}H} NMR δ_{P1} ($^1J_{PtP}$)	^{31}P{^{1}H} NMR δ_{P2} ($^1J_{PtP}$)
PtMe(OTf)(DPCB-OMe) (**3a**)[a]	1.17 (*c*)		4.7 (558)		89.2 (6792)	176.6 (1626)
PtMe(OTf)(DPCB) (**3b**)[a]	1.06 (*c*)		5.0 (545)		98.1 (6819)	186.2 (1618)
PtMe(OTf)(DPCB-CF_3) (**3c**)[a]	1.29 (*c*)		5.8 (545)		107.6 (6821)	194.1 (1604)
[PtMe(ethylene)(DPCB-OMe)]OTf (**4a**)[a]	1.08 (60.4)	5.02 (56.8)	5.1 (505)	88.2 (105)	126.5 (4879)	153.4 (1528)
[PtMe(ethylene)(DPCB)]OTf (**4b**)[a]	1.12 (61.0)	5.11 (57.1)	5.2 (502)	89.7 (103)	133.5 (4919)	161.9 (1520)
[PtMe(ethylene)(DPCB-CF_3)]OTf (**4c**)[a]	1.22 (60.5)	5.22 (58.9)	5.6 (489)	91.2 (100)	142.0 (4980)	172.4 (1496)
[PtMe(ethylene)(phen)]BF_4[b]	0.93 (71)	4.54 (br)	−6.7 (673)	71.3 (br)		
[PtMe(ethylene)(Dip-$DABD^{Me}$)]BF_4[b]	0.18 (70)	3.72 (br)	−4.7 (—)	73.8 (192)		
[PtMe(ethylene)(Det-$DABD^{Me}$)]BF_4[b]	0.13 (70)	3.68 (68)	−5.1 (660)	74.0 (190)		
[PtMe(ethylene)(Ph-$DABD^{Me}$)]BF_4[b]	0.20 (70)	3.71 (br)	−4.8 (660)	72.2 (br)		

[a] In CD_2Cl_2 at 20 °C. [b] In $CDCl_3$ at 25 °C. The data were taken from ref 12. phen = 1,10-phenathroline. Dip-$DABD^{Me}$ = 1,4-bis(2,6-diisopropylphenyl)-2,3-dimethyl-1,4-diazabutadiene. Det-$DABD^{Me}$ = 1,4-bis(2,6-diethylphenyl)-2,3-dimethyl-1,4-diazabutadiene. Ph-$DABD^{Me}$ = 1,4-diphenyl-2,3-dimethyl-1,4-diazabutadiene. [c] Not observed due to broadening.

We next examined NMR data listed in Table 3. The methyl proton signals of **2a**−**d** are observed as the $A_3A'_3$ part of an $A_3A'_3XX'$ spin system, as typically seen for *cis*-dimethylbis(phosphine)platinum(II) complexes. The $^2J_{PtH}$ values for these signals (80.0−81.9 Hz) are intermediate between those of diphosphine (ca. 70 Hz) and diimine (ca. 87 Hz) complexes.[11] Furthermore, the $^1J_{PtC}$ values observed for the PtMe carbon signals (711−723 Hz) are in the middle of the diphosphine (ca. 600 Hz) and diimine (ca. 800 Hz) complexes. Thus, the intermediate magnitude of trans-influence has been evidenced by NMR spectroscopy as well. The ^{31}P NMR signals are shifted to lower fields in the order **2a** < **2b** < **2c** < **2d**, reflecting the variation in the chemical shifts of free DPCB-Y. The $^1J_{PtP}$ values are at ca. 1590 Hz, the value of which is somewhat smaller than those of diphosphine complexes (ca. 1780 Hz).

The ^{195}Pt{^{1}H} NMR spectra were observed for **2a**−**c** and compared with the data of diimine and diphosphine complexes. Complexes **2a**−**c** exhibited triplet signals due to the coupling with the two phosphorus nuclei. The chemical shifts were again intermediate between those of the diimine and diphosphine complexes. For the DPCB-Y complex series, the ^{195}Pt signals were gradually shifted downfield as the electron-withdrawing nature of Y increases: the chemical shifts showed a good Hammett correlation with the σ_p values of Y (r^2 = 0.999): $\delta_{Pt} = 139(3)\sigma_p - 3848(1)$.

Monomethylplatinum(II) Complexes. It has been found that DPCB-Y ligands possess intermediate ability of σ-donation between diimine and diphosphine ligands. On the other hand, the structural variations between coordinated and uncoordinated ligands have suggested the occurrence of π-back-donation to a considerable extent. For evaluating further the π-accepting ability of DPCB-Y ligands, we next introduced ethylene onto $[PtMe(DPCB\text{-}Y)]^+OTf^-$ moieties and examined them by NMR spectroscopy. Thus, PtMe(OTf)(DPCB-Y) (**3a**−**c**) were synthesized from **2a**−**c** and treated with ethylene in CD_2Cl_2 (Scheme 1). The resulting ethylene complexes (**4a**−**c**) were oily materials at ambient temperature and could not be isolated as analytically pure compounds, but their formations were unequivocally confirmed by NMR spectroscopy (see Experimental Section).

Table 4 lists the selected NMR data for **4a**−**c**, together with the data for **3a**−**c** and related diimine complexes. As typically seen for the diimine complexes,[12]

(11) (a) Scollard, J. D.; Day, M.; Labinger. J. A.; Bercaw, J. E. *Helv. Chim. Acta* **2001**, *84*, 3247. (b) van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706. (c) Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439. (d) Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1979**, *169*, 107.

the ^{1}H NMR signal of ethylene coordinated to a Pt(II) center generally appears at around δ 4.0,[10b,13] the values of which are significantly higher than that of free ethylene (δ 5.30). This is due to the π-back-donation from platinum to ethylene. Similarly, the ethylene carbon signal appears at a much higher field (δ 63−78) than that of free ethylene (δ 123.3). On the other hand, the ^{1}H and ^{13}C NMR signals of ethylene ligands in **4a**−**c** are observed at exceptionally low magnetic fields. The ^{1}H NMR chemical shifts, very close to free ethylene, are particularly remarkable. Although we may not exclude the possibility that the ring current of 2,4,6-tri-*tert*-butylphenyl groups causes downfield shifts of the ethylene proton signals, since the diimine analogues with similar geometrical structures show the signals in normal regions, the unusual chemical shifts observed for **4a**−**c** should be attributed to extremely low dπ-electron density on the platinum, caused by DPCB-Y ligands. It is also clear that the signals are shifted to lower fields as the electron-withdrawing ability of para-substituents Y increases. Thus, these observations are fully consistent with the occurrence of strong π-back-donation from platinum to DPCB-Y, which is sensitive to the electronic nature of Y.

Ethylene Polymerization Using Monomethylpalladium(II) Complexes. Considering the structural resemblance between diphosphinidenecyclobutene and diimine ligands, application of DPCB-Y ligands to the Brookhart catalysts for ethylene polymerization is an interesting subject.[14,15] Although the methylplatinum complexes described above were totally inactive, the palladium analogues successfully catalyzed the polymerization. Since the results with **1b**, **1e**, and **1f** as the ligands have been reported,[3a] we herein deal with the effects of substituents Y on the catalytic activity of DPCB-Y complexes.

Dimethylpalladium complexes $PdMe_2$(DPCB-Y) (**5a**−**d**) were prepared by the reactions of $PdMe_2$(tmeda)[16] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) or $PdMe_2$(cod)[17] (cod = 1,5-cyclooctadiene) with **1a**−**d** in Et_2O. The complexes were treated with 1 molar quantity of $H(OEt_2)_2BAr_4$[18] (Ar = 3,5-bis(trifluoromethyl)phenyl) in chlorobenzene at room temperature and then heated at 70 °C under the pressure of ethylene (10 atm) for 1 h, affording a white precipitate of polyethylene. Table 5 summarizes the results. The catalytic activity increased in the order **5a** < **5b** < **5d** < **5c**. Thus, there is a tendency except for **5d** that electron-withdrawing substituents Y at the para positions of 1,2-phenyl groups enhance the catalytic activity. The reactions with **5c** and **5d** formed relatively high molecular weight polymers, while the molecular weight distributions are notably wide, indicating the participation of several active species.

Table 5. Ethylene Polymerization Catalyzed by Methylpalladium Complexes with DPCB-Y Ligands[a]

precursor complex	activity (kg/h·mol cat)	M_w[b]	M_w/M_n[b]
5a	104	13 000	7.1
5b	128	13 000	5.4
5c	210	43 000	23.7
5d	147	101 000	51.6

[a] Reactions were performed in chlorobenzene (20 mL) at 70 °C under the pressure of ethylene (10 atm) for 1 h using 10 μmol of catalysts generated from the precursor complexes and $H(OEt_2)_2BAr_4$ (Ar= 3,5-$(CF_3)_2C_6H_3$). [b] Determined by GPC based on polyethylene standards.

Conclusion

It has been confirmed that the DPCB-Y ligands with sp^2-hybridized phosphorus atoms exhibit a middle range of trans-influence as compared with diimines and diphosphines, showing moderate σ-donating ability of the ligands. On the other hand, the DPCB-Y ligands have been found to act as remarkably strong π-acceptors in the coordination sphere of platinum. The complexes possess widely spread π-conjugation systems, and the dπ-electron density of platinum is significantly affected by substituents Y. Therefore, it is possible to finely tune the electronic property of the platinum center by the choice of Y. These findings are consistent with the observations in catalytic reactions and serve as a basis of further applications of DPCB-Y ligands.

Experimental Section

General Considerations. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Nitrogen gas was dried by passing through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Varian Mercury 300 spectrometers: ^{1}H, 300.10 MHz; ^{13}C, 75.46 MHz; ^{31}P, 121.49 MHz; ^{195}Pt, 64.25 MHz. Chemical shifts are reported in δ (ppm), referenced to ^{1}H (of residual protons) and ^{13}C signals of deuterated solvents as internal standards or to ^{31}P and ^{195}Pt signals of 85% H_3PO_4 and K_2PtCl_4 in H_2O as external standards, respectively. GLC analysis was performed on a Shimadzu GC-14B instrument equipped with a FID detector and a CBP-1 capillary column (25 m × 0.25 mm). GPC analysis of polyethylene was performed on a Waters 150C system using polyethylene standards (1,2,4-trichlorobenzene, 145 °C). Elemental analysis was performed on a Perkin-Elmer 2400II CHN analyzer. Et_2O and toluene were dried over sodium benzophenone ketyl and distilled prior to use. CH_2Cl_2 and chlorobenzene were dried over CaH_2, distilled, and stored under a nitrogen atmosphere. CD_2Cl_2 and $CDCl_3$ were purified by passing through a short Al_2O_3 column and stored under a nitrogen atmosphere.

Preparation of DPCB-Y (1a−d). The ligands were synthesized by slightly modified literature methods.[8,19] The identification data are listed below except for **1b**, which is a

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(15) For related studies on ethylene polymerization using sp^2-hybridyzed phosphorus ligands, see: (a) Daugulis, A.; Brookhart, M.; White, P. S. *Organometallics* **2002**, *21*, 5935. (b) Ionkin, A.; Marshall, W. *Chem. Commun.* **2003**, 710. (c) Moores, A.; Mézailles, N.; Ricard, L.; Mathey, F.; Le Floch, P. *Chem. Commun.* **2003**, 1914. (d) Spencer, L. P.; Altwer, R.; Wei, P.; Gelmini, L.; Gauld, J.; Stephan, D. W. *Organometallics* **2003**, *22*, 3841.
(16) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.
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(18) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.
(19) Yoshifuji, M.; Ichikawa, Y.; Yamada, N.; Toyota, K. *Chem. Commun.* **1998**, 27.

known compound.[8] Some parts of the data are revised from the preliminary communication.[3a]

1a. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.39 (s, 18H, *p*-*t*-Bu), 1.54 (s, 36H, *o*-*t*-Bu), 3.67 (s, 3H, OCH3), 6.31 (d, $^3J_{HH}$ = 9.0 Hz, 4H, *m*-Ar), 6.43 (d, $^3J_{HH}$ = 9.0 Hz, 4H, *o*-Ar), 7.37 (s, 4H, *m*-PAr). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ 31.6 (s, *p*-C*Me*$_3$), 33.1 (virtual triplet, *J* = 3 Hz, *o*-C*Me*$_3$), 35.1 (s, *p*-*C*Me$_3$), 38.3 (s, *o*-*C*Me$_3$), 54.9 (s, OMe), 113.1 (s, *m*-Ar), 121.8 (s, *m*-PAr), 124.5 (s, *ipso*-Ar), 129.8 (s, *o*-Ar), 135.9 (virtual triplet, *J* = 28 Hz, *ipso*-PAr), 149.9 (s, *p*-PAr), 154.4 (t, J_{PC} = 6 Hz, P=C*C*), 154.9 (s, *o*-PAr), 159.0 (s, *p*-Ar), 176.6 (dd, J_{PC} = 17 and 10 Hz, P=C). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C): δ 162.6 (s). Anal. Calcd for $C_{54}H_{72}O_2P_2$: C, 79.56; H, 8.90. Found: C, 79.17; H, 9.28.

1c. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.36 (s, 18H, *p*-*t*-Bu), 1.52 (s, 36H, *o*-*t*-Bu), 6.57 (d, $^3J_{HH}$ = 8.1 Hz, 4H, *o*-Ar), 7.06 (d, $^3J_{HH}$ = 8.1 Hz, 4H, *m*-Ar), 7.35 (s, 4H, *m*-PAr). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ 31.5 (s, *p*-C*Me*$_3$), 33.2 (virtual triplet, *J* = 3 Hz, *o*-C*Me*$_3$), 35.1 (s, *p*-*C*Me$_3$), 38.3 (s, *o*-*C*Me$_3$), 122.0 (s, *m*-PAr), 123.8 (q, $^1J_{FC}$ = 272 Hz, CF_3), 124.7 (q, $^3J_{FC}$ = 4 Hz, *m*-Ar), 128.2 (s, *o*-Ar), 129.4 (q, $^2J_{FC}$ = 32 Hz, *p*-Ar), 134.6 (virtual triplet, *J* = 28 Hz, *ipso*-PAr), 134.8 (q, $^5J_{FC}$ = 1 Hz, *ipso*-Ar), 150.8 (s, *p*-PAr), 153.6 (t, J_{PC} = 7 Hz, P=C*C*), 154.9 (s, *o*-PAr), 174.7 (dd, J_{PC} = 17 and 10 Hz, P=C). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C): δ 180.7 (s). Anal. Calcd for $C_{54}H_{66}F_6P_2$: C, 72.79; H, 7.47. Found: C, 73.03; H, 7.31.

1d. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.19 (s, 18H, *p*-*t*-Bu), 1.58 (s, 36H, *o*-*t*-Bu), 7.17 (s, 4H, *o*-Ar), 7.24 (s, 4H, *m*-PAr), 7.52 (s, 2H, *p*-Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ 31.1 (s, *p*-C*Me*$_3$), 33.5 (virtual triplet, *J* = 3 Hz, *o*-C*Me*$_3$), 35.0 (s, *p*-*C*Me$_3$), 38.5 (s, *o*-*C*Me$_3$), 121.7 (s, *p*-Ar), 122.2 (s, *m*-PAr), 122.6 (q, $^1J_{FC}$ = 273 Hz, CF_3), 127.6 (s, *o*-Ar), 131.2 (q, $^2J_{FC}$ = 33 Hz, *m*-Ar), 132.8 (virtual triplet, *J* = 27 Hz, *ipso*-PAr), 133.3 (s, *ipso*-Ar), 150.2 (s, *p*-PAr), 152.4 (t, J_{PC} = 7 Hz, P=C*C*), 153.9 (s, *o*-PAr), 173.4 (dd, J_{PC} = 17 and 10 Hz, P=C). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C): δ 192.4 (s). Anal. Calcd for $C_{56}H_{64}F_{12}P_2$: C, 65.49; H, 6.28. Found: C, 65.58; H, 6.39.

Preparation of PtMe$_2$(DPCB-Y) (2a−d). A typical procedure is reported for **2a**. To a suspension of $[PtMe_2(\mu\text{-}SMe_2)]_2$[7] (86.2 mg, 0.15 mmol) in Et_2O (5 mL) was added DPCB-OMe (**1a**) (244 mg, 0.30 mmol), and the mixture was stirred at room temperature for 12 h in the dark. The initially yellow mixture was gradually turned to an orange suspension. Volatile materials were removed by pumping, and the resulting reddish orange solid was washed with Et_2O (2 mL) and dried under vacuum (193 mg, 94%). This product was adequately pure for NMR examination and further chemical conversion. A crystalline product suitable for X-ray structural analysis was obtained by recrystallization from toluene. Complexes **2b**, **2c**, and **2d** were similarly prepared using the corresponding DPCB-Y ligands in 99, 85, and 82% yields, respectively.

2a. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.05 ($A_3A_3'XX'$, $^2J_{PtH}$ = 80.2 Hz, 6H, PtMe), 1.46 (s, 18H, *p*-*t*-Bu), 1.64 (s, 36H, *o*-*t*-Bu), 3.71 (s, 6H, OMe), 6.39 (d, $^3J_{HH}$ = 8.4 Hz, 4H, *m*-Ar), 6.76 (d, $^3J_{HH}$ = 8.4 Hz, 4H, *o*-Ar), 7.59 (s, 4H, *m*-PAr). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ −2.0 (dd, $^2J_{PC}$ = 126 and 9 Hz, $^1J_{PtC}$ = 722 Hz, PtMe), 31.6 (s, *p*-C*Me*$_3$), 33.5 (s, *o*-C*Me*$_3$), 35.4 (s, *p*-*C*Me$_3$), 38.9 (s, *o*-*C*Me$_3$), 55.1 (s, OMe), 113.5 (*m*-Ar), 122.7 (s, *m*-PAr), 124.4 (s, *ipso*-Ar), 127.3 (m, *ipso*-PAr), 129.0 (s, *o*-Ar), 146.7 (dd, J_{PC} = 59 and 38 Hz, P=C*C*), 152.3 (s, *p*-PAr), 157.0 (s, *o*-PAr), 159.5 (s, *p*-Ar), 171.0 (dd, J_{PC} = 35 and 30 Hz, P=C). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C): δ 164.7 (s, $^1J_{PtP}$ = 1594 Hz). Anal. Calcd for $C_{56}H_{78}O_2P_2Pt$: C, 64.66; H, 7.56. Found: C, 64.46; H, 7.64.

2b. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.06 ($A_3A'_3XX'$, $^2J_{PtH}$ = 80.3 Hz, 6H, PtMe), 1.43 (s, 18H, *p*-*t*-Bu), 1.62 (s, 36H, *o*-*t*-Bu), 6.81 (d, $^3J_{HH}$ = 7.9 Hz, 4H, *o*-Ph), 6.86 (t, $^3J_{HH}$ = 7.9 Hz, 4H, *m*-Ph), 7.11 (t, $^3J_{HH}$ = 7.9 Hz, 2H, *p*-Ph), 7.57 (d, $^4J_{PH}$ = 1.6 Hz, 4H, *m*-PAr). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ -1.9 (dd, $^2J_{PC}$ = 126 and 9 Hz, $^1J_{PtC}$ = 723 Hz, PtMe), 31.5 (s, *p*-C*Me*$_3$), 33.5 (s, *o*-C*Me*$_3$), 35.4 (s, *p*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 122.8 (s, *m*-PAr), 126.9 (m, *ipso*-PAr), 127.4 (s, *o*-Ph), 128.1 (s, *m*-Ph), 128.6 (s, *p*-Ph), 131.8 (s, *ipso*-Ph), 147.8 (dd, J_{PC} = 60 and 40 Hz, P=C*C*), 152.6 (s, *p*-PAr), 156.9 (s, *o*-PAr), 170.7 (dd, J_{PC} = 36 and 30 Hz, P=C). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C): δ 171.6 (s, $^1J_{PtP}$ = 1590 Hz). Anal. Calcd for $C_{54}H_{74}P_2Pt$: C, 66.17; H, 7.61. Found: C, 65.86; H 7.61.

2c. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.13 ($A_3A_3'XX'$, $^2J_{PtH}$ = 80.0 Hz, 6H, PtMe), 1.43 (s, 18H, *p*-*t*-Bu), 1.62 (s, 36H, *o*-*t*-Bu), 6.87 (d, $^3J_{HH}$ = 8.3 Hz, 4H, *o*-Ar), 7.12 (d, $^3J_{HH}$ = 8.3 Hz, 4H, *m*-Ar), 7.59 (s, 4H, *m*-PAr). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ −1.1 (dd, $^2J_{PC}$ = 126 and 10 Hz, $^1J_{PtC}$ = 721 Hz, PtMe), 31.5 (s, *p*-C*Me*$_3$), 33.6 (s, *o*-C*Me*$_3$), 35.4 (s, *p*-*C*Me$_3$), 38.9 (s, *o*-*C*Me$_3$), 123.0 (s, *m*-PAr), 123.8 (q, $^1J_{FC}$ = 272 Hz, CF_3), 125.2 (q, $^3J_{PC}$ = 4 Hz, *m*-Ar), 126.3 (m, *ipso*-PAr), 127.2 (s, *o*-Ar), 130.0 (q, $^2J_{FC}$ = 32 Hz, *p*-Ar), 134.9 (s, *ipso*-Ar), 146.1 (dd, J_{PC} = 61 and 38 Hz, P=C*C*), 153.1 (s, *p*-PAr), 156.9 (s, *o*-PAr), 169.2 (dd, J_{PC} = 35 and 29 Hz, P=C). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C): δ 181.8 (s, $^1J_{PtP}$ = 1558 Hz). Anal. Calcd for $C_{56}H_{72}F_6P_2Pt$: C, 60.26; H, 6.50. Found: C, 60.12; H, 6.37.

2d. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.02 ($A_3A_3'XX'$, $^2J_{PtH}$ = 81.9 Hz, 6H, PtMe), 1.37 (s, 18H, *p*-*t*-Bu), 1.64 (s, 36H, *o*-*t*-Bu), 7.61 (d, $^4J_{PH}$ = 1.6 Hz, 4H, *m*-PAr), 7.69 (s, 6H, *o*- and *p*-Ar). ^{13}C-{^{1}H} NMR ($CDCl_3$, 20 °C): δ −1.7 (dd, $^2J_{PC}$ = 126 and 9 Hz, $^1J_{PtC}$ = 711 Hz, PtMe), 31.1 (s, *p*-C*Me*$_3$), 33.7 (s, *o*-C*Me*$_3$), 35.4 (s, *p*-*C*Me$_3$), 39.0 (s, *o*-*C*Me$_3$), 122.2 (s, *p*-Ar), 122.4 (q, $^1J_{FC}$ = 273 Hz, CF_3), 123.6 (s, *m*-PAr), 123.9 (m, *ipso*-PAr), 126.8 (s, *o*-Ar), 132.2 (q, $^2J_{FC}$ = 34 Hz, *m*-Ar), 133.4 (s, *ipso*-Ar), 143.7 (dd, J_{PC} = 59 and 38 Hz, P=C*C*), 153.5 (s, *p*-PAr), 155.5 (s, *o*-PAr), 166.7 (dd, J_{PC} = 34 and 30 Hz, P=C). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C): δ 193.7 (s, $^1J_{PtP}$ = 1605 Hz). Anal. Calcd for $C_{58}H_{70}F_{12}P_2Pt$: C, 55.63; H, 5.63. Found: C, 55.58; H, 5.73.

X-ray Diffraction Study for 2a. A red prism having approximate dimensions of 0.40 × 0.40 × 0.08 mm was grown from a toluene solution and mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Indexing was performed from 1??? oscillations, which were exposed for 0.8 min. The unit cell dimensions and systematic absences (*h*0*l*: *l* ± 2*n*; 0*k*0: *k* ± 2*n*) uniquely indicated the space group *P*21/*c* (#14). The intensity data were collected at 23 ± 1 °C to a maximum 2θ value of 55.0°. A total of 138 images, corresponding to 220.8° oscillation angles, were collected with two different goniometer settings. Exposure time was 1.30 min per degree, and the camera radius was 127.40 mm. Readout was performed in the 0.125 mm pixel mode. Of the 46 685 reflections collected, 12 146 were unique (R_{int} = 0.029); equivalent reflections were merged. The data were corrected for Lorentz and polarization effects and absorption (NUMABS). All calculations were performed with the TEXSAN Crystal Structure Analysis Package provided by Rigaku Corp. The structure was solved by heavy atom Patterson methods (PATTY) and expanded using Fourier techniques (DIRDIF94). All non-hydrogen atoms were refined anisotropically. In the final cycles of refinement, hydrogen atoms were located at idealized positions (d(C−H) = 0.95 Å) with isotropic temperature factors (B_{iso} = 1.20$B_{bonded\ atom}$) and were included in calculation without refinement of their parameters. The function minimized in least-squares was $\sum w(F_o^2 - F_c^2)^2$ ($w = 1/[\sigma^2(F_o^2)]$). Crystal data and details of data collection and refinement are summarized in Table 6. Additional information is available as Supporting Information.

Preparation of PtMe(OTf)(DPCB-Y) (3a−c). A typical procedure is as follows. To a suspension of **2a** (208 mg, 0.20 mmol) in Et_2O (5 mL) was added an Et_2O solution of trifluoromethanesulfuric acid (HOTf) (0.675 M, 296 μL, 0.20 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 3 h in the dark. The initially red color of the system gradually turned to orange. The resulting precipitate was collected by filtration, washed with Et_2O (2 mL), and dried under vacuum to give **3a** (210 mg, 89%), which was analytically pure without further purification. Complexes **3b** and **3c** were similarly prepared in 82 and 85% yields, respectively.

Table 6. Crystal Data and Details of the Structure Determination for 2a

formula	$C_{56}H_{78}O_2P_2Pt$
fw	1040.27
cryst size, mm	0.4 × 0.4 × 0.08
cryst syst	monoclinic
no. of reflns used for unit cell determination (2θ range, deg)	69 298 (3.5−55.0)
a (Å)	14.8898(2)
b (Å)	12.9644(2)
c (Å)	28.4114(5)
β (deg)	103.1688(6)
V (Å^3)	5340.2(2)
space group	$P21/c$ (#14)
Z	4
d_{calcd} (g cm^{-3})	1.294
μ(Mo Kα) (cm^{-1})	27.14
diffractometer	Rigaku RAXIS-RAPID (imaging plate)
temp, °C	23
2θ max (deg)	55.0
no. of reflns collected	46685
no. of unique reflns	12146 (R_{int} = 0.029)
transmn factors	0.3815−0.7970
no. of obsd reflns	12 146
no. of variables	550
R indices[a]	R_1 = 0.029 ($I \geq 2.0\sigma(I)$) R = 0.048 R_w = 0.105 GOF = 1.07
max. Δ/σ in final cycle	0.009
max. and min. peak (e Å^{-3})	0.93, −1.42

[a] Function minimized = $\sum w(F_o^2 - F_c^2)^2$; $w = (1/[\sigma^2(F_o^2)]$. R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. $R = \sum(F_o^2 - F_c^2)/\sum(F_o^2)$. $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o and N_v stand for the number of observations and variables, respectively.

3a. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.17 (dd, $^3J_{PC}$ = 10.1 and 2.9 Hz, 3H, PtMe), 1.45 (s, 9H, *p*-*t*-Bu), 1.46 (s, 9H, *p*-*t*-Bu), 1.64 (d, $^5J_{PH}$ = 1.1 Hz, 18H, *o*-*t*-Bu), 1.68 (d, $^5J_{PH}$ = 1.3 Hz, 18H, *o*-*t*-Bu), 3.70 (s, 3H, OMe), 3.71 (s, 3H, OMe), 6.45 (dd, $^3J_{HH}$ = 8.8 Hz, J_{PH} = 1.5 Hz, 4H, *m*-Ar), 6.73 (dd, $^3J_{HH}$ = 9.0 Hz, J_{PH} = 2.2 Hz, 2H, *o*-Ar), 6.78 (dd, $^3J_{HH}$ = 8.8 Hz, J_{PH} = 2.2 Hz, 2H, *o*-Ar), 7.62 (d, $^4J_{PH}$ = 2.9 Hz, 2H, *m*-PAr), 7.70 (d, $^4J_{PH}$ = 4.4 Hz, 2H, *m*-PAr). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 4.68 (dd, $^2J_{PC}$ = 102 and 6 Hz, $^1J_{PtC}$ = 558 Hz, PtMe), 31.4 (s, *p*-C*Me*$_3$), 31.6 (s, *p*-C*Me*$_3$), 33.9 (s, *o*-C*Me*$_3$), 34.2 (s, *o*-C*Me*$_3$), 35.7 (s, *p*-*C*Me$_3$), 35.9 (s, *p*-*C*Me$_3$), 38.9 (s, *o*-*C*Me$_3$), 40.0 (s, *o*-*C*Me$_3$), 55.6 (s, OMe), 114.0 (d, J_{PC} = 2 Hz, *m*-Ar), 114.3 (d, J_{PC} = 4 Hz, *m*-Ar), 118.7 (d, $^1J_{PC}$ = 46 Hz, *ipso*-PAr), 122.9 (s, *ipso*-Ar), 123.1 (s, *ipso*-Ar), 123.5 (d, $^3J_{PC}$ = 7 Hz, *m*-PAr), 124.6 (d, $^3J_{PC}$ = 11 Hz, *m*-PAr), 127.6 (d, $^1J_{PC}$ = 12 Hz, *ipso*-PAr), 129.8 (d, $^4J_{PC}$ = 7 Hz, *o*-Ar), 129.9 (d, $^4J_{PC}$ = 7 Hz, *o*-Ar), 148.9 (dd, J_{PC} = 59 and 33 Hz, P=C*C*), 151.3 (dd, J_{PC} = 54 and 27 Hz, P=C*C*), 153.9 (d, $^4J_{PC}$ = 2 Hz, *p*-PAr), 155.5 (d, $^4J_{PC}$ = 3 Hz, *p*-PAr), 157.5 (s, *o*-PAr), 161.1 (d, J_{PC} = 4 Hz, *p*-Ar), 161.2 (d, J_{PC} = 4 Hz, *p*-Ar), 163.5 (dd, J_{PC} = 93 and 25 Hz, P=C), 167.1 (dd, J_{PC} = 47 and 6 Hz, P=C). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 89.2 (d, $^1J_{PtP}$ = 6792 Hz, $^2J_{PP}$ = 12 Hz, trans to OTf), 176.6 (d, $^1J_{PtP}$ = 1626 Hz, $^2J_{PP}$ = 12 Hz, trans to Me). Anal. Calcd for $C_{56}H_{75}O_5SF_3P_2Pt$: C, 57.28; H, 6.44. Found: C, 57.24; H, 6.48.

3b. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.06 (dd, ^3JPH = 9.9 and 2.7 Hz, 3H, PtMe), 1.42 (s, 9H, *p*-*t*-Bu), 1.44 (s, 9H, *p*-*t*-Bu), 1.63 (d, $^5J_{PH}$ = 1.1 Hz, 18H, *o*-*t*-Bu), 1.66 (d, $^5J_{PH}$ = 1.3 Hz, 18H, *o*-*t*-Bu), 6.79 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *o*-Ph), 6.83 (d, $^3J_{HH}$ = 8.4 Hz, 2H, *o*-Ph), 6.91 (t, $^3J_{HH}$ = 8.1 Hz, 4H, *m*-Ph), 7.17 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *p*-Ph), 7.19 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *p*-Ph), 7.53 (d, $^4J_{PH}$ = 2.7 Hz, 2H, *m*-PAr), 7.65 (d, $^4J_{PH}$ = 4.2 Hz, 2H, *m*-PAr). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ 5.0 (dd, $^2J_{PC}$ = 101 and 6 Hz, $^1J_{PtC}$ = 545 Hz, PtMe), 31.2 (*p*-C*Me*$_3$), 31.4 (*p*-C*Me*3), 33.8 (d, $^4J_{PC}$ = 2 Hz, *o*-C*Me*$_3$), 34.1 (s, *o*-C*Me*$_3$), 35.3 (s, *p*-C*Me*$_3$), 35.5 (s, *p*-*C*Me$_3$), 38.4 (s, *o*-*C*Me$_3$), 39.6 (d, $^3J_{PC}$ = 1 Hz, *o*-*C*Me$_3$), 118.2 (d, $^1J_{PC}$ = 46 Hz, *ipso*-PAr), 123.0 (d, $^3J_{PC}$ = 7 Hz, *m*-PAr), 123.3 (d, $^3J_{PC}$ = 11 Hz, *m*-PAr), 126.8 (d, $^1J_{PC}$ = 13 Hz, *ipso*-PAr), 127.5 (dd, J_{PC} = 6 and 1 Hz, *o*-Ph), 127.6 (dd, J_{PC} = 6 and 2 Hz, *o*-Ph), 128.3 (d, J_{PC} = 2 Hz, *m*-Ph), 128.5 (d, J_{PC} = 2 Hz, *m*-Ph), 129.9 (d, J_{PC} = 4 Hz, *ipso*-Ph), 130.1 (s, *p*-Ph), 130.3 (d, J_{PC} = 13 Hz, *ipso*-Ph), 149.3 (dd, J_{PC} = 59 and 33 Hz, P=C−*C*), 151.7 (dd, J_{PC} = 54 and 27 Hz, P=C−*C*), 153.5 (d, $^4J_{PC}$ = 2 Hz, *p*-PAr), 155.2 (d, $^4J_{PC}$ = 3 Hz, *p*-PAr), 157.1 (d, $^2J_{PC}$ = 2 Hz, *o*-PAr), 157.1 (s, *o*-PAr), 162.2 (dd, J_{PC} = 92 and 25 Hz, P=C), 166.3 (dd, J_{PC} = 48 and 5 Hz, P=C). ^{31}P-{^{1}H} NMR ($CDCl_3$, 20 °C): δ 98.1 (d, $^2J_{PP}$ = 14 Hz, $^1J_{PtP}$ = 6819 Hz, trans to OTf), 186.2 (d, $^2J_{PP}$ = 14 Hz, $^1J_{PtP}$ = 1618 Hz, trans to Me). Anal. Calcd for $C_{54}H_{71}F_3O_3P_2SPt$: C, 58.21; H, 6.42. Found: C, 57.99; H 6.48.

3c. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.29 (dd, $^3J_{PH}$ = 9.9 and 3.1 Hz, 3H, PtMe), 1.44 (s, 18H, *p*-*t*-Bu), 1.63 (s, 18H, *o*-*t*-Bu), 1.67 (s, 18H, *o*-*t*-Bu), 6.87 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *o*-Ar), 6.90 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *o*-Ar), 7.21 (d, $^3J_{HH}$ = 8.0 Hz, 4H, *m*-Ar), 7.61 (d, $^4J_{PH}$ = 2.7 Hz, 2H, *m*-PAr), 7.71 (d, $^4J_{PH}$ = 4.6 Hz, 2H, *m*-PAr). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 5.75 (dd, $^2J_{PC}$ = 101 and 6 Hz, $^1J_{PtC}$ = 545 Hz, PtMe), 31.1 (s, *p*-C*Me*$_3$), 31.4 (s, *p*-C*Me*$_3$), 33.8 (s, *o*-C*Me*$_3$), 34.2 (s, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 35.8 (s, *p*-*C*Me$_3$), 38.7 (s, *o*-*C*Me$_3$), 39.9 (s, *o*-*C*Me$_3$), 117.6 (d, $^1J_{PC}$ = 46 Hz, *ipso*-PAr), 123.7 (q, $^1J_{FC}$ = 273 Hz, CF_3), 123.9 (q, $^1J_{FC}$ = 273 Hz, CF_3), 123.7 (d, $^3J_{PC}$ = 7 Hz, *m*-PAr), 123.9 (d, $^3J_{PC}$ = 11 Hz, *m*-PAr), 125.7 (q, $^3J_{PC}$ = 4 Hz, *m*-Ar), 125.7 (q, $^3J_{PC}$ = 4 Hz, *m*-Ar), 126.5 (d, $^1J_{PC}$ = 13 Hz, *ipso*-PAr), 127.7 (d, *J*PC = 6 Hz, *o*-Ar), 127.9 (d, J_{PC} = 6 Hz, *o*-Ar), 131.2 (m, *p*-Ar), 133.3 (s, *ipso*-Ar), 133.7 (s, *ipso*-Ar), 148.1 (dd, J_{PC} = 59 and 34 Hz, P=C−*C*), 150.7 (dd, J_{PC} = 54 and 26 Hz, P=C−*C*), 154.4 (d, $^4J_{PC}$ = 2 Hz, *p*-PAr), 156.1 (d, $^4J_{PC}$ = 1 Hz, *p*-PAr), 157.3 (s, *o*-PAr), 157.4 (s, *o*-PAr), 161.1 (dd, J_{PC} = 94 and 26 Hz, P=C), 165.6 (dd, J_{PC} = 48 and 5 Hz, P=C). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 107.5 (d, $^2J_{PP}$ = 15 Hz, $^1J_{PtP}$ = 6821 Hz, trans to OTf), 194.1 (d, $^2J_{PP}$ = 15 Hz, $^1J_{PtP}$ = 1604 Hz, trans to Me). Anal. Calcd for $C_{56}H_{69}O_3SF_9P_2Pt$: C, 53.80; H, 5.56. Found: C, 54.10; H, 5.86.

Preparation of [PtMe(η^2-C_2H_4)(DPCB-OMe)]OTf (4a). Complex **3a** (23.5 mg, 20 μmol) was placed in an NMR sample tube equipped with a rubber septum cap and dissolved in CD_2Cl_2 (0.6 mL) under an argon atmosphere. The solution was treated with ethylene (1 atm) at 0 °C and examined by NMR spectroscopy, showing the quantitative formation of ethylene-coordinated complex **4a**. The complex was obtained as a reddish oily material by evaporating the solution under reduced pressure, while no satisfactory elemental analysis data were obtained. The NMR data for **4a**−**c** are as follows.

4a. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.08 (dd, $^3J_{PH}$ = 8.7 and 7.8 Hz, $^2J_{PtH}$ = 60.4 Hz, 3H, PtMe), 1.46 (s, 9H, *p*-*t*-Bu), 1.47 (s, 9H, *p*-*t*-Bu), 1.58 (d, $^5J_{PH}$ = 1.3 Hz, 18H, *o*-*t*-Bu), 1.59 (d, $^5J_{PH}$ = 1.3 Hz, 18H, *o*-*t*-Bu), 3.75 (s, 3H, OMe), 3.76 (s, 3H, MeO), 5.02 (t, $^3J_{PH}$ = 5.0 Hz, $^2J_{PtH}$ = 56.8 Hz, 4H, η^2-C_2H_4), 6.52 (d, $^3J_{HH}$ = 9.0 Hz, 4H, *m*-Ar), 6.88 (dd, $^3J_{HH}$ = 9.0 Hz, J_{PH} = 2.0 Hz, 2H, *o*-Ar), 6.90 (dd, $^3J_{HH}$ = 9.0 Hz, J_{PH} = 2.2 Hz, 2H, *o*-Ar), 7.75 (d, $^4J_{PH}$ = 3.3 Hz, 2H, *m*-PAr), 7.77 (d, $^4J_{PH}$ = 4.4 Hz, 2H, *m*-PAr). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 5.09 (dd, $^2J_{PC}$ = 99 and 6 Hz, $^1J_{PtC}$ = 505 Hz, PtMe), 31.3 (s, *p*-C*Me*$_3$), 31.4 (s, *p*-C*Me*$_3$), 33.9 (s, *o*-C*Me*$_3$), 34.0 (s, *o*-C*Me*$_3$), 35.9 (s, *p*-*C*Me$_3$), 36.0 (*p*-*C*Me$_3$), 39.3 (s, *o*-*C*Me$_3$), 39.8 (d, $^3J_{PC}$ = 1 Hz, *o*-*C*Me$_3$), 55.8 (s, OMe), 55.9 (s, OMe), 88.2 (d, $^2J_{PC}$ = 14 Hz, $^1J_{PtC}$ = 105 Hz, η^2-C_2H_4), 114.6 (s, *m*-Ph), 117.8 (d, $^1J_{PC}$ = 30 Hz, *ipso*-PAr), 121.4 (s, *ipso*-Ar), 121.6 (s, *ipso*-Ar), 123.3 (dd, J_{PC} = 29 and 7 Hz, *ipso*-PAr), 124.8 (d, $^3J_{PC}$ = 8 Hz, *m*-PAr), 125.0 (d, $^3J_{PC}$ = 10 Hz, *m*-PAr), 130.6 (d, $^4J_{PC}$ = 4 Hz, *o*-Ar), 131.2 (d, $^4J_{PC}$ = 6 Hz, *o*-Ar), 151.4 (dd, J_{PC} = 52 and 26 Hz, P=C−*C*), 152.6 (dd, J_{PC} = 57 and 32 Hz, P=C−*C*), 155.7 (d, $^4J_{PC}$ = 2 Hz, *p*-PAr), 156.6 (d, $^4J_{PC}$ = 3 Hz, *p*-PAr), 157.5 (s, *o*-PAr), 158.0 (d, J_{PC} = 3 Hz, *p*-PAr), 162.5 (d, J_{PC} = 4 Hz, *p*-Ar), 162.9 (dd, J_{PC} = 4 Hz, *p*-Ar), 171.8 (dd, J_{PC} = 47 and 14 Hz, P=C), 174.8 (dd, J_{PC} = 66 and 24 Hz, P=C). ^{31}P{^{1}H} NMR (CD_2Cl_2,

20 °C): δ 126.5 (s, $^1J_{PtP}$ = 4879 Hz, trans to C_2H_4), 153.4 (s, $^1J_{PtP}$ = 1528 Hz, trans to Me).

4b. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.12 (dd, $^3J_{PH}$ = 8.8 and 7.8 Hz, $^2J_{PtH}$ = 61.0 Hz, 3H, PtMe), 1.46 (s, 9H, *p*-*t*-Bu), 1.46 (s, 9H, *p*-*t*-Bu), 1.58 (d, $^5J_{PH}$ = 1.2 Hz, 18H, *o*-*t*-Bu), 1.59 (d, $^5J_{PH}$ = 1.2 Hz, 18H, *o*-*t*-Bu), 5.11 (t, $^3J_{PH}$ = 5.1 Hz, $^2J_{PtH}$ = 57.1 Hz, 4H, η^2-C_2H_4), 6.94 (d, $^3J_{HH}$ = 8.3 Hz, 2H, *o*-Ph), 6.96 (d, $^3J_{HH}$ = 8.3 Hz, 2H, *o*-Ph), 7.03 (t, $^3J_{HH}$ = 8.1 Hz, 4H, *m*-Ph), 7.33 (m, 2H, *p*-Ph), 7.74 (d, $^4J_{PH}$ = 2.9 Hz, 2H, *m*-PAr), 7.77 (d, $^4J_{PH}$ = 4.4 Hz, 2H, *m*-PAr). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 5.2 (dd, $^2J_{PC}$ = 99 and 5 Hz, $^1J_{PtC}$ = 502 Hz, PtMe), 31.2 (*p*-C*Me*$_3$), 31.3 (s, *p*-C*Me*$_3$), 33.9 (*o*-C*Me*$_3$), 34.1 (*o*-C*Me*$_3$), 35.9 (s, *p*-*C*Me$_3$), 36.0 (s, *p*-*C*Me$_3$), 39.2 (s, *o*-*C*Me$_3$), 39.8 (s, *o*-*C*Me$_3$), 89.7 (d, $^2J_{PC}$ = 13 Hz, $^1J_{PtC}$ = 103 Hz, η^2-C_2H_4), 117.1 (d, $^1J_{PC}$ = 30 Hz, *ipso*-PAr), 122.8 (dd, J_{PC} = 26 and 7 Hz, *ipso*-PAr), 125.0 (d, $^3J_{PC}$ = 8 Hz, *m*-PAr), 125.3 (d, $^3J_{PC}$ = 12 Hz, *m*-PAr), 128.6 (d, J_{PC} = 7 Hz, *o*-Ph), 129.0 (d, J_{PC} = 7 Hz, *o*-Ph), 129.1 (s, *p*-Ph), 129.2 (s, *m*-Ph), 132.2 (d, J_{PC} = 3 Hz, *ipso*-Ph), 132.5 (d, J_{PC} = 5 Hz, *ipso*-Ph), 152.6 (dd, J_{PC} = 54 and 28 Hz, P=C−*C*), 153.7 (dd, J_{PC} = 57 and 31 Hz, P=C−*C*), 156.2 (s, *p*-PAr), 157.1 (s, *p*-PAr), 157.6 (s, *o*-PAr), 158.1 (s, *o*-PAr), 171.7 (dd, J_{PC} = 48 and 13 Hz, P=C), 174.3 (dd, J_{PC} = 69 and 22 Hz, P=C). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 133.5 (s, $^1J_{PtP}$ = 4919 Hz, trans to C_2H_4), 161.9 (s, $^1J_{PtP}$ = 1520 Hz, trans to Me).

4c. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.22 (dd, $^3J_{PH}$ = 7.9 and 8.6 Hz, $^2J_{PtH}$ = 60.5 Hz, 3H, PtMe), 1.45 (s, 9H, *p*-*t*-Bu), 1.46 (s, 9H, *p*-*t*-Bu), 1.58 (d, $^5J_{PH}$ = 1.5 Hz, 18H, *o*-*t*-Bu), 1.59 (d, $^5J_{PH}$ = 1.1 Hz, 18H, *o*-*t*-Bu), 5.22 (t, $^3J_{HH}$ = 5.0 Hz, $^2J_{PtH}$ = 58.9 Hz, 4H, η^2-C_2H_4), 6.99 (d, $^3J_{HH}$ = 8.4 Hz, 2H, *o*-Ar), 7.01 (d, $^3J_{HH}$ = 8.4 Hz, 2H, *o*-Ar), 7.29 (d, $^3J_{HH}$ = 8.4 Hz, 4H, *m*-Ar), 7.75 (d, $^4J_{PH}$ = 3.3 Hz, 2H, *m*-PAr), 7.78 (d, $^4J_{PH}$ = 4.6 Hz, 2H, *m*-PAr). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 5.59 (dd, $^2J_{PC}$ = 97 and 6 Hz, $^1J_{PtC}$ = 498 Hz, PtMe), 31.1 (s, *p*-C*Me*$_3$), 31.1 (s, *p*-C*Me*$_3$), 33.7 (s, *o*-C*Me*$_3$), 34.0 (s, *o*-C*Me*$_3$), 35.8 (s, *p*-*C*Me$_3$), 35.9 (s, *p*-*C*Me$_3$), 39.1 (s, *o*-*C*Me$_3$), 39.7 (d, ^3JPC = 1 Hz, *o*-*C*Me$_3$), 91.2 (d, $^2J_{PC}$ = 13 Hz, $^1J_{PtC}$ = 100 Hz, η^2-C_2H_4), 123.4 (q, $^1J_{FC}$ = 272 Hz, CF_3), 116.2 (d, $^1J_{PC}$ = 29 Hz, *ipso*-PAr), 120.7 (q, $^1J_{FC}$ = 320 Hz, CF_3SO_3), 122.5 (dd, J_{PC} = 31 and 8 Hz, *ipso*-PAr), 124.8 (d, $^3J_{PC}$ = 7 Hz, *m*-PAr), 125.2 (d, $^3J_{PC}$ = 11 Hz, *m*-PAr), 126.0 (s, *m*-Ar), 128.5 (d, J_{PC} = 4 Hz, *o*-Ar), 128.8 (d, J_{PC} = 4 Hz, *o*-Ar), 132.0 (s, *ipso*-Ar), 132.1 (s, *ipso*-Ar), 132.6 (qd, $^2J_{FC}$ = 33 Hz, J_{PC} = 5 Hz, *p*-Ar), 150.7 (dd, J_{PC} = 56 and 30 Hz, P=C−*C*), 151.6 (dd, J_{PC} = 59 and 34 Hz, P=C−*C*), 156.3 (d, $^4J_{PC}$ = 2 Hz, *p*-PAr), 157.2 (d, $^4J_{PC}$ = 3 Hz, *p*-PAr), 157.4 (d, $^2J_{PC}$ = 1 Hz, *o*-PAr), 157.9 (d, $^2J_{PC}$ = 3 Hz, *o*-PAr), 170.2 (dd, J_{PC} = 48 and 12 Hz, P=C), 172.3 (dd, J_{PC} = 69 and 23 Hz, P=C). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 142.0 (s, $^1J_{PtP}$ = 4980 Hz, trans to C_2H_4), 172.4 (d, $^1J_{PtP}$ = 1496 Hz, trans to Me).

Preparation of $PtMe_2$(DPCB-Y) (5a−d). A typical procedure is reported for **5a**. To a suspension of $PdMe_2$(tmeda)[16] (76.0 mg, 0.30 mmol) in Et_2O (5 mL) was added DPCB-OMe (**1a**) (244 mg, 0.30 mmol), and the mixture was stirred at room temperature for 12 h in the dark. The resulting orange solid was collected by filtration, washed with Et_2O (2 mL), and dried under vacuum to give **5a**, which was analytically pure (265 mg, 93%). Complexes **5b** and **5c** were similarly prepared using **1b** and **1c** in 94 and 80% yields, respectively. Since the reaction of $PdMe_2$(tmeda) with **1d** was not complete, **5d** was prepared from $PdMe_2$(cod)[17] instead of $PdMe_2$(tmeda) in 82% yield.

5a. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 0.53 ($A_3A_3'XX'$, 6H, PdMe), 1.45 (s, 18H, *p*-*t*-Bu), 1.60 (s, 36H, *o*-*t*-Bu), 3.70 (s, 6H, OMe), 6.41 (d, $^3J_{HH}$ = 8.6 Hz, 4H, *m*-Ar), 6.69 (d, $^3J_{HH}$ = 8.6 Hz, 4H, *o*-Ar), 7.58 (d, $^4J_{PH}$ = 1.8 Hz, 4H, *m*-PAr). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 2.1 (dd, $^2J_{PC}$ = 120 and 9 Hz, PdMe), 31.7 (s, *p*-C*Me*$_3$), 33.6 (s, *o*-C*Me*$_3$), 35.7 (s, *p*-*C*Me$_3$), 39.1 (s, *o*-*C*Me$_3$), 55.5 (s, OMe), 113.8 (s, *m*-Ar), 123.1 (s, *m*-PAr), 124.1 (s, *ipso*-Ar), 128.6 (m, *ipso*-PAr), 129.8 (s, *o*-Ar), 149.9 (dd, J_{PC} = 53 and 36 Hz, P=C−*C*), 152.7 (s, *p*-PAr), 156.9 (s, *o*-PAr), 160.4 (s, *p*-Ar), 173.0 (dd, J_{PC} = 24 and 21 Hz, P=C). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 156.8 (s). Anal. Calcd for $C_{56}H_{78}O_2P_2Pd$: C, 70.68; H, 8.26. Found: C, 71.03; H, 8.34.

5b. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 0.55 ($A_3A'_3XX'$, 6H, PdMe), 1.44 (s, 18H, *p*-*t*-Bu), 1.59 (s, 36H, *o*-*t*-Bu), 6.75 (d, $^3J_{HH}$ = 8.5 Hz, 4H, *o*-Ph), 6.89 (t, $^3J_{HH}$ = 7.9 Hz, 4H, *m*-Ph), 7.11 (m, $^3J_{HH}$ = 7.9 Hz, 2H, *p*-Ph), 7.56 (d, $^4J_{PH}$ = 2.1 Hz, 4H, *m*-PAr). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 2.2 (dd, $^2J_{PC}$ = 121 and 8 Hz, PdMe), 31.6 (s, *p*-C*Me*$_3$), 33.6 (s, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 39.0 (s, *o*-*C*Me$_3$), 123.2 (s, *m*-PAr), 128.1 (m, *ipso*-PAr), 128.2 (s, *o*-Ph), 128.5 (s, *m*-Ph), 129.4 (s, *p*-Ph), 131.5 (s, *ipso*-Ph), 151.0 (dd, J_{PC} = 55 and 36 Hz, P=C), 153.0 (s, *p*-PAr), 156.9 (s, *o*-PAr), 172.6 (dd, J_{PC} = 26 and 21 Hz, P=C−*C*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 164.0 (s). Anal. Calcd for $C_{54}H_{74}P_2Pd$: C, 72.75; H 8.37. Found: C, 72.50; H, 8.26.

5c. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 0.61 ($A_3A_3'XX'$, 6H, PdMe), 1.43 (s, 18H, *p*-*t*-Bu), 1.59 (s, 36H, *o*-*t*-Bu), 6.82 (d, $^3J_{HH}$ = 8.2 Hz, 4H, *o*-Ar), 7.16 (d, $^3J_{HH}$ = 8.2 Hz, 4H, *m*-Ar), 7.58 (d, $^4J_{PH}$ = 1.8 Hz, 4H, *m*-PAr). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 2.9 (dd, $^2J_{PC}$ = 121 and 10 Hz, PdMe), 31.6 (s, *p*-*C*Me$_3$), 33.7 (s, *o*-C*Me*$_3$), 35.7 (s, *p*-*C*Me$_3$), 39.1 (s, *o*-*C*Me$_3$), 123.4 (s, *m*-PAr), 124.1 (q, $^1J_{FC}$ = 272 Hz, CF_3), 125.5 (q, $^3J_{FC}$ = 4 Hz, *m*-Ar), 127.5 (m, *ipso*-PAr), 128.2 (s, *o*-Ar), 130.5 (q, $^2J_{FC}$ = 33 Hz, *p*-Ar), 134.7 (s, *ipso*-Ar), 149.5 (dd, J_{PC} = 55 and 37 Hz, P=C−*C*), 153.4 (s, *p*-PAr), 156.9 (s, *o*-PAr), 171.1 (dd, J_{PC} = 24 and 21 Hz, P=C). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 173.8 (s). Anal. Calcd for $C_{56}H_{72}F_6P_2Pd$: C, 65.46; H, 7.06. Found: C, 65.35; H, 6.87.

5d. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 0.48 ($A_3A_3'XX'$, 6H, PdMe), 1.36 (s, 18H, *p*-*t*-Bu), 1.62 (s, 36H, *o*-*t*-Bu), 7.59 (d, $^4J_{PH}$ = 1.6 Hz, 4H, *m*-PAr), 7.59 (s, 4H, *o*-Ar), 7.71 (s, 2H, *p*-Ar). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 2.4 (dd, $^2J_{PC}$ = 121 and 10 Hz, PdMe), 31.2 (s, *p*-C*Me*$_3$), 33.8 (s, *o*-C*Me*3), 35.7 (s, *p*-*C*Me3), 39.2 (s, *o*-*C*Me3), 123.0 (q, $^1J_{FC}$ = 273 Hz, CF3), 123.1 (s, *p*-Ar), 123.8 (s, *m*-PAr), 125.0 (m, *ipso*-PAr), 127.9 (s, *o*-Ar), 132.3 (q, $^2J_{FC}$ = 34 Hz, *m*-Ar), 133.2 (s, *ipso*-Ar), 147.5 (dd, J_{PC} = 55 and 37 Hz, P=C−*C*), 153.6 (s, *p*-PAr), 155.6 (s, *o*-PAr), 168.2 (dd, J_{PC} = 24 and 21 Hz, P=C). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 185.9 (s). Anal. Calcd for $C_{58}H_{70}F_{12}P_2Pd$: C, 59.87; H, 6.06. Found: C, 59.73; H, 6.28.

Polymerization of Ethylene. To a solution of **5a** (9.9 mg, 10 μmol) in chlorobenzene (2 mL) was added a chlorobenzene solution (3 mL) of $H(OEt_2)_2BAr_4$[18] (10.7 mg, 10.6 μmol). The resulting solution was quickly transferred into a 150 mL pressure bottle by cannulation and diluted with chlorobenzene (15 mL). Ethylene (10 atm) was charged, and the mixture was mechanically stirred at 70 °C for 1 h under constant pressure. The mixture was poured into MeOH (100 mL), and the resulting precipitate was collected by filtration and dried under vacuum to give a white solid of polyethylene (1.04 g). ^{1}H NMR (1,2,4-trichlorobenzene/C_6D_6, 130 °C): δ 0.90 (m, CH_3, 2% of total H), 1.33 (CH_2, 95% of total H), 2.01 (m, allylic H, 1% of total H), 4.94 (m, terminal vinyl H), 5.40 (m, internal vinyl H), 5.78 (m, terminal vinyl H). ^{13}C{^{1}H} NMR (1,2,4-trichlorobenzene/C_6D_6, 130 °C): δ 14.1 (s, CH_3), 30.0 (s, CH_2), 32.8, 33.9 (each s, allylic C).

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Supporting Information Available: Details of the structure determination of **2a**, including an atomic numbering scheme and tables of atomic coordinates, thermal parameters, and full bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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