Equilibrium Studies of the Binding of Unsaturated Fatty Acid Methyl Esters to Palladium(II)

Kesete Y. Ghebreyessus, Arkady Ellern, and Robert J. Angelici*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received December 14, 2004

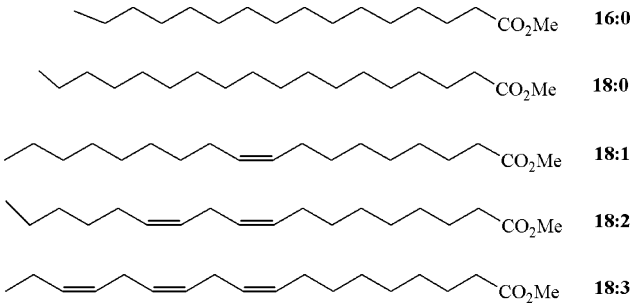
Cationic palladium(II)−olefin complexes $[CpPd(PR_3)(olefin)]BF_4$ (PR_3 = PPh_3, $PMePh_2$, PEt_3, PMe_3; olefin = methyl oleate (18:1), methyl linoleate (18:2), methyl linolenate (18:3), *cis*-3-hexene, 1,4-pentadiene) have been synthesized and characterized. (For 18:1, 18:2, and 18:3, the first number represents the chain length while the second indicates the number of double bonds). The diene (1,4-pentadiene and 18:2) and triene (18:3) ligands also form binuclear complexes $\{[CpPd(PR_3)]_2(olefin)\}^{2+}$ containing two coordinated $[CpPd(PR_3)]^+$ units. The crystal structure of $\{[CpPd(PMe_3)]_2(1,4\text{-pentadiene})\}(BF_4)_2$ (**5b**) was determined by X-ray crystallography. In all of the complexes, ^1H and $^{13}C\{^1H\}$ NMR spectra establish the presence of the η^2-coordinated fatty acid methyl ester and alkene ligands. Equilibrium constants for the formation of the $[CpPd(PR_3)(olefin)]^+$ complexes with 18:1, 18:2, 18:3, and *cis*-3-hexene show that the binding abilities of the large unsaturated fatty acid methyl esters to $[CpPd(PR_3)]^+$ are similar to those of simple *cis*-olefins, such as *cis*-3-hexene and *cis*-2-butene. The equilibrium constants for the binding of $[CpPd(PR_3)]^+$ to 18:1 and *cis*-3-hexene increase with the increasing electron-donating ability and decreasing size of the phosphines: PPh_3 < $PMePh_2$ < PEt_3 < PMe_3.

Introduction

One of the major challenges for the development of vegetable oils into feedstocks for the synthesis of chemicals[1] now derived from petroleum is the separation of the different fatty acids that comprise these oils.[2] Soybean oil, which is typical of such oils, consists of two saturated fatty acids, palmitic (16:0, 10.6%) and stearic (18:0, 4.7%), and three unsaturated fatty acids, oleic (18:1, 24.3%), linoleic (18:2, 53.2%), and linolenic (18:3, 7.2%). (The first number in parentheses represents the chain length, while the second indicates the number of double bonds.) Their methyl esters are shown in Chart 1.

These methyl esters are obtained by transesterification of the vegetable oils (triacylglycerols). This mixture of fatty acid methyl esters (FAMEs) is produced commercially and is known as biodiesel.[3] Because of their similar molecular weights and physical properties, it is not possible to separate them by distillation. Considering the presence of *cis*-olefinic groups in 18:1, 18:2, and 18:3, one possible approach to their separation could involve selective coordination of the double bonds to transition-metal complexes. This has already been demonstrated in widely used liquid- and gas-phase chromatographic separations of these fatty acid methyl esters on stationary phases that are impregnated with $AgNO_3$.[4,5] Although highly effective for analytical applications, these methods are not economical for the large-scale separation of the individual fatty acid esters.

Chart 1



To determine whether the binding abilities of 18:1, 18:2, and 18:3 are sufficiently different toward transition-metal complexes to allow them to be separated from each other, we sought to determine equilibrium constants for their coordination to $[CpPd(PR_3)]^+$, where Cp = η^5-C_5H_5. To our knowledge, no studies of transition-metal binding to fatty acid derivatives have been reported previously. The $[CpPd(PR_3)]^+$ system was chosen because Kurosawa and co-workers[6a] had already measured K values for the reactions in eq 1 for a variety

$$[CpPd(PR_3)(o\text{-}MeC_6H_4CN)]BF_4 + \text{olefin} \rightleftharpoons [CpPd(PR_3)(\text{olefin})]BF_4 + o\text{-}MeC_6H_4CN \quad (1)$$

of simple olefins: e.g., ethylene, 1-butene, *cis*-2-butene,

* To whom correspondence should be addressed. Phone: (515) 294-2603. Fax: (515) 294-0105. E-mail: angelici@iastate.edu.

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(2) Heidrich, J. F. *J. Am. Oil Chem. Soc*. **1984**, *61*, 271.

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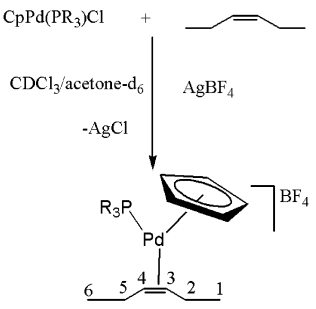
10.1021/om049009q CCC: $30.25
Publication on Web 03/04/2005

Scheme 1



3a, $PR_3 = PPh_3$; **3b**, $PR_3 = PMePh_2$; **3c**, $PR_3 = PMe_3$

trans-2-butene, and styrene. During the course of the equilibrium studies with 18:1, 18:2, and 18:3, it was necessary to characterize the composition of the complexes and the binding sites of the fatty acid methyl esters with two and three double bonds. It is these investigations of the $[CpPd(PR_3)(olefin)]^+$ and $\{[CpPd(PR_3)]_2(olefin)\}^{2+}$complexes that we report herein.

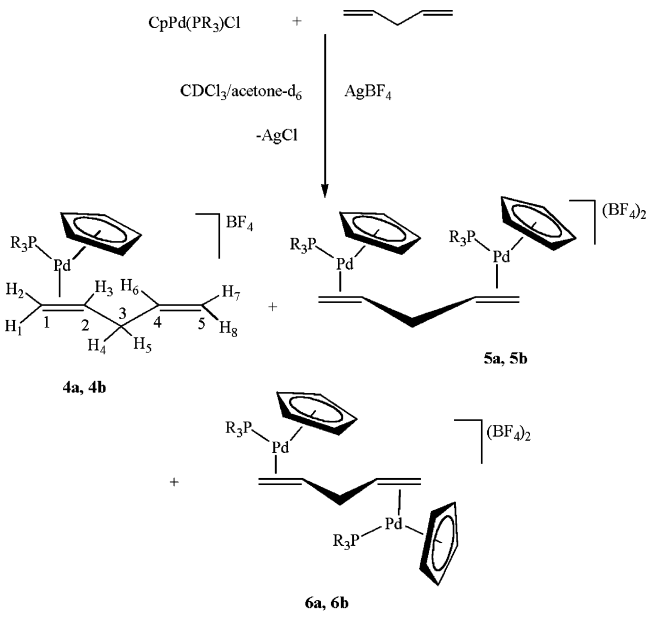
Results and Discussion

Synthesis and Characterization of the Complexes. (a) $CpPd(PR_3)Cl$ ($PR_3 = PMePh_2$ (1), PMe_3 (2)). By a procedure used for the synthesis of $CpPd(PR_3)Cl$ ($PR_3 = PPh_3$, PEt_3, PBu_3),[6,7] compounds **1** and **2** were prepared by the reaction of the binuclear chloride-bridged palladium(II) complexes $(R_3P)_2Pd_2Cl_4$ ($PR_3 = PMePh_2$, PMe_3) with cyclopentadienylthallium in tetrahydrofuran at room temperature; the green air-stable $CpPd(PR_3)Cl$ products were characterized by their elemental analyses and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra.

(b) $[CpPd(PR_3)(cis\text{-}3\text{-hexene})]BF_4$ ($PR_3 = PPh_3$ (3a), $PMePh_2$ (3b), PMe_3 (3c)). The complexes of *cis*-3-hexene were prepared and characterized in order to facilitate NMR assignments to the more complicated spectra of the analogous complexes of 18:1. Reactions of the $CpPd(PR_3)Cl$ complexes (0.11 mmol) with *cis*-3-hexene (0.33 mmol) in chloroform-*d*/acetone-d_6 in the presence of silver tetrafluoroborate gave complexes **3a**−**c** (Scheme 1). Coordination of the olefin to Pd(II) was evidenced by a substantial upfield shift of the olefinic protons from 5.34 ppm in free *cis*-3-hexene to 3.95, 4.02, and 4.40 ppm in **3a**−**c**, respectively. Like the other $[CpPd(PR_3)(olefin)]BF_4$ complexes, **3a**−**c** were not sufficiently stable to be isolated as pure solids.

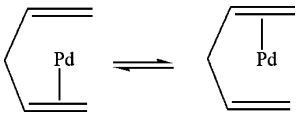
(c) $[CpPd(PR_3)(1,4\text{-pentadiene})]BF_4$ (4a,b) and $\{[CpPd(PR_3)]_2(1,4\text{-pentadiene})\}(BF_4)_2$ (5a,b, 6a,b). These complexes were prepared and characterized as relatively simple models of the 1,4-pentadiene unit in the complexes of 18:2. The addition of 0.15−0.33 mmol of 1,4-pentadiene and solid $CpPd(PR_3)Cl$ (0.11 mmol) to a suspension of silver tetrafluoroborate in chloroform-*d*/acetone-d_6 (7:1) resulted in the formation of the three types of complexes **4**−**6** (Scheme 2); in **4** the 1,4-pentadiene is bonded to one $[CpPd(PR_3)]^+$ unit, while two $[CpPd(PR_3)]^+$ units are bonded in the others (**5** and **6**). The relative abundances of complexes **4**−**6**, as determined from peak intensities in the ^1H NMR spectra, are dependent upon the amount of 1,4-pentadiene used. When a large excess of the 1,4-pentadiene ligand (3 equiv) is used, the mononuclear complexes **4a**,**b** are formed as major products with only trace amounts of **5a**,**b** and **6a**,**b**. On the other hand, when a small amount (1.5 equiv) of the free 1,4-pentadiene is used, the binuclear compounds **5a**,**b** and **6a**,**b** predominate. Therefore, the complexes **4**−**6** are in rapid equilibrium, their relative amounts depending on the concentration of 1,4-pentadiene. Characterization of the mononuclear (**4a**,**b**) and binuclear (**5a**,**b** and **6a**,**b**) complexes was established by means of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

Scheme 2



$PR_3 = PPh_3$ (**4a, 5a, 6a**); $PR_3 = PMe_3$ (**4b, 5b, 6b**)

Scheme 3



The ^1H NMR spectrum of **4a** shows three olefinic resonances (instead of the six expected for an η^2-coordinated 1,4-pentadiene ligand) at 5.13 ppm ($H_{3,6}$), 4.73 ppm ($H_{2,7}$), and 4.31 ppm ($H_{1,8}$), which are approximate averages of the chemical shifts of free 1,4-pentadiene and the 1,4-pentadiene ligand with both double bonds coordinated in **5a** and **6a**. For example, the chemical shift for $H_{3,6}$ in **4a** is 5.13 ppm, while the average for these protons in free 1,4-pentadiene (5.86 ppm) and **5a** (4.14 ppm) is 5.00 ppm. These ^1H NMR results suggest that the two terminal CH_2 and the two internal CH protons are exchanging rapidly, as shown in Scheme 3. The mechanism for this process could involve Pd dissociation from one double bond and coordination to the other or PR_3 dissociation or Cp ring slippage accompanied by coordination to the other double bond. The resonance due to the Cp protons in **4a** is a doublet at 5.88 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 35.51 ppm. The $^{13}C\{^1H\}$ NMR spectrum of **4a** is also consistent with this exchange process. The olefinic carbon resonances appear as two singlets at 116.80 ppm ($C_{2,4}$) and 101.00 ppm ($C_{1,5}$). These chemical shifts are also approximate averages of

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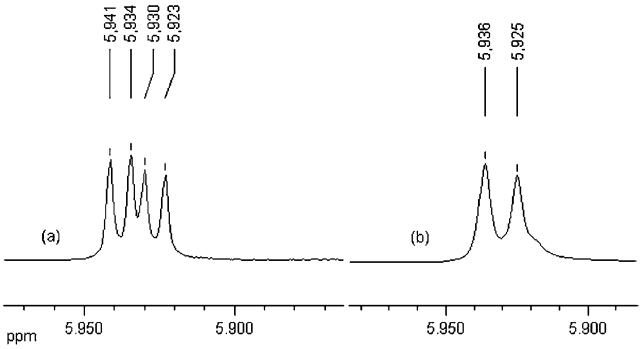


Figure 1. ^{1}H NMR spectra of **5a** and **6a** in the Cp region in $CDCl_3$/acetone-d_6: (a) ^{31}P coupled; (b) ^{31}P decoupled.

those for free 1,4-pentadiene and the 1,4-pentadiene ligand with both double bonds coordinated in **5a** and **6a**. For example, the chemical shift for $C_{2,4}$ in **4a** is 116.80 ppm, while the average value of free 1,4-pentadiene (135.5 ppm) and **5a** (98.40 ppm) is 117.0 ppm. The resonance for the Cp carbons is observed as a doublet at 103.88 ppm with a P−C coupling constant of 2.0 Hz. To slow the exchange process and determine if one of these compounds is favored at low temperature, the $^{13}C\{^1H\}$ NMR spectrum of **4a**−**6a** was recorded at −80 °C. However, no additional peaks were observed, suggesting that **4a** remains fluxional at −80 °C. Also, there was no significant change in the ratio of **4a**−**6a**. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **4b** are similar to those of **4a**; they also indicate rapid migration of the $[CpPd(PMe_3)]^+$ unit between the two double bonds.

The spectral features of the binuclear complexes $\{[CpPd(PPh_3)]_2(1,4\text{-pentadiene})\}^{2+}$ (**5a** and **6a**) are described below. Figure 1 shows the ^{1}H NMR spectrum of the binuclear complexes **5a** and **6a** in the Cp region, with and without ^{31}P decoupling. Without ^{31}P decoupling, the Cp protons of **5a** and **6a** give rise to two doublet peaks at 5.94 and 5.93 ppm, while the ^{31}P-decoupled spectrum gives two singlets. The two Cp and ^{31}P signals indicate that two binuclear compounds $\{[CpPd(PPh_3)_2]_2(1,4\text{-pentadiene})\}^{2+}$ (**5a** and **6a**) are present in solution. In the $^{31}P\{^1H\}$ NMR spectrum, **5a** displays a singlet resonance at 37.90 ppm, indicating effective mirror symmetry of the molecule. Likewise, **6a** displays a singlet resonance at 37.40 ppm, indicating the presence of two equivalent phosphorus atoms. The two isomers **5a** and **6a** are proposed to have structures that differ by the faces through which the $[CpPd(PPh_3)]^+$ units are coordinated to the 1,4-pentadiene. In one isomer (**5a**) both $[CpPd(PPh_3)]^+$ units are on the same side of the 1,4-pentadiene, when it is drawn (Scheme 2) in the planar conformation. In the other isomer (**6a**), the $[CpPd(PPh_3)]^+$ units are on opposite sides of the planar 1,4-pentadiene. It is not possible to interconvert these isomers by rotating around any of the C−C single bonds. NMR studies of **5b** also show that it exists as the two isomers **5b** and **6b**, but in this case it was possible to obtain crystals of **5b**, whose structure was established by an X-ray diffraction analysis (see below). It should be noted that when crystals of **5b** were dissolved in CD_3NO_2, the ^{1}H NMR spectrum showed the presence of **4b**−**6b**, as expected for this rapidly equilibrating mixture.

The η^2 coordination of the olefinic groups in **5a** and **6a** was also established by the pronounced upfield ^{1}H and $^{13}C\{^1H\}$ NMR shifts of the coordinated olefinic protons and carbons compared to those of the free 1,4-pentadiene. For instance, in the $^{13}C\{^1H\}$ NMR spectrum of **5a**, the olefinic signals at 98.46 ppm ($C_{1,5}$) and 65.19 ppm ($C_{2,4}$) are substantially upfield of those at 135.5 ppm ($C_{2,4}$) and 115.5 ppm ($C_{1,5}$) in the free 1,4-pentadiene ligand. The $^{13}C\{^1H\}$ NMR spectrum of **5a** also displays a doublet at 103.30 ppm corresponding to the Cp carbons. No significant change in the $^{13}C\{^1H\}$ NMR spectra of **5a** and **6a** was observed when the temperature was lowered to −80 °C.

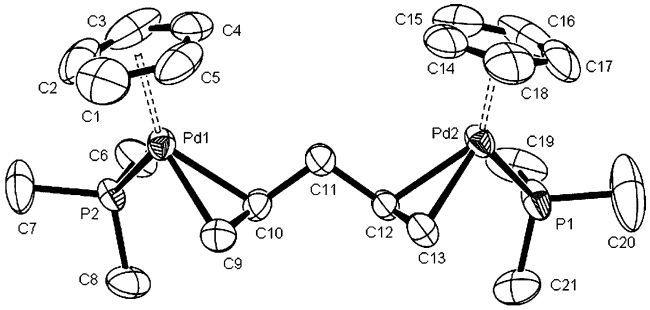


Figure 2. ORTEP drawing of the $\{[CpPd(PMe_3)]_2(1,4\text{-pentadiene})\}^{2+}$ cation in **5b** showing the atom-numbering scheme (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pd(1)−C(9), 2.163(8); Pd(1)−C(10), 2.184(7); Pd(2)−C(12), 2.187(7); Pd(2)−C(13), 2.209(7); Pd(1)−P(2), 2.271(2); Pd(2)−P(1), 2.256(2); C(9)−C(10), 1.36(1); C(12)−C(13), 1.43(1). Selected bond angles (deg): C(10)−Pd(1)−P(2), 93.6(2); C(9)−Pd(1)−P(2), 98.7(2); C(12)−Pd(2)−P(1), 94.5(2); C(13)−Pd(2)−P(1), 100.1(1).

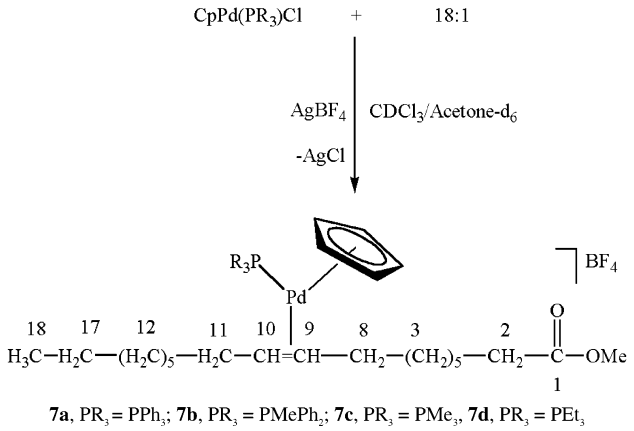
The $^{13}C\{^1H\}$ NMR spectrum of **6a** displays signals at 94.40 ppm ($C_{2,4}$) and 64.99 ppm ($C_{1,5}$) for the olefinic carbons; these compare to those at 135.5 ppm ($C_{2,4}$) and 115.5 ppm ($C_{1,5}$) in free 1,4-pentadiene. The $^{13}C\{^1H\}$ NMR spectrum of **6a** also displays a doublet at 104.23 ppm corresponding to the Cp carbons. Spectral data for **5b** and **6b** are quite similar to those of **5a** and **6a** discussed above.

An ORTEP view, together with selected bond distances and angles, of **5b** is given in Figure 2. Each palladium is coordinated to cyclopentadienyl (Cp), PMe_3, and olefin ligands, and the $[CpPd(PMe_3)]^+$ groups are on the same side of the 1,4-pentadiene. A similar coordination geometry around the palladium atom was found in the analogous $[CpPd(PEt_3)(CH_2{=}CHC_6H_5)]BF_4$[6,8] and related complexes with substituted styrene ligands.[6b] The Pd(1)−C(9) (2.163(8) Å), Pd(1)−C(10) (2.184(7) Å), Pd(2)−C(12) (2.187(7) Å), and Pd(2)−C(13) bond lengths (2.209(7) Å) are comparable to those in $[CpPd(PEt_3)(CH_2{=}CHC_6H_5)]BF_4$.[6,8] The C(9)=C(10) bond distance (1.36(1) Å) is well within the range of coordinated carbon−carbon double bonds observed in $[CpPd(PEt_3)(CH_2{=}CHC_6H_5)]BF_4$[6,8] and related substituted styrene complexes,[6b] but the C(12)=C(13) bond distance (1.43(2) Å) is longer than expected and probably reflects the relatively large standard deviations for **5b**.

(d) $[CpPd(PR_3)(18{:}1)]BF_4$ (PR_3 = PPh_3 (7a), $PMePh_2$ (7b), PMe_3 (7c), PEt_3 (7d)). The methyl oleate (18:1) complexes $[CpPd(PR_3)(18{:}1)]BF_4$ (**7a**−**d**), though of limited stability, were prepared from $CpPd(PR_3)Cl$ (0.11

(8) Miki, K.; Yama, M.; Kai, Y.; Kasai, N. *J. Organomet. Chem.* **1982**, *239*, 417.

Scheme 4



7a, $PR_3 = PPh_3$; **7b**, $PR_3 = PMePh_2$; **7c**, $PR_3 = PMe_3$, **7d**, $PR_3 = PEt_3$

mmol) and methyl oleate (0.33 mmol) in the presence of silver tetrafluoroborate (Scheme 4). Attempted isolation of the complexes as pure solids by precipitation and/or crystallization was not successful. Washing the resulting precipitate with hexanes to remove excess 18:1 led to the decomposition products $[CpPd(PR_3)_2](BF_4)_2$[6a] and free 18:1. However, the relatively high stability of the complexes in the presence of excess 18:1 was exploited in their characterization and identification in solution.

Coordination of methyl oleate (18:1) to the Pd(II) center is clearly indicated by the ^1H and $^{13}C\{^1H\}$ NMR spectra. In the ^1H NMR spectrum a large upfield shift is observed for the coordinated olefinic protons in complexes **7a**−**d** relative to the uncoordinated olefin. Such shielding of olefinic protons is common in η^2-olefin complexes of transition metals.[9,10] The chemical shifts of the coordinated olefinic protons occur at 4.08 ppm (**7a**), 4.10 ppm (**7b**), 4.52 ppm (**7c**), and 4.38 ppm (**7d**). The higher upfield chemical shifts observed for the PPh_3 and $PMePh_2$ complexes **7a**,**b** are probably associated with diamagnetic shielding by the phenyl rings. Since distinct ^1H NMR resonances for free (5.34 ppm) and coordinated 18:1 (4.08 ppm) in **7a** (Figure 3) are observed, exchange between the free and coordinated olefin is slow on the NMR time scale. The resonances due to the Cp protons appear as doublets at 5.73, 5.77, 5.81, and 5.74 ppm for **7a**−**d**, respectively, as a result of coupling to phosphorus. These signals are shifted by about 0.2 ppm downfield compared to those for the corresponding $CpPd(PR_3)Cl$ complexes (∼5.56 ppm). Assignments for protons H_2, H_8, $H_{9,10}$, H_{11}, H_{17}, and H_{18} of methyl oleate in the complexes (see the Experimental Section) are based on previous assignments for those protons in the free unsaturated fatty acid methyl ester.[11] Assignments for C_1, C_2, C_8, C_9, C_{10}, C_{11}, C_{17}, and C_{18} of the methyl oleate in the $^{13}C\{^1H\}$ NMR spectra of **7a**−**d** were made on the basis of previous assignments for those carbons in the free unsaturated fatty acid methyl ester.[12] The olefinic carbons in complexes **7a**−**d** occur as two peaks at 97.27 ppm (C_9) and 97.40 ppm (C_{10}) for **7a**, at 95.54 ppm (C_9) and 95.52 ppm (C_{10}) for **7b**, at 93.34 ppm (C_9) and 93.47 ppm (C_{10}) for **7c**, and at 93.34 ppm (C_{10}) and 93.19 ppm (C_9) for **7d**; these are upfield of those at 129.72 ppm (C_9) and 129.97 ppm (C_{10}) for free 18:1.[12b] The $^{13}C\{^1H\}$ NMR resonances for the Cp ligand occur as doublets at 104.85 ppm (**7a**), 103.51 ppm (**7b**), 102.38 ppm (**7c**), and 102.48 ppm (**7d**). The $^{13}C\{^1H\}$ resonance for the C=O group is observed at 173.35 ppm, while the OMe signal is observed at 51.05 ppm in **7a**.

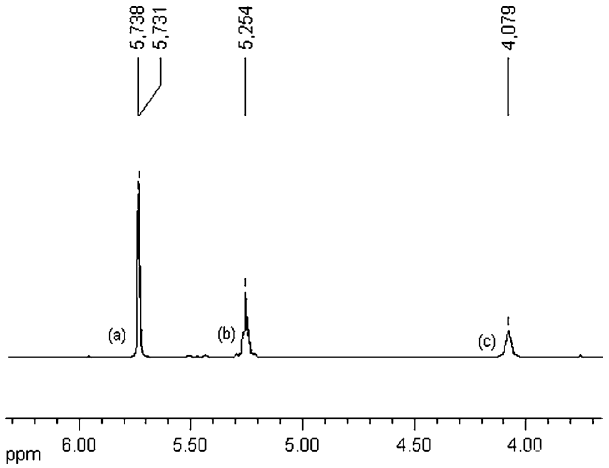


Figure 3. ^1H NMR spectrum of **7a** in $CDCl_3$/acetone-d_6: (a) Cp; (b) free 18:1; (c) coordinated 18:1.

(e) $[CpPd(PR_3)(18:2)]BF_4$ (8a,b) and $\{[CpPd(PR_3)]_2(18:2)\}(BF_4)_2$ (9a,b). The methyl linoleate (18:2) complexes $[CpPd(PR_3)(18:2)]BF_4$ (**8a**,**b**) and $\{[CpPd(PR_3)]_2(18:2)\}(BF_4)_2$ (**9a**,**b**) were prepared in the reaction of $CpPd(PR_3)Cl$ (0.11 mmol) with methyl linoleate (0.33 mmol) in the presence of silver tetrafluoroborate, as shown in Scheme 5. Like **7a**,**b,** compounds **8** and **9** could not be isolated in pure form, due to their limited stability and gradual decomposition to $[CpPd(PR_3)_2]^{2+}$ and free 18:2 as the main products. The synthesis of **8** and **9** in chloroform-*d*/acetone-d_6 (7:1) produced a red solution after filtration of the silver chloride precipitate. ^1H and $^{13}C\{^1H\}$ NMR spectra of these solutions show signals for the coordinated olefin protons and carbons that are significantly upfield of the corresponding signals in free 18:2. Assignments for protons H_2, H_8, $H_{9,10}$, H_{11}, $H_{12,13}$, H_{14}, H_{17}, and H_{18} of methyl linoleate in the complexes (see the Experimental Section) are based on previous assignments for those protons in the free unsaturated fatty acid methyl ester.[11] Assignments for C_1, C_2, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{17}, and C_{18} of the methyl linoleate in the $^{13}C\{^1H\}$ NMR spectra of **8** and **9** were made on the basis of previous assignments for those carbons in the free unsaturated fatty acid methyl ester.[12] The methyl linoleate complexes present

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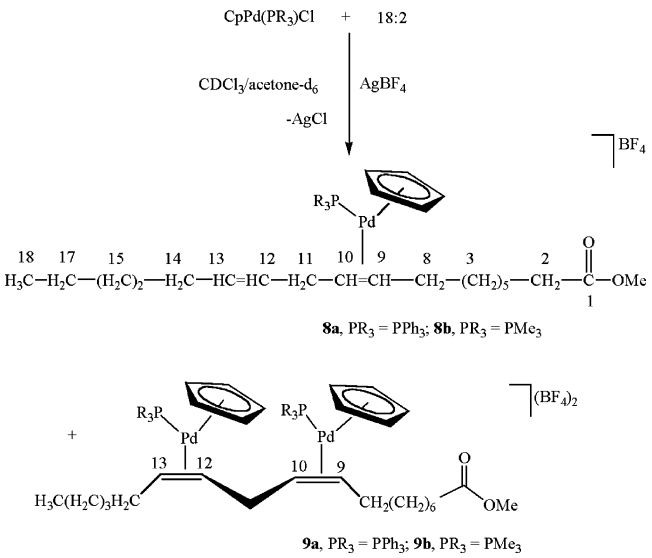
Scheme 5



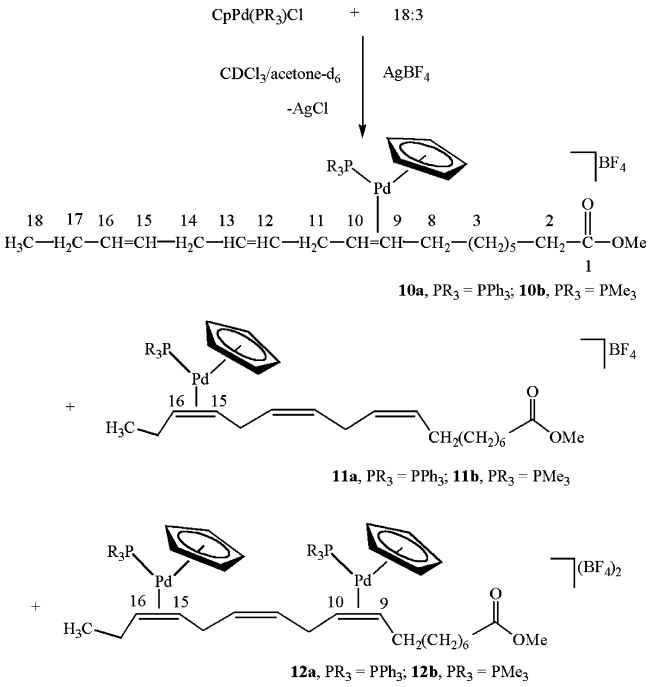
in solution contain either one coordinated $[CpPd(PR_3)]^+$ unit (**8**) or two (**9**). Identification of these compounds was achieved by comparison of their ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra with those of $[CpPd(PR_3)(18:1)]^+$ (**7a**,**b**) and $\{[CpPd(PR_3)]_2(1,4\text{-pentadiene})\}^{2+}$ (**5a**,**b, 6a**,**b**). Since complexes **8b** and **9b** exhibit spectroscopic features similar to those of **8a** and **9a**, a detailed discussion of only **8a** and **9a** is presented here.

In ^1H and $^{13}C\{^1H\}$ NMR spectra of the mixture of complexes **8a** and **9a** are peaks that may be assigned on the basis of their relative intensities to a complex with the composition $[CpPd(PPh_3)(18:2)]^+$ (**8a**), whose structure is proposed to be that shown in Scheme 5, in which the $[CpPd(PPh_3)]^+$ unit is coordinated to C_9 and C_{10}. The following ^1H and $^{13}C\{^1H\}$ NMR data favor this site for $[CpPd(PPh_3)]^+$ coordination rather than at C_{12} and C_{13}, but they do not exclude the possibility of $C_{12,13}$ coordination. However, there is no evidence for two isomers of $[CpPd(PPh_3)(18:2)]^+$ in which $[CpPd(PPh_3)]^+$ is coordinated at $C_{9,10}$ or $C_{12,13}$. The ^1H NMR spectrum of **8a** shows a broad multiplet centered at 4.06 ppm for the coordinated olefinic protons, which is very similar to that for $H_{9,10}$ (4.08 ppm) in $[CpPd(PPh_3)(18:1)]^+$ (**7a**). The uncoordinated olefinic protons in **8a** occur as a broad multiplet at 5.43 ppm, which is very similar to $H_{12,13}$ at 5.36 ppm in free 18:2. The $^{13}C\{^1H\}$ NMR spectrum of **8a** shows singlets at 94.87 and 94.90 ppm, which are considerably upfield of C_9 (127.88 ppm) and C_{10} (128.01 ppm) in free 18:2 but are similar to those for C_9 (97.27 ppm) and C_{10} (97.40 ppm) in $[CpPd(PPh_3)(18:1)]^+$ (**7a**). The uncoordinated olefin carbons in **8a** give rise to peaks at 131.82 and 131.95 ppm, respectively, which are close to those of C_{12} (129.99 ppm) and C_{13} (130.16 ppm) in free 18:2. The assignment of $[CpPd(PPh_3)]^+$ bonding to $C_{9,10}$ rather than $C_{12,13}$ is based primarily on the fact that the chemical shifts of $C_{12,13}$ (131.82 and 131.95 ppm) of the uncoordinated olefin in **8a** are more similar to those of $C_{12,13}$ (129.99, 130.16 ppm) in free 18:2 than they are to $C_{9,10}$ (127.88, 128.01 ppm) in free 18:2. Supporting the structural assignment for **8a** in Scheme 5 is the Cp doublet at 5.75 ppm, which is similar to that (5.73 ppm) of $[CpPd(PPh_3)(18:1)]^+$ (**7a**) and the $^{31}P\{^1H\}$ singlet at 37.87 ppm, which is similar to that (38.51 ppm) in **7a.** The observation of separate olefinic signals for the coordinated and uncoordinated double bonds in **8a** indicates that the $[CpPd(PPh_3)]^+$ group is not rapidly migrating between the two double bonds, as was observed in $[CpPd(PPh_3)(1,4\text{-pentadiene})](BF_4)$ (**4a**). The long *cis* hydrocarbon chains on C_9 and C_{13} would be expected to prevent the two olefins from achieving a parallel orientation that would allow a rapid transfer of the $[CpPd(PPh_3)]^+$ unit from one olefin to the other.

The electrospray ionization spectra (ESI) of chloroform/acetone solutions of **8a** and **9a** and free 18:2 show peaks at *m/z* 695 for $[(Cp)Pd(PPh_3)(18:2)]^+$, at *m/z* 903 for $[(Cp)Pd_2(PPh_3)(18:2)]^{2+}$, and at *m/z* 953 for $[(Cp)Pd_2(18:2)]^+$. The isotopic pattern for the peaks is consistent with the presence of two Pd atoms in the *m/z* 903 and 953 fragments. Treatment of a chloroform-*d*/acetone-d_6 solution of **8a** and **9a** with equimolar $[(n\text{-}Bu)_4N]Cl$ led to an instantaneous color change from red to green; the ^1H NMR spectrum showed the products to be $CpPd(PPh_3)Cl$ and free 18:2.

The binuclear complex $\{[CpPd(PPh_3)]_2(18:2)\}^{2+}$ (**9a**), in which the $[CpPd(PR_3)]^+$ unit is coordinated to the $C_{9,10}$ and $C_{12,13}$ sites shown in Scheme 5, is detected as a minor product. The intensity ratio of the Cp protons in the ^1H NMR spectra of **8a** and **9a** was about 5:1. The ^1H NMR spectrum of **9a** exhibits doublet peaks at 5.87 and 5.86 ppm for the Cp protons; these resonances are similar to those (5.94 ppm) observed for $\{[CpPd(PPh_3)]_2(1,4\text{-pentadiene})\}^{2+}$ (**5a**) (Scheme 2). Resonances for the coordinated olefinic protons are observed as multiplets at higher fields (4.00 and 3.89 ppm) as compared to those for free 18:2 at 5.36 ppm. The $^{31}P\{^1H\}$ NMR spectrum of **9a** exhibits two separate singlet resonances at 38.37 and 38.32 ppm with approximately equal intensities due to the nonequivalent PPh_3 ligands, as expected for a molecule lacking mirror symmetry. These resonances are similar to that (37.40 ppm) observed in $\{[CpPd(PPh_3)]_2(1,4\text{-pentadiene})\}^{2+}$ (**5a**). The presence of two nonequivalent $^{31}P\{^1H\}$ signals and two Cp groups in the ^1H NMR spectrum of **9a** also indicates the asymmetric nature of the methyl linoleate (18:2) ligand. In the $^{13}C\{^1H\}$ NMR spectrum of **9a**, resonances due to the Cp carbons are observed as doublets at 103.54 and 103.65 ppm, which are similar to 103.30 ppm in $\{[CpPd(PPh_3)]_2(1,4\text{-pentadiene})\}(BF_4)_2$ (**5a**). The coordinated olefinic carbon resonances are observed at 94.92 ppm (C_9), 95.06 ppm (C_{10}), 97.14 ppm (C_{12}), and 97.28 ppm (C_{13}), which are considerably upfield of those (127.07 ppm (C_9), 129.85 ppm (C_{10}), 129.65 ppm (C_{12}) and 130.20 ppm (C_{13})) in free 18:2. The $^{13}C\{^1H\}$ chemical shift assignments for the coordinated olefinic carbons, high field for $C_{9,10}$ and low field for $C_{12,13}$, are based on the fact that the chemical shifts for $C_{9,10}$ are at higher field than those of $C_{12,13}$ in free 18:2.[12] For the binuclear complex **9a**, there is the possibility of forming two isomers in which the $[CpPd(PR_3)]^+$ groups are coordinated on either the same side or opposite sides of the 1,4-pentadiene unit, as observed for $\{[CpPd(PPh_3)]_2(1,4\text{-pentadiene})\}(BF_4)_2$ (**5a,b** and **6a**,**b**) (Scheme 2). However, all the NMR data indicate the presence of only one isomer. When the ^1H and $^{13}C\{^1H\}$ NMR spectra of the binuclear complex **9a** are compared to those of $\{[CpPd(PR_3)]_2(1,4\text{-pentadiene})\}(BF_4)_2$ (**5a**,**b** and **6a**,**b**), the more likely structure is that shown in Scheme 5,

Scheme 6



where the $[CpPd(PR_3)]^+$ groups are on the same side of the 1,4-pentadiene unit, similar to that of $\{[CpPd(PMe_3)]_2$(1,4-pentadiene)$\}(BF_4)_2$ (**5b**), which was characterized by an X-ray crystal structure analysis.

(f) $[CpPd(PR_3)(18:3)]BF_4$ (10a,b, 11a,b) and $\{[CpPd(PR_3)]_2(18:3)\}(BF_4)_2$ (12a,b). The methyl linolenate (18:3) complexes **10**−**12** (Scheme 6) were prepared by addition of 0.33 mmol of methyl linolenate and 0.11 mmol of $CpPd(PR_3)Cl$ to a chloroform-*d*/acetone-d_6 (7:1) solution of silver tetrafluoroborate at 0 °C. Like **8** and **9,** compounds **10**−**12** could not be isolated in pure form, due to their limited stability and gradual decomposition to $[CpPd(PR_3)_2]^{2+}$ and free 18:3 as the main products. The synthesis of **10**−**12** in chloroform-*d*/acetone-d_6 (7:1) produced a red solution after filtration of the silver chloride precipitate. Assignments for protons H_2, H_8, $H_{9,10}$, H_{11}, $H_{12,13}$, H_{14}, $H_{15,16}$, H_{17}, and H_{18} of methyl linolenate in the complexes (see the Experimental Section) are based on previous assignments for those protons in the free unsaturated fatty acid methyl ester.[11] Assignments for C_1, C_2, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, and C_{18} of the methyl linolenate in the $^{13}C\{^1H\}$ NMR spectra of **10**−**12** were made on the basis of previous assignments for those carbons in the free unsaturated fatty acid methyl ester.[12] ^1H and $^{13}C\{^1H\}$ NMR spectra of these solutions show signals for the coordinated olefin protons and carbons that are shifted significantly upfield of the corresponding signals in free 18:3. The relative abundances of complexes **10a**−**12a**, as determined by the relative peak intensities, depends on the concentration of the $[CpPd(PPh_3)]^+$ units. For example, when 0.33 mmol of the $[CpPd(PPh_3)(o\text{-}MeC_6H_4CN)]BF_4$ complex was added instead of 0.11 mmol, the relative amounts of **11a** and **12a** increased while that of **10a** decreased. Attempts to coordinate three $[CpPd(PR_3)]^+$ units by using a 4-fold excess (0.44 mmol) of the $CpPd(PR_3)Cl$ complexes gave no evidence for trimetalated 18:3. The methyl linolenate complexes present in solution contain either one coordinated $[CpPd(PR_3)]^+$ unit (**10** and **11**) or two (**12**). Since complexes **10b**−**12b** exhibit spectroscopic features similar to those of **10a**−**12a**, a detailed discussion of only **10a**−**12a** is presented here.

In the reactions of $CpPd(PPh_3)Cl$ with 18:3, the three species (**10a**−**12a**) shown in Scheme 6 were detected by both their ^1H and $^{13}C\{^1H\}$ NMR spectra. The relative amounts of **10a**−**12a** were about 3:1:1, as determined from their ^1H NMR spectra. Clearly, the coordination behavior of 18:3 with $CpPd(PPh_3)Cl$ is considerably more complicated than that observed for the analogous complexes of 18:1 and 18:2, due to the presence of three double bonds. However, analysis of the ^1H and $^{13}C\{^1H\}$ NMR spectra of the mixture shows peaks that correspond to two, not three, monometalated complexes with the composition $[CpPd(PPh_3)(18:3)]^+$ (**10a** and **11a**) whose structures are proposed to be those shown in Scheme 6, in which the $[CpPd(PPh_3)]^+$ is coordinated to $C_{9,10}$, and $C_{15,16}$, respectively. Compounds **10a** and **11a** have the same composition and very similar ^1H and $^{13}C\{^1H\}$ NMR spectra. The only difference between them is the coordination site of the $[CpPd(PPh_3)]^+$ unit on the triene ligand. Assignments of the signals are discussed separately for compounds **10a** and **11a**.

The ^1H NMR spectrum of **10a** shows a broad multiplet at 4.09 ppm attributed to the coordinated olefinic protons ($H_{9,10}$) which is very similar to that for $H_{9,10}$ (4.08 ppm) in $[CpPd(PPh_3)(18:1)]^+$ (**7a**). Resonances for the uncoordinated olefinic protons in **10a** are observed as broad multiplets at 5.42 ppm ($H_{12,13}$) and 5.48 ppm ($H_{15,16}$), which are close to those $H_{12,13,15,16}$ (5.36 ppm) in free 18:3. Supporting this structural assignment is the doublet peak at 5.79 ppm assigned to the Cp protons, which is similar to that (5.73 ppm) of $[CpPd(PPh_3)(18:1)]^+$ (**7a**). The $^{31}P\{^1H\}$ NMR spectrum of **10a** shows a singlet at 37.87 ppm which is similar to that (38.51 ppm) in **7a**. The $^{13}C\{^1H\}$ NMR spectrum of **10a** shows a doublet resonance at 104.72 ppm assigned to the Cp carbons, which is similar to that (104.85 ppm) for **7a**. Resonances for the coordinated olefinic carbons are observed at 94.56 ppm (C_9) and 94.60 ppm (C_{10}), which are considerably upfield of those (127.05 ppm (C_9) and 127.67 ppm (C_{10})) in free 18:3 but similar to those for C_9 (97.27 ppm) and C_{10} (97.40 ppm) in $[CpPd(PPh_3)(18:1)]^+$ (**7a**). The $^{13}C\{^1H\}$ NMR spectrum of **10a** also shows resonances for the uncoordinated olefinic carbons, $C_{12,13}$ (131.14, 131.96 ppm) and $C_{15,16}$ (132.35, 133.96 ppm), which are more similar to those for $C_{12,13}$ (128.17, 128.20 ppm) and $C_{15,16}$ (131.85, 130.17 ppm) than to those for $C_{9,10}$ (127.05, 127.67 ppm) in free 18:3. Although the NMR data support the structure of **10a** shown in Scheme 6, they do not completely exclude the possibility of $[CpPd(PPh_3)]^+$ coordination at one of the other double bonds.

The spectral features of $[CpPd(PPh_3)(18:3)]^+$ (**11a**) described below favor the $C_{15,16}$ site for $[CpPd(PPh_3)]^+$ coordination rather than the $C_{12,13}$ site, but they do not exclude the possibility of $C_{12,13}$ coordination. The ^1H NMR spectrum of **11a** exhibits a broad multiplet at 4.06 ppm for the coordinated olefinic protons ($H_{15,16}$) which is considerably upfield of 5.36 ppm ($H_{15,16}$) in free 18:3.[11] Resonances for the uncoordinated olefinic protons in **11a** are observed as broad multiplets at 5.38 ppm ($H_{9,10}$) and 5.44 ppm ($H_{12,13}$), which are close to those of $H_{9,10,12,13}$ (5.36 ppm) in free 18:3. The ^1H NMR signal

for the Cp ligand is observed as a doublet at 5.81 ppm. The $^{31}P\{^1H\}$ NMR spectrum displays a singlet at 35.33 ppm. In the $^{13}C\{^1H\}$ NMR spectrum of **11a**, the Cp carbons give rise to a doublet at 104.64 ppm with a P−C coupling constant of 2.0 Hz. Resonances for the coordinated olefinic carbons are observed at 97.14 ppm (C_{15}) and 98.92 ppm (C_{16}), which are considerably upfield of C_{15} (130.17 ppm) and C_{16} (131.85 ppm) in free 18:3. The $^{13}C\{^1H\}$ NMR spectrum of **11a** also shows resonances for the uncoordinated olefinic carbons $C_{12,13}$ (128.88, 129.95 ppm), and $C_{9,10}$ (125.60, 125.81 ppm), which are more similar to $C_{12,13}$ (128.17, 128.20 ppm) and $C_{9,10}$ (127.05, 127.67 ppm) than to $C_{15,16}$ (130.17, 131.85 ppm) in free 18:3, which is the primary reason for assigning $[CpPd(PPh_3)]^+$ coordination to $C_{15,16}$ rather than $C_{12,13}$.

The dimetalated $\{[CpPd(PPh_3)]_2(18:3)\}^{2+}$ (**12a**), in which the $[CpPd(PPh_3)]^+$ unit is proposed to be coordinated to the $C_{9,10}$ and $C_{15,16}$ positions, as shown in Scheme 6, was detected as a minor product. While the following ^1H and $^{13}C\{^1H\}$ NMR spectra favor the $C_{9,10}$ and $C_{15,16}$ sites for $[CpPd(PPh_3)]^+$ coordination rather than to $C_{9,10}$ and $C_{12,13}$ or $C_{12,13}$ and $C_{15,16}$, they do not completely exclude the possibility of these other coordination modes. However, there is evidence for only one dimetalated complex. The ^1H NMR spectrum of **12a** shows broad multiplet resonances attributed to the coordinated olefinic protons at 4.05 ppm ($H_{9,10}$) and 4.01 ppm ($H_{15,16}$), which are considerably upfield of 5.36 ppm in free 18:3. The doublet resonances at 5.91 and 5.92 ppm are assigned to the Cp protons, and these resonances are very similar to that (5.94 ppm) for $\{[CpPd(PPh_3)]_2(1,4\text{-pentadiene})\}^{2+}$ (**5a**) (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum displays singlet resonances at 38.37 and 38.32 ppm, which are similar to that (37.40 ppm) for $\{[CpPd(PPh_3)]_2(1,4\text{-pentadiene})\}^{2+}$ (**5a**). The $^{13}C\{^1H\}$ NMR spectrum of **12a** shows doublet peaks at 104.94 and 104.86 ppm due to the Cp carbons which are similar to that (103.30 ppm) observed in **5a**. Resonances for the coordinated olefinic carbons in **12a** are observed at 94.55 ppm (C_9), 94.65 ppm (C_{10}), 94.80 ppm (C_{15}), and 94.82 ppm (C_{16}) which are considerably upfield of those in free 18:3 at 127.05 ppm (C_9), 127.67 ppm (C_{10}), 130.17 ppm (C_{15}), and 131.85 ppm (C_{16}). The $^{13}C\{^1H\}$ chemical shift assignments for the coordinated olefinic carbons, high field to $C_{9,10}$ and low field to $C_{15,16}$, in **12a** are made on the basis of the fact that the resonances for $C_{9,10}$ are upfield of those for $C_{15,16}$ in free 18:3.[12] The uncoordinated olefinic carbons are observed at 126.25 ppm (C_{12}) and 126.45 ppm (C_{13}), which are more similar to $C_{12,13}$ (128.17, 128.20 ppm) than they are to $C_{15,16}$ (130.17, 131.85 ppm) in free 18:3. The observation of two distinct doublet signals for the Cp protons and carbons in the NMR spectrum of **12a** agrees with the presence of two inequivalent $[CpPd(PPh_3)]^+$ units coordinated to the triene (18:3). The observation of four distinct signals for the coordinated double bonds and two signals for the uncoordinated olefinic double bonds in the $^{13}C\{^1H\}$ NMR spectrum of **12a** is also consistent with the inequivalence of the three olefinic groups in **12a**.

Equilibrium Studies. Equilibrium constants for the binding of unsaturated fatty acid methyl esters and *cis*-3-hexene to $[CpPd(PR_3)]^+$ were determined in $CDCl_3$ solvent at 25.0 °C for the reactions shown in Scheme 7. Previously Kurosawa and co-workers[6a] reported K_1 values also in $CDCl_3$ solvent at 23.0 °C for the binding of simple olefins.

Scheme 7

$$[CpPd(PR_3)(o\text{-}MeC_6H_4CN)]BF_4 + \text{olefin} \overset{K_1}{\rightleftharpoons} [CpPd(PR_3)(\text{olefin})]BF_4 + o\text{-}MeC_6H_4CN$$

$$[CpPd(PPh_3)(o\text{-}MeC_6H_4CN)]BF_4 + [CpPd(PPh_3)(18:2)]BF_4 \overset{K_2}{\rightleftharpoons} \{[CpPd(PPh_3)]_2(18:2)\}(BF_4)_2 + o\text{-}MeC_6H_4CN$$

$$[CpPd(PPh_3)(o\text{-}MeC_6H_4CN)]BF_4 + 18:3 \overset{K_1(\mathbf{10a})}{\rightleftharpoons} [CpPd(PPh_3)(18:3)]BF_4 + o\text{-}MeC_6H_4CN$$

10a

$$[CpPd(PPh_3)(o\text{-}MeC_6H_4CN)]BF_4 + 18:3 \overset{K_1(\mathbf{11a})}{\rightleftharpoons} [CpPd(PPh_3)(18:3)]BF_4 + o\text{-}MeC_6H_4CN$$

11a

$$[CpPd(PPh_3)(o\text{-}MeC_6H_4CN)]BF_4 + [CpPd(PPh_3)(18:3)]BF_4 \overset{K_2(\mathbf{10a})}{\rightleftharpoons} \{[CpPd(PPh_3)]_2(18:3)\}(BF_4)_2 + o\text{-}MeC_6H_4CN$$

10a

$$[CpPd(PPh_3)(o\text{-}MeC_6H_4CN)]BF_4 + [CpPd(PPh_3)(18:3)]BF_4 \overset{K_2(\mathbf{11a})}{\rightleftharpoons} \{[CpPd(PPh_3)]_2(18:3)]BF_4 + o\text{-}MeC_6H_4CN$$

11a

The equilibrium expressions shown in Scheme 7 are defined as follows: K_1 is the equilibrium constant for the formation of the mononuclear complexes $[CpPd(PR_3)(\text{olefin})]BF_4$ (olefin = *cis*-3-hexene, 18:1, and 18:2). K_2 is the equilibrium constant for the formation of the binuclear methyl linoleate complex $\{[CpPd(PR_3)]_2(18:2)\}(BF_4)_2$ with two $[CpPd(PR_3)]^+$ units coordinated at the C_9-C_{10} and $C_{12}-C_{13}$ positions. K_1(**10a**) is the equilibrium constant for the formation of the mononuclear methyl linolenate complex $[CpPd(PPh_3)(18:3)]BF_4$ (**10a**) with one $[CpPd(PPh_3)]^+$ unit coordinated at the C_9-C_{10} position, whereas K_1(**11a**) is the equilibrium constant for the formation of $[CpPd(PPh_3)(18:3)]BF_4$ (**11a**) with one $[CpPd(PPh_3)]^+$ unit coordinated at the $C_{15}-C_{16}$ position. K_2(**10a**) and K_2(**11a**) are equilibrium constants for the formation of the binuclear methyl linolenate complex $\{[CpPd(PPh_3)]_2(18:3)\}(BF_4)_2$ (**12a**), in which two $[CpPd(PPh_3)]^+$ units are coordinated at the C_9-C_{10} and $C_{15}-C_{16}$ positions.

The ^1H NMR spectra of the reaction mixtures, recorded within 3−5 min of mixing, showed that the reactions had already achieved equilibrium. The presence of well-separated resonances for the free and coordinated olefins indicates that the exchange between the free and coordinated olefin is slow on the NMR time scale. Since ^1H NMR signals were unambiguously assignable to the *o*-tolunitrile and olefin species in solution, integrations of the Cp and *o*-tolunitrile proton signals using methyl β-naphthyl ether as an internal standard gave concentrations of the reactants and

Table 1. Equilibrium Constants for the Formation of [CpPd(PR$_3$)(olefin)]BF$_4$ and {[CpPd(PR$_3$)]$_2$(olefin)}(BF$_4$)$_2$ in CDCl$_3$ at 25 °C According to Scheme 7

compd	PR$_3$	olefin	K_1	K_2
3a	PPh_3	*cis*-3-hexene	0.43 ± 0.02	
3b	$PMePh_2$	*cis*-3-hexene	3.2 ± 0.1	
3c	PMe_3	*cis*-3-hexene	21.1 ± 0.1	
7a	PPh_3	18:1	0.19 ± 0.01	
7b	$PMePh_2$	18:1	1.64 ± 0.05	
7d	PEt_3	18:1	2.50 ± 0.05	
7c	PMe_3	18:1	5.52 ± 0.06	
8	PPh_3	18:2	0.22 ± 0.02	0.11 ± 0.01
10	PPh_3	18:3	0.17 ± 0.02 (**10a**)	0.20 ± 0.02 (**10a**)
10	PPh_3	18:3	0.072 ± 0.009 (**11a**)	0.47 ± 0.04 (**11a**)
7a	PPh_3	18:1	0.56 ± 0.11[a]	
7a	PPh_3	18:1	0.43 ± 0.11[b]	
7a	PPh_3	18:1	0.37 ± 0.11[c]	
7a	PPh_3	18:1	0.30 ± 0.11[d]	

[a] At −10.0 ± 0.1 °C. [b] At −5.0 ± 0.1 °C. [c] At 5.0 ± 0.1 °C. [d] At 10.0 ± 0.1 °C.

products which allowed the equilibrium constants to be calculated. The equilibrium constants for *cis*-3-hexene and the fatty acid methyl esters (18:1, 18:2, and 18:3) determined by this method are presented in Table 1. The K_1 values for the *cis*-3-hexene complexes [CpPd(PR$_3$)(*cis*-3-hexene)]BF$_4$ increase with the phosphines in the order: PPh_3 (0.43) < $PMePh_2$ (3.21) < PMe_3 (21.1). A similar trend in the K_1 values was observed for the methyl oleate [CpPd(PR$_3$)(18:1)]BF$_4$ complexes: PPh_3 (0.19) < $PMePh_2$ (1.64) < PEt_3 (2.50) < PMe_3 (5.52). The cone angles and the pK_a values[13] for these phosphines are PPh_3 (145°, 2.73), $PMePh_2$ (136°, 4.57), PEt_3 (132°, 8.69), and PMe_3 (118°, 8.65). Since PMe_3 and PEt_3 have very similar basicities and, therefore, electron-donating abilities, the lower K_1 for the PEt_3 complex (2.50) as compared with that (5.52) for the PMe_3 complex is probably due to the greater steric effect of PEt_3. The PEt_3 and $PMePh_2$ ligands have similar cone angles (132 vs 136°), but 18:1 binds more strongly to the PEt_3 complex, as indicated by the K_1 values (2.50 vs 1.64). This difference in K_1 values suggests that the more strongly donating PEt_3 ligand promotes strong olefin coordination by back-bonding. Thus, both electronic and steric effects of the phosphine ligand appear to play a role in the observed trend in K_1 values. It should be noted that PPh_3 is both the most bulky and least basic of the phosphines, which results in its complex having the lowest K_1 value.

K_1 values for the formation of the [CpPd(PPh_3)(olefin)]BF$_4$ complexes are nearly the same (within a factor of 2) for *cis*-3-hexene, 18:1, and 18:2. Moreover, these values are similar to those reported[6a] previously for *cis*-2-butene (0.22 ± 0.05); however, they are significantly larger than those of *trans*-olefins, e.g., *trans*-2-butene (0.04), but smaller than those of terminal olefins, e.g., 1-butene (1.14), styrene (0.63), and ethylene (13.5 ± 0.6).[6a]

The equilibrium constant (K_1) for the formation of [CpPd(PPh_3)(18:1)]$^+$ was also measured at 10.0 ± 0.1, 5.0 ± 0.1, −5.0 ± 0.1, and −10.0 ± 0.1 °C (Table 1). The thermodynamic parameters calculated from a van't Hoff plot (−ln(K_1) vs 1/T) of these data are $\Delta H° = -16.7 \pm 1$ kJ mol^{-1}, $\Delta G° = +2.3$ kJ mol^{-1} at 5 °C, and $\Delta S° = -68.5 \pm 4$ J mol^{-1} K^{-1}. The relatively small $\Delta H°$ value implies that the Pd−olefin and Pd−nitrile bond energies are very similar. The negative entropy ($\Delta S°$) value for this reaction is consistent with a greater loss in degrees of freedom when the large 18:1 coordinates to palladium(II) in place of *o*-tolunitrile.

In the case of 18:2 (Scheme 5), an equilibrium mixture of complexes involving coordination to one or two double bonds was observed. The major observed product was the mononuclear [CpPd(PPh_3)(18:2)]BF$_4$ species, while the {[CpPd(PPh_3)]$_2$(18:2)}(BF$_4$)$_2$ binuclear species was produced as a minor product. In this system, K_1 (0.22) is 2 times larger than K_2 (0.11).

In the reactions of [CpPd((PPh_3)(*o*-MeC$_6$H$_4$CN)](BF$_4$) with 18:3, equilibrium mixtures contain two isomeric mononuclear [CpPd(PPh_3)(18:3)]$^+$ complexes (**10a** and **11a**) and the binuclear [CpPd(PPh_3)]$_2$(18:3)]$^{2+}$ (**12a**). The K_1(**10a**) value (0.17) for the formation of isomer **10a** is very similar to that of K_1 (0.19 ± 0.01) for the binding of 18:1 in [CpPd(PPh_3)(18:1)]$^+$. The K_2(**10a**) value for the binding of the second [CpPd(PPh_3)]$^+$ to **10a** to give **12a** is essentially the same as K_1(**10a**), which indicates that the presence of the first [CpPd(PPh_3)]$^+$ on 18:3 does not reduce the binding to the second [CpPd(PPh_3)]$^+$ unit. The K_1(**11a**) value (0.072) for the formation of isomer **11a** is about half of the value (0.17) of K_1(**10a**). Although the difference between K_1(**10a**) and K_1(**11a**) is not large, it is not obvious why on the basis of their structures (Scheme 6) there would be a significant difference in K_1(**10a**) and K_1(**11a**) values. The low stability of **11a** is also evident in the relatively high value of K_2(**11a**) (0.47) for the addition of the second [CpPd(PPh_3)]$^+$ unit to **11a**.

Perhaps the most significant result of these studies is that the K_1 values for *cis*-3-hexene (0.43), 18:1 (0.19), 18:2 (0.22), and 18:3 (0.17) (for the major isomer) are all very similar; the slightly higher value for *cis*-3-hexene may reflect the overall smaller size of this olefin. In addition, the K_2 values for 18:2 (0.11) and 18:3 (0.20) for the major isomer **10a** are also similar, which indicates that the binding of one [CpPd(PPh_3)]$^+$ unit does not substantially reduce the binding ability of the diene or triene to the second [CpPd(PPh_3)]$^+$ unit.

Conclusions

Cationic Pd(II)−olefin complexes of the type [CpPd(PR$_3$)(olefin)]BF$_4$ (PR$_3$ = PPh_3, $PMePh_2$, PEt_3, PMe_3; olefin = 18:1, 18:2, 18:3, *cis*-3-hexene, 1,4-pentadiene) and {[CpPd(PR$_3$)]$_2$(olefin)}$^{2+}$ (olefin = 1,4-pentadiene, 18:2, 18:3) have been characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy in solution. Equilibrium constants for the formation of these complexes have led to the following observations. (a) Olefin binding increases significantly with the PR$_3$ ligand in the complexes in the order PPh_3 < $PMePh_2$ < PEt_3 < PMe_3. (b) Equilibrium constants (K_1) for the binding of all of the *cis*-olefins to [CpPd(PPh_3)]$^+$ are similar. Since this is also true for 18:1, 18:2, and 18:3, it will be difficult to separate these fatty acid methyl esters from each other on the basis of their ability to coordinate to one [CpPd(PPh_3)]$^+$ unit. (c) Equilibrium constants (K_2) for the binding of a second [CpPd(PPh_3)]$^+$ unit to the diene (18:2) and triene (18:3) are also similar to each other and

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to their K_1 values, which shows that the binding of one $[CpPd(PPh_3)]^+$ unit does not significantly reduce the ability of a 1,4-diene or 1,4-triene to bind to a second $[CpPd(PPh_3)]^+$ unit.

Experimental Section

All of the reactions were carried out under an argon atmosphere. Diethyl ether, methylene chloride, hexanes, and tetrahydrofuran were purified on alumina using a Solv-Tek solvent purification system, as described by Grubbs and coworkers.[14] Acetone was refluxed over and distilled from $CaSO_4$.[15] $[CpPd(PPh_3)(o\text{-}MeC_6H_4CN)]BF_4$,[6a] $CpPd(PPh_3)Cl$,[7] $CpPd(PEt_3)Cl$,[7] and $(PR_3)_2Pd_2Cl_4$[16] were synthesized by literature procedures. All other chemicals were reagent grade and were used as received. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DRX-400 spectrometer. Proton and carbon chemical shifts were measured relative to internal deuterated solvents, while 85% H_3PO_4 (aqueous) was the external reference for phosphorus chemical shifts; positive values are downfield of the respective reference. See H and C labels in the schemes for the ^1H and ^{13}C NMR assignments. In the $^{31}P\{^1H\}$ spectra of the $[CpPd(PR_3)(olefin)]BF_4$ complexes, small amounts of the $[CpPd(PR_3)_2]BF_4$ complexes were often detected.[6a]

Syntheses of the Complexes CpPd(PR$_3$)Cl (PR$_3$ = PMePh$_2$ (1), PMe$_3$ (2)). The complexes were synthesized by following the literature method for $CpPd(PPh_3)Cl$.[6,7] Thallium cyclopentadienyl (0.31 g, 1.10 mmol) was suspended in 100 mL of tetrahydrofuran (THF), and $(PR_3)_2Pd_2Cl_4$ (0.50 g, 0.57 mmol) was added. The mixture immediately changed color to green and was stirred at room temperature for 1 h. The resulting solution was filtered to remove thallium chloride. The solvent was removed under reduced pressure to leave a dark green solid. The solid was dissolved in a minimum amount of benzene and layered with hexane to yield dark green needles of the desired products in 60−70% yield. Anal. Calcd for $C_{18}H_{18}PPdCl$ (**1**): C, 53.09; H, 4.45. Found: C, 52.99; H, 4.45. Anal. Calcd for $C_8H_{14}PPdCl$ (**2**): C, 33.94; H, 4.98. Found: C, 34.26; H, 5.06.

1: ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.40−7.65 (m, 10H, Ph), 5.57 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 2.15 (d, $^2J_{PH}$ = 11.6 Hz, 3H, P*Me*Ph$_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 134.59 (d, $^1J_{PC}$ = 49.2 Hz, C_i), 132.11 (d, $^2J_{PC}$ = 11.9 Hz, C_o), 130.71 (d, $^4J_{PC}$ = 2.7 Hz, C_p), 128.73 (d, $^3J_{PC}$ = 10.9 Hz, C_m), 100.94 (d, J_{PC} = 2.6 Hz, C_5H_5), 15.41 (d, $^1J_{PC}$ = 33.3 Hz, P*Me*Ph$_2$); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C) δ 23.44 ($PMePh_2$).

2: ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 5.71 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 1.61 (d, $^2J_{PH}$ = 12.0 Hz, 9H, PMe_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 99.48 (d, J_{PC} = 2.7 Hz, C_5H_5), 18.68 (d, $^1J_{PC}$ = 32.1 Hz, PMe_3); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C) δ 0.47 (PMe_3).

Syntheses of [CpPd(PR$_3$)(*cis*-3-hexene)]BF$_4$ (PR$_3$ = PPh$_3$ (3a), PMePh$_2$ (3b), PMe$_3$ (3c)). A suspension of $AgBF_4$ (0.10 mmol) in a chloroform/acetone (1:1) (10.0 mL) solvent mixture was treated with 0.33 mmol of *cis*-3-hexene. To this mixture was added solid $CpPd(PR_3)Cl$ (0.10 mmol) with stirring at 0 °C. After it was stirred for 15 min, the red solution was filtered to remove AgCl. The filtrate was layered with hexane to yield a red-brown precipitate of the complexes. Attempted purification to remove the excess olefin resulted in gradual decomposition of the products. Hence, the complexes were prepared in situ and characterized in chloroform-*d*/acetone-d_6 (7:1) solvent mixtures.

3a: ^1H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 7.40−7.50 (m, 15H, Ph), 5.65 (d, J_{PH} = 2.8 Hz, 5H, C_5H_5), 3.95 (m, 2H, $H_{3,4}$), 2.04 (m, 4H, $H_{2,5}$), 0.88 (t, $^3J_{HH}$ = 7.6 Hz, 6H, $H_{1,6}$).

3b: ^1H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 7.30−7.50 (m, 10H, Ph), 5.71 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 4.02 (m, 2H, $H_{3,4}$), 2.17 (d, $^2J_{PH}$ = 11.6 Hz, 3H, P*Me*Ph$_2$) 2.05 (m, 4H, $H_{2,5}$), 0.92 (t, $^3J_{HH}$ = 7.5 Hz, 6H, $H_{1,6}$).

3c: ^1H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.71 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 4.40 (m, 2H, $H_{3,4}$), 2.11 (m, 4H, $H_{2,5}$), 1.53 (d, $^3J_{PH}$ = 12.4 Hz, 9H, $3CH_3$), 0.99 (t, $^3J_{HH}$ = 7.6 Hz, 6H, $H_{1,6}$).

Syntheses of [CpPd(PR$_3$)(1,4-pentadiene)]BF$_4$ (4a,b) and {[CpPd(PR$_3$)]$_2$(1,4-pentadiene)}(BF$_4$)$_2$ (5a,b and 6a,b). The same procedure as for the synthesis of **3a**−**c** above was followed for the synthesis of **4**−**6**.

4a (PR$_3$ = PPh$_3$): ^1H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 7.50 (m, 15H, Ph), 5.88 (d, J_{PH} = 2.8 Hz, 5H, C_5H_5), 5.13 (m, 2H, $H_{3,6}$), 4.73 (m, 2H, $H_{2,7}$), 4.31 (m, 2H, $H_{1,8}$), 3.21 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 2.8 Hz, 2H, $H_{4,5}$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 133.30 (d, $^2J_{PC}$ = 11.6 Hz, C_o), 132.08 (d, $^4J_{PC}$ = 2.8 Hz, C_p), 129.17 (d, $^3J_{PC}$ = 11.2 Hz, C_m), 128.06 (d,$^1J_{PC}$ = 50.0 Hz, C_i), 116.80 ($C_{2,4}$), 103.88 (d, J_{PC} = 2.0 Hz, C_5H_5),101.00 ($C_{1,5}$), 44.12 (C_3); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C) δ 35.51 (PPh_3).

4b (PR$_3$ = PMe$_3$): ^1H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.94 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 5.64 (m, 2H, $H_{3,6}$), 5.05 (m, 2H, $H_{2,7}$), 4.78 (m, 2H, $H_{1,8}$), 3.59 (d, $^3J_{HH}$ = 8.0 Hz, 2H, $H_{4,5}$), 1.64 (d, $^2J_{PH}$ = 12.8 Hz, 9H, $3CH_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 116.06 ($C_{2,4}$), 101.61 (d, J_{PC} = 2.4 Hz, C_5H_5), 99.04 ($C_{1,5}$), 37.64 (C_3), 18.13 (d, $^1J_{PC}$ = 32.2 Hz, CH_3); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.45 (PMe_3).

5a (PR$_3$ = PPh$_3$): ^1H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 7.31−7.70 (m, 30H, $2PPh_3$), 5.94 (d, J_{PH} = 2.1 Hz, 10H, C_5H_5), 4.86 (m, 2H, $H_{3,6}$), 3.86 (m, 4H, $H_{1,2,7,8}$), 2.93 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 2.8 Hz, 2H, $H_{4,5}$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 133.44 (d, $^2J_{PC}$ = 10.8 Hz, C_o), 131.93 (C_p), 129.35 (d,$^3J_{PC}$ = 9.0 Hz, C_m), 128.10 (d, $^1J_{PC}$ = 48.9 Hz, C_i), 104.23 (d, J_{PC} = 1.6 Hz, C_5H_5), 98.46 ($C_{2,4}$), 65.19 ($C_{1,5}$), 37.58 (C_3); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C) δ 37.90.

5b (PR$_3$ = PMe$_3$): ^1H NMR (400 MHz, CD_3NO_2, 25 °C) δ 6.08 (d, J_{PH} = 2.4 Hz, 10H, C_5H_5), 4.87 (m, 1H, $H_{3,6}$), 4.62 (m, 4H, $H_{1,2,7,8}$), 3.73 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 2.0 Hz, 2H, $H_{4,5}$), 1.71 (d $^2J_{PH}$ = 12.4 Hz, 9H, $3CH_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3NO_2, 25 °C) δ 102.95 (d, J_{PC} = 1.5 Hz, C_5H_5), 94.66 ($C_{2,4}$), 67.89 ($C_{1,5}$), 42.90 (C_3), 17.62 (d, $^1J_{PC}$ = 33.1 Hz, CH_3); $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_3NO_2, 25 °C) δ 5.88 (PMe_3).

6a (PR$_3$ = PPh$_3$): ^1H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 7.31−7.70 (m, 30H, $2PPh_3$), 5.93 (d, J_{PH} = 2.1 Hz, 10H, C_5H_5), 4.14 (m, 2H, $H_{3,6}$), 3.72 (m, 2H, $H_{1,2,7,8}$), 2.85 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 2.8 Hz, 2H, $H_{4,5}$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 133.35 (d, $^2J_{PC}$ = 10.8 Hz, C_o), 131.22 (C_p), 129.09 (d, $^3J_{PC}$ = 9.0 Hz, C_m), 104.23 (d, J_{PC} = 1.6 Hz, C_5H_5), 94.40 ($C_{2,4}$), 64.99 ($C_{1,5}$), 37.17 (C_3); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C) δ 37.40 (PPh_3).

6b (PR$_3$ = PMe$_3$): ^1H NMR (400 MHz, CD_3NO_2, 25 °C) δ 6.07 (d, J_{PH} = 2.4 Hz, 10H, C_5H_5), 5.13 (m, 2H, $H_{3,6}$), 4.76 (m, 4H, $H_{1,2,7,8}$), 3.68 (dd, $^3J_{HH}$ = 7.6 Hz, $^2J_{HH}$ = 2.0 Hz, 2H, $H_{4,5}$), 1.71 (d, $^2J_{PH}$ = 12.4 Hz, 9H, $3CH_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3NO_2, 25 °C) δ 102.80 (d, J_{PC} = 2.1 Hz, C_5H_5), 97.50 ($C_{2,4}$), 67.89 ($C_{1,5}$), 47.50 (C_3), 17.60 (d, $^1J_{PC}$ = 33.0 Hz, CH_3); $^{31}P\{^1H\}$ NMR (162 MHz, CD_3NO_2, 25 °C) δ 5.86 (PMe_3).

Syntheses of [CpPd(PR$_3$)(18:1)]BF$_4$ (PR$_3$ = PPh$_3$ (7a), PMePh$_2$ (7b), PMe$_3$ (7c), PEt$_3$ (7d)). As described for the synthesis of the *cis*-3-hexene complexes, the complexes $[CpPd(PR_3)(18:1)]BF_4$ (PR_3 = PPh_3 (**7a**), $PMePh_2$ (**7b**), PMe_3 (**7c**), PEt_3 (**7d**)) were all synthesized by the following method. To a suspension of $AgBF_4$ (0.11 mmol) in a chloroform/acetone (1:1) (10.0 mL) solvent mixture was added 0.33 mmol of methyl oleate (18:1). To this solution was added solid $CpPd(PR_3)Cl$ (0.11 mmol) with stirring at 0 °C. After it was stirred for 15

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min, the red solution was filtered to remove AgCl. The filtrate was layered with hexane to yield a red-brown precipitate. Subsequent purification attempts to remove the excess 18:1 resulted in decomposition. Hence, further reactions and characterizations of the complexes were conducted in chloroform-*d*/acetone-d_6 (7:1) solution.

7a: ^{1}H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 7.51 (m, 15H, Ph), 5.73 (d, J_{PH} = 2.8 Hz, 5H, C_5H_5), 4.08 (m, 2H, $H_{9,10}$), 3.51 (s, 3H, OMe), 2.31 (m, 2H, H_{11}), 2.23 (t, $^3J_{HH}$ = 7.2 Hz, 2H, H_2), 2.11 (m, 2H, H_8), 1.34 (m, 2H, H_{17}), 1.20 (m, 20H, $H_{3,12}$), 0.85 (t, $^3J_{HH}$ = 7.0 Hz, 3H, H_{18}); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.69 (C=O), 133.25 (d, $^2J_{PC}$ = 11.5 Hz, C_o), 132.22 (d, $^4J_{PC}$ = 2.7 C_p), 129.4 (d, $^1J_{PC}$ = 20.7 Hz, C_i), 128.05 (C_m), 104.85 (d, J_{PC} = 1.9 Hz, C_5H_5), 97.40 (C_{10}), 97.27 (C_9), 50.96 (OMe), 35.52 (C_2), 32.47 (C_{11}), 31.41 (C_8), 31.30−24.38, ($C_{3,12}$), 22.26 (C_{17}), 13.66 (C_{18}); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 38.51 (PPh_3).

7b: ^{1}H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 7.40−7.65 (m, 10H, Ph), 5.77 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 4.10 (m, 2H, $H_{9,10}$), 3.52 (s, 3H, OMe), 2.32 (m, 2H, H_{11}), 2.25 (t, $^3J_{HH}$ = 7.2 Hz, 2H, H_2), 2.15 (d, $^2J_{PH}$ = 11.6 Hz, 9H, P*Me*Ph_2), 2.13 (m, 2H, H_8), 1.57 (m, 2H, H_{17}), 1.21 (m, 20H, $H_{3,12}$), 0.83 (t, $^3J_{HH}$ = 7.0 Hz, 3H, H_{18}); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.53 (C=O), 134.59 (d, $^1J_{PC}$ = 49.2 Hz, C_i), 132.11 (d, $^2J_{PC}$ = 11.9 Hz, C_o), 130.71 (d, $^4J_{PC}$ = 2.7 Hz, C_p), 128.73 (d, $^3J_{PC}$ = 10.9 Hz, C_m), 103.51 (d, J_{PC} = 1.8 Hz, C_5H_5), 95.54 (C_{10}), 95.52 (C_9), 51.94 (OMe), 35.52 (C_2), 32.47 (C_{11}), 31.41 (C_8), 31.30−24.33 ($C_{3,12}$), 22.24 (C_{17}), 15.41 (d, $^1J_{PC}$ = 33.3 Hz, P*Me*Ph_2), 13.66 (C_{18}); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 38.41 ($PMePh_2$).

7c: ^{1}H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.81 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 4.52 (m, 2H, $H_{9,10}$), 3.58 (s, 3H, OMe), 2.17 (m, 4H, $H_{8,11}$), 1.92 (m, 2H, H_2), 1.63 (d, $^2J_{PH}$ = 12.4 Hz, 9H, $3CH_3$), 1.54 (m, 2H, H_{17}), 1.24 (m, 20H, $H_{3,12}$), 0.87 (t, $^3J_{HH}$ = 7.0 Hz, 3H, H_{18}); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.66 (C=O), 102.38 (d, J_{PC} = 2.1 Hz, C_5H_5), 93.47 (C_{10}), 93.34 (C_9), 50.93 (OMe), 33.49 (C_2), 33.39 (C_{11}), 33.02 (C_8), 31.44−24.39 ($C_{3,12}$), 22.22 (C_{17}), 17.12 (d, $^1J_{PC}$ = 32.90 Hz, PMe_3), 13.63 (C_{18}); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 4.85 (PMe_3).

7d: ^{1}H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.74 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 4.38 (m, 2H, $H_{9,10}$), 3.48 (s, 3H, OMe), 1.97 (m, 4H, $H_{8,11}$), 1.83 (m, 6H, $3CH_2$), 1.72 (m, 2H, H_2), 1.42 (m, 2H, H_{17}), 1.11 (m, 20H, $H_{3,12}$), 0.95 (m, 9H, $3CH_3$), 0.70 (t,$^3J_{HH}$ = 7.0 Hz, 3H, H_{18}); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.51 (C=O), 102.48 (d, J_{PC} = 2.2 Hz, C_5H_5), 93.34 (C_{10}), 93.19 (C_9), 50.83 (OMe), 33.39 (C_2), 33.35 (C_{11}), 33.05 (C_8), 31.44−24.30 ($C_{3,12}$), 19.12 (C_{17}), 17.00 (d, $^1J_{PC}$ = 28.2 Hz, PEt_3), 13.40 (C_{18}), 7.91 (d, $^2J_{PC}$ = 19.3, PEt_3); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 42.52 (PEt_3).

Syntheses of [CpPd(PR$_3$)(18:2)]BF$_4$ (8a,b) and {[CpPd(PR$_3$)]$_2$(18:2)}(BF$_4$)$_2$ (9a,b). The same procedure as for the synthesis of complexes **7a**−**c** was followed for the synthesis of **8** and **9.**

8a (**PR$_3$ = PPh$_3$**): ^{1}H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 7.49−7.52 (m, 15H, Ph), 5.75 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 5.43 (m, 2H, $H_{12,13}$), 4.06 (m, 2H, $H_{9,10}$), 3.60 (s, 3H, OMe), 3.01 (m, 1H, H_{11}), 2.65 (m, 1H, H_8), 2.20 (t, $^3J_{HH}$ = 6.4 Hz, 2H, H_2), 2.12 (m, 2H, H_{14}), 1.52 (m, 2H, H_{17}), 1.22 (m, 14H, $H_{3,15}$), 0.80 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_{18}); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.64 (C=O), 133.41 (d, $^1J_{PC}$ = 20.4 Hz, C_i), 132.36 (d, $^2J_{PC}$ = 13.2 Hz, C_o), 132.20 (d, $^4J_{PC}$ = 2.1 Hz, C_p), 129.25 (C_{13}), 129.14 (C_{12}), 125.94 (d, $^3J_{PC}$ = 8.0 Hz, C_m), 104.75 (d, J_{PC} = 2.0 Hz, C_5H_5), 94.94 (C_{10}), 94.87 (C_9), 50.91 (OMe), 33.54 (C_2), 33.48 (C_{11}), 32.60 (C_8), 30.93 (C_{14}), 30.84−24.35 ($C_{3,15}$), 21.98 (C_{17}), 13.49 (C_{18}); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 33.69 (PPh_3).

8b (**PR$_3$ = PMe$_3$**): ^{1}H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.74 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 5.34 (m, 2H, $H_{12,13}$), 4.45 (m, 2H, $H_{9,10}$), 3.67 (s, 3H, OMe), 3.03 (m, 1H, H_{11}), 2.63 (m, 1H, H_8), 2.25 (t, $^3J_{HH}$ = 6.6 Hz, 2H, H_2), 2.15 (m, 2H, H_{14}), 1.54 (d, $^2J_{PH}$ = 12.4 Hz, 9H, $3PMe_3$), 1.50 (m, 2H, H_{17}), 1.26 (m, 14H, $H_{3,15}$), 0.87 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_{18}); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.80 (C=O), 131.95 (C_{13}), 131.83 (C_{12}), 102.38 (d, J_{PC} = 1.4 Hz, C_5H_5), 91.22 (C_{10}), 91.18 (C_9), 50.95 (OMe), 33.57 (C_2), 33.48 (C_{11}), 32.64 (C_8), 30.95 (C_{14}), 30.80−24.37 ($C_{3,15}$), 21.92 (C_{17}), 17.17 (d $^1J_{PC}$ = 32.8 Hz, PMe_3), 13.49 (C_{18}); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 4.84 (PMe_3).

9a (PR$_3$ = PPh$_3$): ^{1}H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 7.49−7.52 (m, 15H, Ph), 5.87 (d, J_{PH} = 1.6 Hz, 5H, C_5H_5), 5.86 (d, J_{PH} = 1.6 Hz, 5H, C_5H_5), 5.43 (m, 2H, $H_{12,13}$), 4.00 (m, 2H, $H_{12,13}$), 3.89 (m, 2H, $H_{9,10}$), 3.60 (s, 3H, OMe), 3.01 (m, 2H, H_{11}), 2.65 (m, 2H, H_8), 2.20 (t, $^3J_{HH}$ = 6.4 Hz, 2H, H_2), 2.12 (m, 2H, H_{14}), 1.52 (m, 2H, H_{17}), 1.22 (m, 14H, $H_{3,15}$), 0.82 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_{18}); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.64 (C=O), 133.41 (d, $^1J_{PC}$ = 20.4 Hz, C_i), 132.36 (d, $^2J_{PC}$ = 13.2 Hz, C_o), 132.20 (d, $^4J_{PC}$ = 2.1 Hz, C_p), 125.94 (d, $^3J_{PC}$ = 8.0 Hz, C_m), 101.38 (d, J_{PC} = 1.5 Hz, C_5H_5), 101.30 (d, J_{PC} = 1.5 Hz, C_5H_5), 97.28 (C_{13}), 97.14 (C_{12}), 94.91 (C_{10}), 94.87 (C_9), 50.91 (OMe), 33.54 (C_2), 33.48 (C_{11}), 32.60 (C_8), 30.93 (C_{14}), 30.84−21.98, ($C_{3,15}$), 13.49 (C_{18}); ^{31}P-{^{1}H} NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 38.37, (PPh_3), 38.32 (PPh_3).

9b (PR$_3$ = PMe$_3$): ^{1}H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.84 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 5.82 (d, J_{PH} = 2.3 Hz, 5H, C_5H_5), 4.32 (m, 2H, $H_{12,13}$), 4.30 (m, 2H, $H_{9,10}$), 3.31 (s, 3H, OMe), 3.09 (m, 2H, H_{11}), 2.63 (m, 2H, H_8), 2.22 (t, $^3J_{HH}$ = 6.5 Hz, 2H, H_2), 2.17 (m, 2H, H_{14}), 1.57 (d, $^2J_{PH}$ = 12.4 Hz, 9H, $3PMe_3$), 1.55 (d, $^2J_{PH}$ = 12.4 Hz, 9H, $3PMe_3$), 1.50 (m, 2H, H_{17}), 1.19 (m, 14H, $H_{3,15}$), 0.80 (t, $^3J_{HH}$ = 7.0 Hz, 3H, H_{18}); ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.75 (C=O), 102.76 (d, J_{PC} = 1.5 Hz, C_5H_5), 102.74 (d, J_{PC} = 1.5 Hz, C_5H_5), 93.27 (C_{13}), 93.11 (C_{12}), 91.22 (C_{10}), 91.18 (C_9), 51.0 (OMe), 33.48 (C_2), 33.38 (C_{11}), 32.60 (C_8), 30.93 (C_{14}), 30.82−21.94 ($C_{3,15}$), 17.15 (d $^1J_{PC}$ = 32.7 Hz, PMe_3), 17.13 (d, $^1J_{PC}$ = 32.6 Hz, PMe_3), 13.49 (C_{18}); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 4.26 (PMe_3), 4.08 (PMe_3).

Syntheses of [CpPd(PR$_3$)(18:3)]BF$_4$ (10a,b and 11a,b) and {[CpPd(PR$_3$)]$_2$(18:3)}(BF$_4$)$_2$ (12a,b). The same procedure as for the synthesis of complexes **7a**−**c** was followed for the synthesis of **10**−**12**.

10a (PR$_3$ = PPh$_3$): ^{1}H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 7.48−7.50 (m, 15H, Ph), 5.79 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 5.42 (m, 2H, $H_{15,16}$), 5.29 (m, 2H, $H_{12,13}$), 4.09 (m, 2H, $H_{9,10}$), 3.66 (s, 3H, OMe), 3.08 (m, 1H, H_{11}), 2.80 (m, 1H, H_{14}), 2.21 (t, $^3J_{HH}$ = 6.5 Hz, 2H, H_2), 2.15 (m, 2H, H_8), 1.52 (m, 2H, H_{17}), 1.22 (m, 10H, H_3), 0.84 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_{18}); ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.57 (C=O), 133.96 (C_{16}), 132.52 (C_{15}), 133.20 (d, $^2J_{PC}$ = 11.3 Hz, C_o), 132.10 (d, $^4J_{PC}$ = 2.2 Hz, C_p), 132.18 (C_{15}), 131.96 (C_{13}), 130.30 (C_{12}), 127.50 (d, $^3J_{PC}$ = 4.0 Hz, C_m), 104.72 (d, J_{PC} = 2.20 Hz, C_5H_5), 94.60 (C_{10}), 94.50 (C_9), 50.97 (OMe), 33.67 (C_2), 32.60 (C_{11}), 31.26 (C_8), 30.84 (C_{14}), 27.27−24.35 (C_3), 21.98 (C_{17}), 13.72 (C_{18}); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 35.27 (PPh_3).

10b (PR$_3$ = PMe$_3$): ^{1}H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.75 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 5.35 (m, 2H, $H_{15,16}$), 5.33 (m, 2H, $H_{12,13}$), 4.35 (m, 2H, $H_{9,10}$), 3.52 (s, 3H, OMe), 3.05 (m, 1H, H_{11}), 2.90 (m, 1H, H_{14}), 2.27 (t, $^3J_{HH}$ = 6.7 Hz, 2H, H_2), 2.18 (m, 2H, H_8), 1.61 (d, $^2J_{PH}$ = 12.3 Hz, 9H, $3PMe_3$), 1.58 (m, 2H, H_{17}), 1.20 (m, 10H, H_3), 0.91 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_{18}); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.83 (C=O), 133.63 (C_{16}), 132.18 (C_{15}), 126.54 (C_{13}), 126.25 (C_{12}), 102.33 (d, J_{PC} = 2.0 Hz, C_5H_5), 90.70 (C_{10}), 90.40 (C_9), 50.96 (OMe), 33.66 (C_2), 32.63 (C_{11}), 31.30 (C_8), 30.94 (C_{14}), 27.37−24.31 (C_3), 21.92 (C_{17}) 17.19 (d, $^1J_{PC}$ = 32.7 Hz, PMe_3), 15.50 (C_{18}); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.22 (PMe_3).

11a (PR$_3$ = PPh$_3$): ^{1}H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 7.48−7.50 (m, 15H, Ph), 5.81 (d, J_{PH} = 2.8 Hz, 5H, C_5H_5), 5.33 (m, 2H, $H_{12,13}$), 5.29 (m, 2H, $H_{9,10}$), 4.01 (m, 2H,

$H_{15,16}$), 3.68 (s, 3H, OMe), 3.08 (m, 1H, H_{11}), 2.85 (m, 1H, H_{14}), 2.20 (t, $^3J_{HH}$ = 6.4 Hz, 2H, H_2), 2.12 (m, 2H, H_8), 1.52 (m, 2H, H_{17}), 1.22 (m, 10H, H_3), 0.80 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_{18}); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.82 (C=O), 133.41 (d, $^1J_{PC}$ = 20.4 Hz, C_i), 132.36 (d, $^2J_{PC}$ = 13.2 Hz, C_o), 132.20 (d, $^4J_{PC}$ = 2.1 Hz, C_p), 127.01 (C_{13}), 126.91 (C_{12}), 125.94 (d, $^3J_{PC}$ = 8.0 Hz, C_m), 125.81 (C_{10}), 125.60 (C_9), 102.40 (d, J_{PC} = 2.1 Hz, C_5H_5), 98.92 (C_{16}), 97.14 (C_{15}), 51.03 (OMe), 33.65 (C_2), 32.60 (C_{11}), 30.61 (C_8), 30.30 (C_{14}), 27.12−24.35 (C_3), 21.98 (C_{17}), 15.72 (C_{18}); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 37.87 (PPh_3).

11b (PR_3 = PMe_3): ^1H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.74 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 5.26 (m, 2H, $H_{12,13}$), 5.23 (m, 2H, $H_{9,10}$), 4.37 (m, 2H, $H_{15,16}$), 3.31 (s, 3H, OMe), 3.06 (m, 1H, H_{11}), 2.80 (m, 1H, H_{14}), 2.23 (t, $^3J_{HH}$ = 6.5 Hz, 2H, H_2), 2.13 (m, 2H, H_8), 1.59 (d, $^2J_{PH}$ = 12.4 Hz, 9H, 3PMe_3), 1.54 (m, 2H, H_{17}), 1.21 (m, 10H, H_3), 0.88 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_{18}); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.81 (C=O), 132.02 (C_{13}), 130.56 (C_{12}), 125.81 (C_{10}), 125.60 (C_9), 102.40 (d, J_{PC} = 2.1 Hz, C_5H_5), 93.17 (C_{16}), 90.91 (C_{15}), 51.03 (OMe), 33.65 (C_2), 32.62 (C_{11}), 31.28 (C_8), 30.89 (C_{14}), 27.17−24.37 (C_3), 21.88 (C_{17}), 17.16 (d, $^1J_{PC}$ = 32.9 Hz, PMe_3), 13.72 (C_{18}); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.13 (PMe_3).

12a (PR_3 = PPh_3): ^1H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 7.48−7.50 (m, 15H, Ph), 5.92 (d, J_{PH} = 2.2 Hz, 5H, C_5H_5), 5.91 (d, J_{PH} = 2.2 Hz, 5H, C_5H_5), 5.33 (m, 2H, $H_{12,13}$), 4.03 (m, 2H, $H_{15,16}$), 4.01 (m, 2H, $H_{9,10}$), 3.69 (s, 3H, OMe), 3.19 (m, 2H, H_{14}), 3.04 (m, 2H, H_{11}), 2.40 (t, $^3J_{HH}$ = 7.0 Hz, 2H, H_2), 2.15 (m, 2H, H_8), 1.52 (m, 2H, H_{17}), 1.22 (m, 10H, H_3), 0.86 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_{18}); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.78 (C=O), 133.41 (d, $^1J_{PC}$ = 20.4 Hz, C_i), 132.36 (d, $^2J_{PC}$ = 13.2 Hz, C_o), 132.20 (d, $^4J_{PC}$ = 2.1 Hz, C_p), 126.41 (C_{13}), 126.25 (C_{12}), 125.94 (d, $^3J_{PC}$ = 8.0 Hz, C_m), 102.78 (d, J_{PC} = 2.0 Hz, C_5H_5), 102.70 (d, J_{PC} = 2.1 Hz, C_5H_5), 94.82 (C_{16}), 94.80 (C_{15}), 94.65 (C_{10}), 94.55 (C_9), 51.07 (OMe), 33.58 (C_2), 32.60 (C_{11}), 29.15 (C_8), 28.91 (C_{14}), 28.61 (C_8), 27.14−24.37 (C_3), 21.96, (C_{17}), 15.78 (C_{18}); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 38.07 (PPh_3), 38.03 (PPh_3).

12b (PR_3 = PMe_3): ^1H NMR (400 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.79 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 5.77 (d, J_{PH} = 2.4 Hz, 5H, C_5H_5), 5.14 (m, 2H, $H_{12,13}$), 4.44 (m, 2H, $H_{15,16}$), 4.33 (m, 2H, $H_{9,10}$), 3.54 (s, 3H, OMe), 3.03 (m, 1H, H_{11}), 2.83 (m, 1H, H_{14}), 2.24 (t, $^3J_{HH}$ = 6.6 Hz, 2H, H_2), 2.15 (m, 2H, H_8), 1.57 (d, $^2J_{PH}$ = 12.4 Hz, 9H, 3PMe_3), 1.55 (m, 2H, H_{17}), 1.24 (m, 10H, H_3), 0.90 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H_{18}); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 173.78 (C=O), 129.95 (C_{13}), 126.91 (C_{12}), 102.78 (d, J_{PC} = 2.0 Hz, C_5H_5), 102.70 (d, J_{PC} = 1.9 Hz, C_5H_5), 95.02 (C_{16}), 93.12 (C_{15}), 90.86 (C_{10}), 90.54 (C_9), 51.05 (OMe), 33.69 (C_2), 32.64 (C_{11}), 31.28 (C_8), 30.86 (C_{14}), 27.30−24.45 (C_3), 22.01 (C_{17}), 17.15 (d, $^1J_{PC}$ = 32.6 Hz, PMe_3), 13.76 (C_{18}); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$/acetone-d_6, 25 °C) δ 5.07 (PMe_3), 5.08 (PMe_3).

Determination of the Equilibrium Constants. Equilibrium constants for the binding of the unsaturated fatty acid methyl esters and *cis*-3-hexene to $[CpPd(PR_3)]^+$ were determined according to Scheme 7 by ^1H NMR analysis (400 MHz) at 25.0 ± 0.1 °C. The initial concentration of the $[CpPd(PR_3)(o\text{-}MeC_6H_4CN)]BF_4$ complexes was 5.24×10^{-2} M. The K values shown in Table 1 are averages of at least three measurements using different concentrations ($(5.24-1.10) \times 10^{-2}$ M) of the alkenes. The errors reported in Table 1 are standard deviations of three different K values calculated from each measurement. Solutions for the equilibrium measurements were prepared in air by adding $CDCl_3$ to $[CpPd(PPh_3)(o\text{-}MeCH_3C_6H_4CN)]BF_4$ and methyl β-naphthyl ether (internal reference) in an NMR tube. Then the free fatty acid methyl ester or *cis*-3-hexene was added at room temperature. The relative concentrations of the complexes were then calculated by integrating the Cp signals of the Pd−olefin and Pd−nitrile complexes and the methyl signals for the free and coordinated nitrile ligand against the methoxy signal (3.90 ppm) of the internal reference. These concentrations were used to calculate the equilibrium constant K:

$$K = \frac{[CpPd(PR_3)(olefin)^+][o\text{-}MeC_6H_4CN]}{[CpPd(PR_3)(o\text{-}MeC_6H_4CN)^+][olefin]}$$

The equilibrium constant for the formation of $[CpPd(PPh_3)(18{:}1)]^+$ was also measured at 10.0 ± 0.1, 5.0 ± 0.1, −5.0 ± 0.1, and −10.0 ± 0.1 °C, from which the thermodynamic parameters were calculated from a plot of $1/T$ vs $-\ln(K_1)$.

To ensure equilibration of the olefins with the $\{CpPd(PR_3)(o\text{-}MeC_6H_4CN)]BF_4$ complexes, a ^1H NMR spectrum was recorded within 3−5 min after each solution was prepared. A second ^1H NMR spectrum was recorded 15 min later. A third ^1H NMR spectrum was recorded ½ h later. No significant difference was observed among the first, second, and third ^1H NMR spectra. This indicates, for all the olefins examined, that equilibrium was established by the time the first spectrum was recorded (less than 10 min from solution preparation).

Table 2. Crystal Data and Structure Refinement Details for 5b

empirical formula	$C_{21}H_{36}B_2F_8O_{4.5}P_2Pd_2$[a]
formula wt	808.86
temp	180(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	*C*2/*c*
unit cell dimens	
a	21.919(5) Å
b	19.441(4) Å
c	16.339(4) Å
α	90°
β	104.285(4)°
γ	90°
V	6747(3) Å^3
Z	8
density (calcd)	1.592 Mg/m^3
abs coeff	1.230 mm^{-1}
F(000)	3216
cryst size	0.30 × 0.15 × 0.08 mm^3
θ range for data collecn	2.46−26.37°
index ranges	
h	−26 to +27
k	−24 to +24
l	−20 to +20
no. of rflns collected	27 365
no. of indep rflns	6889 (*R*(int) = 0.0459)
completeness to *θ* = 26.37°	99.7%
abs cor	semiempirical from equivalents
max, min transmissn	1, 0.72
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	6889/1/402
goodness of fit on F^2	1.041
final *R* indices ($I > 2\sigma(I)$)[b]	
R1	0.0636
wR2	0.1714
R indices (all data)[b]	
R1	0.0915
wR2	0.1955
largest diff peak, hole	2.211, −1.165 e Å^{-3}

[a] H atoms of 4.5 water solvent are not included. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Crystallographic Structural Determination of 5b. Single crystals of the title compound, suitable for X-ray analysis, were obtained from a concentrated solution in chloroform-*d*/acetone-d_6 containing an excess of the 1,4-pentadiene. A crystal selected under ambient conditions (Table 2) was covered with epoxy glue under a layer of solvent, mounted, and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed at 180 K on a Bruker CCD-1000 diffractometer with

Mo Kα (λ = 0.710 73 Å) radiation and a detector−crystal distance of 5.03 cm. The data were collected using a full-sphere routine and were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface, as sampled by multiple equivalent measurements[17] using SADABS software.[18] Positions of the heavy atoms were found by direct methods. The remaining non-hydrogen atoms, including water solvent, were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in a full-matrix anisotropic approximation. All hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The H atoms of water solvent were not assigned or included in the calculations. One organometallic cation, two BF_4^- anions (one plus two halves), and 4.5 water molecules were found in the asymmetric unit in a *c*-centered monoclinic cell. Two halves of the anion lay on a *c*-glide and lead to highly disordered spherically shaped moieties.

(17) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38.

(18) All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Acknowledgment. This project was supported by the National Research Initiative of the USDA Cooperative State Research, Education and Extension Service, Grant No. 2003-35504-12846.

Supporting Information Available: A figure giving a van't Hoff plot of $-\ln(K_1)$ vs $1/T$ for [CpPd(PPh_3)(*o*-MeC_6H_4-CN)]$^+$ + 18:1 = [CpPd(PPh_3)(18:1)]$^+$ + *o*-MeC_6H_4CN (**7a**) and tables of crystal data and structural refinement details, atomic coordinates, isotropic and anisotropic displacement parameters, bond lengths and angles, and hydrogen coordinates for **5b** (these crystallographic data are also available as CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

OM049009Q