Synthesis of Palladium Dimers Bridged by a Range of Phosphinocyclopentadienyl Ligands

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The reaction of [PdClMe(cod)] or $[Pd_2(\mu\text{-}Cl)_2Me_2(AsPh_3)_2]$ with $TlC_5H_4PPh_2$ yields the dppc-bridged complex $[Pd_2Me_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2]$. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.511(5)$ Å, $b = 19.848(8)$ Å, $c = 14.933(5)$ Å, $\beta = 100.31(3)°$, $V = 3065(2)$ Å^3, and $Z = 4$. Least-squares refinement converged at $R = 0.0468$ and $R_w = 0.0614$, based on 7202 reflections with $F > 4.0\sigma(F)$. Analogous reactions of $[Pd_2(\mu\text{-}Cl)_2R_2(AsPh_3)_2]$ (R = Et, Ph, COMe) with $TlC_5H_4PPh_2$ generate $[Pd_2R_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2]$. Similarly, dimethylcyclopentadienyl complexes may be prepared by reaction of $[Pd_2(\mu\text{-}Cl)_2Me_2(NC_5H_3Me_2\text{-}2,6)]$ or $[Pd_2(\mu\text{-}Cl)_2Ph_2(AsPh_3)_2]$ with $TlC_5H_4PMe_2$. Reactions of [PdClMe(cod)] with $TlC_5H_4P(OEt)_2$, or $[Pd_2(\mu\text{-}Cl)_2Me_2(AsPh_3)_2]$ with $LiC_5Me_4PPh_2$, further extend the range of phosphinocyclopentadienyl-bridged palladium complexes. In each case, their NMR spectra indicate that, in contrast to their platinum analogues, they adopt symmetrical, η^5-cyclopentadienyl structures in solution. On standing in solution, the compounds $[Pd_2Me_2(\mu\text{-}\eta^5\text{-}C_5H_4PR_2)_2]$ (R = Me, OEt) undergo coupling of the methyl and phosphino groups, and loss of palladium, to yield $C_5H_4PR_2Me$, each of which has also been prepared from $TlC_5H_4PR_2$ and iodomethane.

Introduction

There has been considerable interest in the use of heterodifunctional ligands for the construction of homo- and heterometallic complexes. Phosphinocyclopentadienyl ligands, in particular, have found widespread use.[1] Complexes containing two diphenylphosphinocyclopentadienyl (dppc) or dimethylphosphinocyclopentadienyl (dmpc) ligands have been prepared,[2–15] including several involving the Group 9 metals.[11–15] Recently, a small number of complexes involving f-element/transition metal species have been prepared.[16–18]

With the exception of our work on organoplatinum derivatives bridged by dppc ligands,[2,19,20] in each case the phosphinocyclopentadienyl ligand coordinates to one metal by means of the phosphino group and to the second through the η^5-cyclopentadienyl moiety. We have shown for platinum, however, that the five-membered ring may coordinate in either of two η^1 modes[19,20] or it may be displaced from the metal altogether.[20] Thus, the dppc ligand exhibits considerable flexibility and may serve to bridge dinuclear complexes with or without a metal–metal bond. In view of these somewhat unexpected findings, we have prepared a series of organopalladium species bridged by dppc or related ligands. These exhibit both structures and reactivity quite different from their platinum analogues.

Results and Discussion

When [PdClMe(cod)] was treated with $TlC_5H_4PPh_2$ in a THF solution, an off-white precipitate of TlCl was formed, along with an orange solution. Isolation of the palladium-containing product at low temperature yielded $[Pd_2Me_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2]$ (**1a**) as an orange solid (eq 1). The complex is soluble in CH_2Cl_2, THF, or benzene and slightly soluble in ether or pentane. In the solid state, the compound is stable for several months when stored at 0 °C under an atmosphere of argon, but it decomposes slowly in solution at ambient temperature. It has been characterized by NMR spectroscopy, elemental analysis, and X-ray diffraction.

The ^1H NMR spectrum of **1a** consists of a doublet at 0.65 ppm, due to the methyl group, two signals at 5.88

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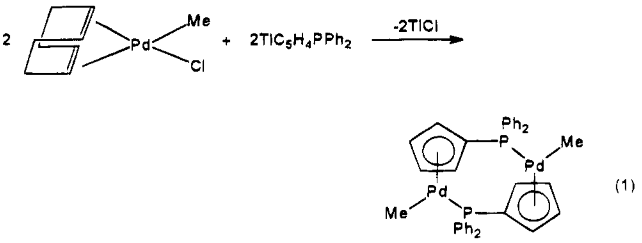

(1)

and 6.21 ppm, due to the two pairs of equivalent cyclopentadienyl ring hydrogens, and a multiplet in the aromatic region. The $^{13}C\{^1H\}$ NMR spectrum exhibits a doublet resonance at −18.7 ppm, assigned to the methyl group, and two multiplets at 98.6 and 106.3 ppm, due to CH carbons of the cyclopentadienyl ring, and is also consistent with the η^5 ring formulation. The $^{31}P\{^1H\}$ NMR spectrum consists of a single resonance at 29.2 ppm, further illustrating the symmetrical nature of the complex in solution. This is in contrast to the analogous platinum complex [$Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2$], which contains one η^5 and one η^1 ring both in the solid state and in solution.[2]

The crystal structure of **1a** belongs to the space group $P2_1/c$, and the molecular structure is shown in Figure 1. Selected bond distances and angles are given in Table 1. The structure reveals that the complex maintains its symmetrical nature, with two η^5 cyclopentadienyl moieties, in the solid state, although the molecule does not possess a center of inversion. The Pd−C distances lie in the ranges 2.293(4)−2.427(4) and 2.307(4)−2.438(4) Å for the two cyclopentadienyl rings. For each ring, three of the Pd−C distances are approximately equal, the longest distance (*ca.* 0.05 Å longer) is that to the *ipso* carbon, and the remaining one is *ca.* 0.10 Å shorter than the other three. Thus, the palladium atoms are slipped toward C(6) and C(11), respectively. In [$Rh_2(CO)_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2$], the Rh−C distances lie in the range 2.248(3)−2.321(4) Å, the Rh−C(*ipso*) distance being the longest by only 0.01 Å,[12] whereas in [$Rh_2(CO)_2(\mu\text{-}\eta^5\text{-}C_5H_4PMe_2)_2$] the Rh−C distances range from 2.232(7) to 2.303(8) Å, with the Rh−C(*ipso*) distance being 2.295(6) Å.[13] The metal−metal distances are not significantly different in the three complexes, however, being 4.141 Å in the palladium complex, and 4.166 and 4.303 Å, respectively, in the rhodium dmpc and dppc compounds. In all these cases, the variations in metal−carbon bond distances are averaged in solution, giving rise to relatively simple NMR spectra.

The ethyl and phenyl derivatives **1b** and **1c**, [$Pd_2R_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2$] (R = Et, Ph), have been prepared by reaction of the appropriate organopalladium dimer [$Pd_2(\mu\text{-}Cl)_2R_2(AsPh_3)_2$] with $TlC_5H_4PPh_2$. They are isolated as orange solids, which are stable under argon, but when exposed to air they decompose more readily than the methyl analogue. The ethyl derivative is also light-sensitive, turning dark brown within 1 h at ambient temperature. The acetylpalladium complex [$Pd_2(COMe)_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2$] (**1d**) has been obtained by treatment of [PdCl(COMe)(cod)] with $TlC_5H_4PPh_2$, but it has proved difficult to isolate in analytically pure form. The solution NMR spectra of **1b−d** are consistent with those of symmetrical structures, in which the cyclopentadienyl rings are coordinated to palladium in a η^5 fashion.

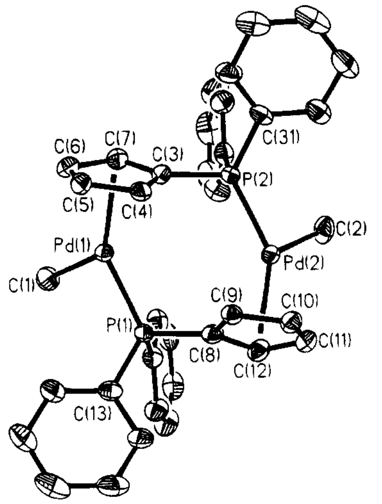

Figure 1. Projection view of the molecular structure of [$Pd_2Me_2(\mu\text{-}C_5H_4PPh_2)_2$] (**1a**) showing the atom-labeling scheme.

Table 1. Selected Bond Distances (Å) and Angles (deg) for [$Pd_2Me_2(\mu\text{-}C_5H_4PPh_2)_2$]

Bond Distances			
Pd(1)−P(1)	2.208(1)	Pd(1)−C(1)	2.054(5)
Pd(1)−C(3)	2.427(4)	Pd(1)−C(4)	2.392(4)
Pd(1)−C(5)	2.394(5)	Pd(1)−C(6)	2.293(4)
Pd(1)−C(7)	2.388(4)	Pd(2)−P(2)	2.213(1)
Pd(2)−C(2)	2.050(4)	Pd(2)−C(8)	2.438(4)
Pd(2)−C(9)	2.391(4)	Pd(2)−C(10)	2.398(4)
Pd(2)−C(11)	2.307(4)	Pd(2)−C(12)	2.394(4)
P(1)−C(8)	1.799(4)	P(1)−C(13)	1.825(4)
P(1)−C(19)	1.829(4)	P(2)−C(3)	1.792(4)
P(2)−C(25)	1.830(4)	P(2)−C(31)	1.833(4)
C(3)−C(4)	1.443(5)	C(3)−C(7)	1.419(5)
C(4)−C(5)	1.422(5)	C(5)−C(6)	1.422(6)
C(6)−C(7)	1.439(6)	C(8)−C(9)	1.447(5)
C(8)−C(12)	1.415(6)	C(9)−C(10)	1.411(5)
C(10)−C(11)	1.424(6)	C(11)−C(12)	1.432(6)
Bond Angles			
P(1)−Pd(1)−C(1)	90.6(1)	P(2)−Pd(2)−C(2)	89.5(1)
C(4)−C(3)−C(7)	107.9(3)	C(3)−C(4)−C(5)	108.3(3)
C(4)−C(5)−C(6)	107.3(3)	C(5)−C(6)−C(7)	108.9(4)
C(3)−C(7)−C(6)	107.2(3)	C(9)−C(8)−C(12)	107.1(3)
C(8)−C(9)−C(10)	108.9(3)	C(9)−C(10)−C(11)	107.1(3)
C(10)−C(11)−C(12)	108.7(4)	C(8)−C(12)−C(11)	107.9(4)

We have extended the series of methylpalladium species to include examples with bridging $C_5H_4PMe_2$ (dmpc), $C_5H_4P(OEt)_2$ (deopc), or $C_5Me_4PPh_2$ (dpptmc) ligands. $TlC_5H_4PMe_2$ was prepared by the method of Rausch,[13] and $LiC_5Me_4PPh_2$ was prepared according to the procedure described by Szymoniak.[21] $TlC_5H_4P(OEt)_2$ was generated in a manner similar to the dppc and dmpc analogues, namely, by treatment of diethyl chlorophosphite with cyclopentadienylthallium in ether, followed by deprotonation with TlOEt (eq 2). The product was obtained as an off-white solid, which is stable when stored under an inert atmosphere and in the absence of light. (It turns dark brown on exposure to light for 48 h.)

$$(EtO)_2PCl + TlC_5H_5 \xrightarrow{-TlCl} (EtO)_2P(C_5H_5) \xrightarrow[EtOH]{+TlOEt} (EtO)_2PC_5H_4Tl \quad (2)$$

The corresponding palladium complexes [$Pd_2Me_2(\mu\text{-}$

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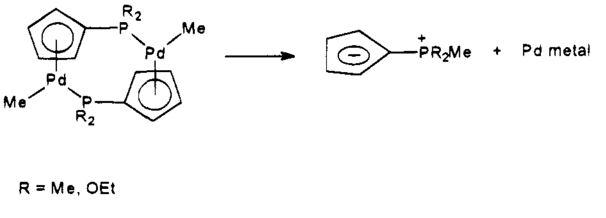
η^5-$C_5H_4PMe_2)_2$] (**2a**), [$Pd_2Me_2\{\mu$-η^5-$C_5H_4P(OEt)_2\}_2$] (**3a**), and [$Pd_2Me_2(\mu$-η^5-$C_5Me_4PPh_2)_2$] (**4a**) were prepared by reaction of either [PdClMe(cod)] or [$Pd_2(\mu$-$Cl)_2Me_2L_2$] (L = $AsPh_3$ or $NC_5H_3Me_2$-2,6) with the appropriate phosphinocyclopentadienyl salt in THF solution. The short reaction times are crucial, and extensive decomposition takes place after longer reaction times. In each case the product is obtained as an orange solid, which decomposes in air and is best stored at low temperature under argon and in the absence of light. The dmpc and deopc compounds, in particular, are very air-sensitive, turning black within 1 h at ambient temperature even in the solid state.

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **2a**, **3a**, and **4a** are also consistent with those of symmetrical dimeric structures. Each complex exhibits one ^{31}P signal and one palladium–methyl resonance in its ^1H and $^{13}C\{^1H\}$ spectra. The $PdCH_3$ ^{13}C resonances appear at 1.8 ppm in **2a** and −0.9 ppm in **4a**, whereas the methyl carbon is more shielded in **3a**, being observed at −20.0 ppm. Two ^1H and two ^{13}C resonances are found for the cyclopentadienyl groups in **2a** and **3a** (the *ipso* carbon is too weak to be observed in either case), and two methyl signals are observed for the tetramethylcyclopentadienyl group in **4a** in its ^1H and $^{13}C\{^1H\}$ spectra.

On standing in solution at ambient temperature, compounds **2a** and **3a** decompose by extrusion of palladium and coupling of the methyl group with the phosphino group to yield the zwitterionic speices $R_2MeP^+C_5H_4^-$ (R = Me, OEt) (eq 3). The identities of the products have been confirmed by comparison of their NMR parameters with those of samples prepared by reaction of $TlC_5H_4PR_2$ with iodomethane. In these reactions, we believe the initial products are of the form ($R_2MeP^+C_5H_4^-$)TlI, which gradually precipitate thallium iodide, allowing isolation of the phosphorus compounds. When the reaction of $TlC_5H_4PMe_2$ with MeI in C_6D_6 solution was monitored by ^1H NMR spectroscopy, signals were observed initially at 0.90 (d, ^2J(P,H) = 13 Hz), 6.37, and 6.77 ppm, but on standing for 24 h these gradually shifted to 0.81, 6.48, and 6.95 ppm, as found for free $Me_3P^+C_5H_4^-$. Similarly, the reaction of $TlC_5H_4P(OEt)_2$ with MeI in C_6D_6 solution after 1 h exhibited cyclopentadienyl signals at 6.59 and 6.83 ppm which, on standing at 0 °C for 24 h, shifted to 6.67 and 6.94 ppm.



(3)

R = Me, OEt

The rates of decomposition of the palladium complexes are strongly dependent on the nature of the phosphinocyclopentadienyl ligand. [$Pd_2Me_2(\mu$-η^5-$C_5H_4PMe_2)_2$] (**2a**) undergoes complete and clean reaction to give $Me_3P^+C_5H_4^-$ and Pd metal within 3 h in CD_2Cl_2 solution at ambient temperature under an inert atmosphere. Decomposition of [$Pd_2Me_2\{\mu$-η^5-$C_5H_4P(OEt)_2\}_2$] (**3a**) to produce $Me(EtO)_2P^+C_5H_4^-$ and Pd metal occurs more slowly, being complete within 48 h. In contrast, the dppc compounds **1a–c** and [$Pd_2Me_2(\mu$-η^5-$C_5Me_4PPh_2)_2$] (**4a**) show no propensity to undergo loss of palladium and coupling of the PPh_2 and organic groups. (They do, however, decompose to give a range of unidentifed species on standing in solution for a prolonged period of time.) The relative rates of reductive elimination from **1a–3a** are not simply related to electronic or steric effects. The electron-donating ability of the PR_2 group lies in the order Me > Ph > OEt, whereas the size decreases in the order Ph > Me > OEt.[22] It is likely that elimination is favored by the small size of the methyl and ethoxy groups, but the strongly electron-releasing nature of the methyl groups may also be important. The lack of reactivity of **4a** is probably due to the bulky nature of the tetramethylcyclopentadienyl group.

We have employed [PdClMe(cod)], [$Pd_2(\mu$-$Cl)_2R_2(AsPh_3)_2$] (R = Me, COMe, Ph, Et), and [$Pd_2(\mu$-$Cl)_2Me_2(NC_5H_3Me_2$-2,6$)_2$] as precursors to the phosphinocyclopentadienyl derivatives. [PdClMe(cod)] has the advantage that the only byproducts of the reaction are thallium chloride and cyclooctadiene, and these are easily removed. Its disadvantage is that some attack of the phosphinocyclopentadienyl on the coordinated diene appears to occur,[23,24] and this reduces the yield of the desired product. The reactions of the triphenylarsine and 2,6-lutidine complexes release 1 equiv of the free ligand and, particularly in the arsine case, this competes for the remaining palladium precursor to give bis(ligand) species of the type [$PdClRL_2$].

Complexes **1a**, **2a**, and **3a** react with tertiary phosphines, although the reactions of **2a** and **3a** are complicated by the decompositions of the complexes themselves. When **1a** was treated with PEt_3 (7 equiv) in C_6D_6 solution, the major product was consistent with the zwitterionic compound[20] *trans*-[$Pd^+Me(PEt_3)_2(Ph_2PC_5H_4^-)$] ($\delta$(H) 0.40 (m, $PdCH_3$); 0.74 (m, PCH_2CH_3); 1.21 (m, PCH_2CH_3); 6.8–8.2 (m, C_5H_4, C_6H_5); δ(P) 0.7 (t), 13.6 (d), ^2J(P,P) = 37 Hz). In $CDCl_3$ solution the reaction proceeded further to give *trans*-[$PdClMe(PEt_3)_2$] (δ(P) 16.8). Treatment of **2a** with PEt_3, $PMePh_2$, or $P(CH_2CH_2CN)_3$ in C_6D_6 solution resulted in the formation of many products, including $Me_3P^+C_5H_4^-$, and **3a** reacted with PEt_3 to generate [$Pd^+Me(PEt_3)_2\{(EtO)_2PC_5H_4^-\}$] ($\delta$(P) 18.9 (d), 143.9 (t), ^2J(P,P) = 44 Hz) as the major product, but showed no tendency to react with PPh_3. The zwitterionic complexes proved to be insufficiently stable to allow their isolation. Complex **4a** was found to be particularly unreactive, being recovered unchanged after treatment with excess PEt_3. In this last instance the lack of reactivity may be due to the presence of the bulky tetramethylcyclopentadienyl group.

These results indicate that changes in the groups attached to phosphorus or on the cyclopentadienyl ring lead to significant changes in stability and reactivity. Further studies of metal complexes containing phosphinocyclopentadienyl ligands are in progress.

Experimental Section

NMR spectra were recorded on a Varian XL-300 FT NMR spectrometer. Chemical shifts are reported relative to TMS

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($^1\mathrm{H}$ and $^{13}\mathrm{C}$) or $\mathrm{H_3PO_4}$ ($^{31}\mathrm{P}$). Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA. [PdClMe(cod)],[25,26] $[\mathrm{Pd_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{Me_2L_2}]$ (L = $\mathrm{AsPh_3}$, 2,6-$\mathrm{NC_5H_3Me_2}$),[25] $\mathrm{TlC_5H_4PPh_2}$,[27] $\mathrm{TlC_5H_4PMe_2}$[13] (δ(P) −63.7 in DMSO-d_6), and $\mathrm{LiC_5Me_4PPh_2}$[21] (δ(H) 2.18, 2.30 (Me); 7.03−7.13, 7.68 (Ph); δ(P) −26.0 in $\mathrm{C_6D_6}$) were prepared by reported methods. The syntheses of $[\mathrm{Pd_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{R_2(AsPh_3)_2}]$ (R = Et, Ph) will be described elsewhere.

Preparation of $\mathbf{TlC_5H_4P(OEt)_2}$. A flask was charged with $\mathrm{TlC_5H_5}$ (3.05 g, 11.3 mmol) under argon. Ether (100 mL) was introduced, followed by $\mathrm{P(OEt)_2Cl}$ (1.69 mL, 1.03 equiv). The reaction mixture was stirred for 45 min and then filtered to remove TlCl. To the resulting colorless solution was added dropwise an ether solution (20 mL) of TlOEt (0.850 mL, 1.05 equiv) over 20 min. The cream-white solid which precipitated was collected by filtration and washed with ether (10 mL). It was protected from light and dried *in vacuo* at ambient temperature for 6 h (3.41 g, 78%). The product was stored under argon at 5 °C in the absence of light. $^1\mathrm{H}$ NMR ($\mathrm{C_6D_6}$): δ(H) 1.18 (t, $^3J(\mathrm{H,H})$ = 7.0 Hz, $\mathrm{C}H_3$); 3.90 (m, $\mathrm{OC}H_2$); 6.14, 6.54 (m, $\mathrm{C_5}H_4$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ(P) 162.8 (s).

Preparation of $[\mathbf{Pd_2Me_2}(\boldsymbol{\mu}\text{-}\boldsymbol{\eta}^5\text{-}\mathbf{C_5H_4PPh_2})_2]$ (1a). [PdClMe(cod)] (0.224 g, 0.845 mmol) and $\mathrm{TlC_5H_4PPh_2}$ (0.436 g, 0.962 mmol) were charged into a 50 mL flask under argon. Tetrahydrofuran (15 mL) was introduced by syringe, and the reaction mixture was stirred for 10 min. The orange mixture was cooled to −78 °C and filtered to remove TlCl. The orange filtrate was evaporated to dryness at 0 °C under reduced pressure, and the resulting solid was washed with ether/pentane (1:1, 15 mL) and dried *in vacuo* to leave the product as an orange solid (0.241 g, 75%). Anal. Calcd for $\mathrm{C_{36}H_{34}P_2Pd_2}$: C, 58.32; H, 4.62. Found: C, 57.79; H, 4.59. $^1\mathrm{H}$ NMR ($\mathrm{C_6D_6}$): δ(H) 0.65 (d, $^3J(\mathrm{P,H})$ = 2.9 Hz, $\mathrm{C}H_3$), 5.88, 6.21 (m, $\mathrm{C_5}H_4$), 7.07−7.82 (m, $\mathrm{C_6}H_5$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ(C) −18.7 (d, $^2J(\mathrm{P,C})$ = 4.8 Hz, $C\mathrm{H_3}$), 98.6 (t, $J(\mathrm{P,C})$ = 7.5 Hz), 106.3 (5-line mult, $J(\mathrm{PC}) + J(\mathrm{P'C})$ = 14.0 Hz, $C_5\mathrm{H_4}$), 129.9, 127.8, 133.6 (s, $C_6\mathrm{H_5}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ(P) 29.2 (s). Crystals suitable for an X-ray diffraction study were obtained from a benzene solution.

Preparation of $[\mathbf{Pd_2Ph_2}(\boldsymbol{\mu}\text{-}\boldsymbol{\eta}^5\text{-}\mathbf{C_5H_4PPh_2})_2]$ (1b). This complex was prepared from $[\mathrm{Pd_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{Ph_2(AsPh_3)_2}]$ (0.103 g, 0.098 mmol) and $\mathrm{TlC_5H_4PPh_2}$ (0.103 g, 0.227 mmol) by a procedure similar to that described above. The crude solid was washed twice with ether/pentane (1:3, 10 mL) and then with pentane (10 mL) and dried *in vacuo* while being protected from light. The product was obtained as an orange solid (0.068 g, 80%). Anal. Calcd for $\mathrm{C_{46}H_{38}P_2Pd_2}$: C, 63.83; H, 4.43. Found: C, 63.13; H, 4.43. $^1\mathrm{H}$ NMR ($\mathrm{CDCl_3}$): δ(H) 5.85, 6.33 (m, $\mathrm{C_5}H_4$), 6.55, 6.67, 6.84 (m, $\mathrm{PdC_6}H_5$), 7.20−7.36 (m, $\mathrm{P(C_6}H_5)_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ(C) 97.4, 106.4 (s, $C_5\mathrm{H_4}$), 122.5, 126.3, 127.4, 129.6, 133.7, 140.2 (s, $C_6\mathrm{H_5}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ(P) 25.1 (s).

Preparation of $[\mathbf{Pd_2Et_2}(\boldsymbol{\mu}\text{-}\boldsymbol{\eta}^5\text{-}\mathbf{C_5H_4PPh_2})_2$ (1c). This complex was prepared analogously from $[\mathrm{Pd_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{Et_2(AsPh_3)_2}]$ (0.429 g, 0.450 mmol) and $\mathrm{TlC_5H_4PPh_2}$ (0.480 g, 1.06 mmol). The crude solid was washed twice with ether/pentane (1:3, 10 mL) and then with pentane (10 mL) and dried *in vacuo* while being protected from light. The product was obtained as an orange-brown solid (0.105 g, 30%). Anal. Calcd for $\mathrm{C_{38}H_{38}P_2Pd_2}$: C, 59.31; H, 4.98. Found: C, 58.63; H, 4.91. $^1\mathrm{H}$ NMR ($\mathrm{C_6D_6}$): δ(H) 1.04 (dt, $^3J(\mathrm{P,H})$ = 2.7 Hz, $^3J(\mathrm{H,H})$ = 7.2 Hz, $\mathrm{C}H_3$), 1.67 (m, $\mathrm{C}H_2$), 5.95, 6.20 (m, $\mathrm{C_5}H_4$), 7.08−7.80 (m, $\mathrm{C_6}H_5$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ(C) 27.6 (s, $C\mathrm{H_3}$), 39.3 (s, $C\mathrm{H_2}$), 92.5 (br), 97.1 (t, $J(\mathrm{P,C})$ = 4.9 Hz, $\mathrm{C_5H_4}$), 111.9−113.3 (m), 116.0 (s, $C_6\mathrm{H_5}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ(P) 28.9 (s).

Preparation of $[\mathbf{Pd_2(COMe)_2}(\boldsymbol{\mu}\text{-}\boldsymbol{\eta}^5\text{-}\mathbf{C_5H_4PPh_2})_2]$ (1d). This complex was prepared analogously from $[\mathrm{Pd_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{(COMe)_2(AsPh_3)_2}]$ (0.199 g, 0.202 mmol) and $\mathrm{TlC_5H_4PPh_2}$ (0.211 g, 0.466 mmol). The crude solid was washed with ether (20 mL), 1:1 ether/pentane (40 mL), and finally pentane (10 mL) and dried *in vacuo* while being protected from light. The product was obtained as an orange-brown solid (0.117 g, 73%). Anal. Calcd for $\mathrm{C_{38}H_{34}O_2P_2Pd_2}$: C, 57.23; H, 4.30. Found: C, 58.95; H, 4.45. $^1\mathrm{H}$ NMR ($\mathrm{CDCl_3}$): δ(H) 2.01 (s, $\mathrm{C}H_3$), 5.91, 6.23 (m, $\mathrm{C_5}H_4$), 7.31−7.58 (m, $\mathrm{C_6}H_5$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ(C) 45.7 (br, $C\mathrm{H_3}$), 95.2, 107.3 (s, $C_5\mathrm{H_4}$), 128.1, 128.9, 130.0, 133.7 ($C_6\mathrm{H_5}$), 213.5 ($C\mathrm{O}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ(P) 17.3 (s).

Preparation of $[\mathbf{Pd_2Me_2}(\boldsymbol{\mu}\text{-}\boldsymbol{\eta}^5\text{-}\mathbf{C_5H_4PMe_2})_2]$ (2a). $\mathrm{TlC_5H_4PMe_2}$ (0.406 g, 1.23 mmol) was placed in a 100 mL flask under argon, and THF (50 mL) was introduced by syringe. The resulting solution was transferred by cannula into a solution of $[\mathrm{Pd_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{Me_2(NC_5H_3Me_2\text{-}2,6)_2}]$ (0.322 g, 0.610 mmol) in THF (75 mL). The mixture was stirred for 5 min and then cooled to −78 °C and filtered through a fritted Schlenk tube packed with alumina (basic). The resulting orange solution was collected at −78 °C and evaporated under reduced pressure at 0 °C to leave an orange solid. The solid was washed with ether/pentane (1:2, 3 mL) and dried *in vacuo* at 0 °C while being protected from light. The product was obtained as a brick red-orange solid (0.123 g, 41%). Anal. Calcd for $\mathrm{C_{16}H_{26}P_2Pd_2}$: C, 38.97; H, 5.32. Found: C, 39.09; H, 5.17. $^1\mathrm{H}$ NMR ($\mathrm{C_6D_6}$): δ(H) 0.58 (d, $^3J(\mathrm{P,H})$ = 3.4 Hz, $\mathrm{PdC}H_3$), 1.15 (d, $^2J(\mathrm{P,H})$ = 10.2 Hz, $\mathrm{P(C}H_3)_2$), 5.83, 6.21 (m, $\mathrm{C_5}H_4$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_7D_8}$, −10 °C): δ(C) 1.8 (s, $\mathrm{Pd}C\mathrm{H_3}$), 17.2 (d, $^1J(\mathrm{P,C})$ = 34.0 Hz, $\mathrm{P(}C\mathrm{H_3)_2}$), 97.6 (t, $J(\mathrm{P,C})$ = 8.0 Hz), 102.7 (5-line mult, $J(\mathrm{P,C}) + J(\mathrm{P',C})$ = 13.5 Hz, $C_5\mathrm{H_4}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ(P) −4.1 (s).

Preparation of $[\mathbf{Pd_2Me_2}\{\boldsymbol{\mu}\text{-}\boldsymbol{\eta}^5\text{-}\mathbf{C_5H_4P(OEt)_2}\}_2]$ (3a). A 50 mL flask was charged with $\mathrm{TlC_5H_4P(OEt)_2}$ (0.244 g, 0.627 mmol) under argon. Tetrahydrofuran (15 mL) was introduced, and the suspension was stirred vigorously. With continued stirring, the suspension was added by cannula to a THF solution (10 mL) of [PdClMe(cod)] (0.165 g, 0.621 mmol). The reaction mixture was stirred for 9 min and then cooled to −78 °C and filtered through a fritted Schlenk tube packed with alumina (basic). The orange-red filtrate was collected at −78 °C, and an additional 20 mL of THF was used to elute the product. The filtrate was concentrated under reduced pressure to leave an oily solid, which was crystallized from ether/petroleum ether at −78 °C. The resulting orange solid was dried *in vacuo* at 0 °C, while being protected from light (0.117 g, 62%). Anal. Calcd for $\mathrm{C_{20}H_{34}O_4P_2Pd_2}$: C, 39.17; H, 5.59. Found: C, 38.60; H, 5.72. $^1\mathrm{H}$ NMR ($\mathrm{C_6D_6}$): δ(H) 1.02 (t, $^3J(\mathrm{H,H})$ = 7.0 Hz, $\mathrm{OCH_2C}H_3$), 1.05 (s, $\mathrm{PdCH_3}$), 3.79 (m, $\mathrm{OC}H_2\mathrm{CH_3}$), 5.78, 6.55 (m, $\mathrm{C_5}H_4$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_7D_8}$, −10 °C): δ(C) −20.0 (s, $\mathrm{Pd}C\mathrm{H_3}$), 16.7 (s, $\mathrm{OCH_2}C\mathrm{H_3}$), 62.7 (s, $\mathrm{O}C\mathrm{H_2CH_3}$), 98.2 (t, $J(\mathrm{P,C})$ = 9.7 Hz), 102.3 (t, $J(\mathrm{P,C})$ = 8.1 Hz, $C_5\mathrm{H_4}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ(P) 137.4 (s).

Preparation of $[\mathbf{Pd_2Me_2}(\boldsymbol{\mu}\text{-}\boldsymbol{\eta}^5\text{-}\mathbf{C_5Me_4PPh_2})_2]$ (4a). A 50 mL flask was charged with $[\mathrm{Pd_2}(\mu\text{-}\mathrm{Cl})_2\mathrm{Me_2(AsPh_3)_2}]$ (0.495 g, 0.534 mmol) and $\mathrm{LiC_5Me_4PPh_2}$ (0.350 g, 1.12 mmol) under argon. Benzene (5 mL) was introduced, and the mixture was stirred for 5 min. The resulting red mixture was filtered to remove LiCl, and the filtrate was evaporated to dryness. The residue was washed with ether (70 mL), leaving the product as an orange solid which was dried *in vacuo* (0.362 g, 79%). Anal. Calcd for $\mathrm{C_{44}H_{50}P_2Pd_2}$: C, 61.91; H, 5.90. Found: C, 60.88, H, 5.16. $^1\mathrm{H}$ NMR ($\mathrm{C_6D_6}$): δ(H) 0.48 (d, $^3J(\mathrm{P,H})$ = 2.9 Hz, $\mathrm{PdC}H_3$), 2.05 (d, $J(\mathrm{P,H})$ = 1.3 Hz), 2.07 (d, $J(\mathrm{P,H})$ = 1.8 Hz, $\mathrm{C_5}Me_4$), 7.02−7.82 (m, $\mathrm{C_6}H_5$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_7D_8}$, −10 °C): δ(C) −0.9 (d, $^2J(\mathrm{P,C})$ = 6.0 Hz, $\mathrm{Pd}C\mathrm{H_3}$), 10.2, 12.9 (s, $\mathrm{C_5}Me_4$), 128.5, 129.5, 134.1 ($C_6\mathrm{H_5}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ(P) 27.7 (s).

Preparation of $\mathbf{C_5H_4PMe_3}$. A 50 mL flask was charged with $\mathrm{TlC_5H_4PMe_2}$ (0.386 g, 1.17 mmol) under argon, and THF (10 mL) was introduced. Iodomethane (80 μL, 1.28 mmol) was added, and the mixture was stirred overnight. The reaction mixture was filtered to remove the yellow precipitate of TlI, and the filtrate was evaporated to dryness. $^1\mathrm{H}$ NMR ($\mathrm{C_6D_6}$): δ(H) 0.81 (d, $^2J(\mathrm{P,H})$ = 13.3 Hz, $\mathrm{P(C}H_3)_3$), 6.47, 6.95 (m, $\mathrm{C_5}H_4$).

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Table 2. Crystallographic Data for $[Pd_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$

formula	$C_{36}H_{34}P_2Pd_2$
formula wt	741.4
color, habit	dark brown, irregularly shaped
space group	$P2_1/c$
a, Å	10.511(5)
b, Å	19.848(8)
c, Å	14.933(5)
β, deg	100.31(3)
cell vol, Å^3	3065(2)
Z	4
D(calcd), Mg/m^3	1.607
temp, K	123
radiation	graphite monochromated Mo Kα ($\lambda = 0.71073$ Å)
crystal dimens, mm	0.4 × 0.3 × 0.2
abs coeff, mm^{-1}	1.302
2*θ* range, deg	3.0 to 60.0
scan speed, deg/min	4.0 to 14.7
scan range (*ω*), deg	1.20 plus Kα separation
independent reflctns	9013
obsd reflctns	7202 ($F > 4.0\sigma(F)$)
abs corrctn	semiempirical
min/max transmission	0.8428/1.0000
no. parameters refined	498
R	0.0468
R_w	0.0614
goodness of fit	1.00

$^{13}C\{^1H\}$ NMR (C_6D_6): δ(C) 13.3 (d, ^1J(P,C) = 59 Hz, P(CH_3)$_3$), 111.8, 114.5 (br, C_5H_4). $^{31}P\{^1H\}$ NMR (C_6D_6): δ(P) −1.2 (s).

Preparation of $C_5H_4P(OEt)_2Me$. $TlC_5H_4P(OEt)_2$ (25 mg, 0.066 mmol) was placed in a 5-mm NMR tube under argon. Benzene-d_6 (0.5 mL) was introduced, followed by iodomethane (4.7 μL, 0.075 mmol). After standing for 24 h, the formation of $C_5H_4PMe(OEt)_2$ was complete, as determined by NMR spectroscopy. ^1H NMR: δ(H) 0.85 (t, ^3J(H,H) = 7.1 Hz, OCH_2CH_3), 1.36 (d, ^2J(P,H) = 14 Hz, PCH_3), 3.63 (m, OCH_2CH_3), 6.67, 6.94 (m, C_5H_4). $^{31}P\{^1H\}$ NMR: δ(P) 74.0 (s).

X-ray Structure Determination. A single crystal of $[Pd_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$ (**1a**) was mounted on a glass fiber in random orientation. Preliminary examination was carried out with Mo Kα radiation using a Siemens R3 automated four-circle diffractometer. Final cell parameters and orientation matrices were obtained by least-squares refinement of 25 automatically centered reflections (20° < 2*θ* < 35°). Axial photographs of the three axes were taken to confirm cell lengths and the lattice symmetry. *ω*-Scans of representative reflections indicated acceptable crystal quality.

Data were collected using the *θ*−2*θ* scan technique, and the intensities of three standard reflections were measured every 50 reflections. As no significant variations in intensities of the standard reflections were observed during data collection, no decay corrections were applied. Empirical absorption corrections were applied to the data using 6 *ψ* curves for reflections with 80° < *χ* < 88°.

Data reduction and structure solution was achieved using the SHELXTL PLUS structure solution software package.[28] The structure was solved by the Patterson method in the monoclinic space group $P2_1/c$ and was refined successfully in this space group. The remaining non-hydrogen atoms were located from subsequent difference Fourier maps. Full matrix least-squares refinement was carried out by minimizing the function $\omega(F_o - F_c)^2$. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were refined isotropically, to convergence. Summaries of crystal data, intensity collection parameters, and final structure refinement parameters are presented in Table 2. Atomic coordinates for **1a** are given in Table 3. All calculations were performed on a VAX Station 3100 computer using SHELXTL PLUS software.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	*y*	*z*	*U*(eq)[a]
Pd(1)	463(1)	2208(1)	1737(1)	15(1)
Pd(2)	1475(1)	4043(1)	2983(1)	15(1)
P(1)	2496(1)	2529(1)	1846(1)	15(1)
P(2)	−608(1)	3791(1)	2680(1)	16(1)
C(1)	524(5)	1747(2)	514(3)	24(1)
C(2)	1030(5)	5029(2)	2653(3)	26(1)
C(3)	−912(4)	2910(2)	2493(3)	18(1)
C(4)	−365(4)	2383(2)	3110(3)	18(1)
C(5)	−855(4)	1754(2)	2743(3)	21(1)
C(6)	−1591(4)	1884(2)	1865(3)	23(1)
C(7)	−1686(4)	2601(2)	1727(3)	20(1)
C(8)	2976(3)	3166(2)	2696(2)	17(1)
C(9)	2788(3)	3120(2)	3631(2)	15(1)
C(10)	3295(4)	3705(2)	4101(3)	19(1)
C(11)	3681(4)	4147(2)	3447(3)	21(1)
C(12)	3540(4)	3802(2)	2593(3)	21(1)
C(13)	3695(4)	1862(2)	2133(3)	19(1)
C(14)	4938(4)	2001(2)	2631(3)	23(1)
C(15)	5837(4)	1487(3)	2835(3)	29(1)
C(16)	5524(5)	833(3)	2536(3)	33(1)
C(17)	4303(5)	691(3)	2056(3)	29(1)
C(18)	3397(4)	1204(2)	1861(3)	22(1)
C(19)	2927(4)	2923(2)	834(3)	20(1)
C(20)	1963(4)	3277(2)	254(3)	23(1)
C(21)	2276(5)	3640(2)	−475(3)	28(1)
C(22)	3532(5)	3641(2)	−640(3)	29(1)
C(23)	4484(5)	3267(3)	−83(3)	31(1)
C(24)	4188(4)	2913(2)	654(3)	25(1)
C(25)	−1513(4)	4160(2)	1634(3)	21(1)
C(26)	−2825(4)	4309(2)	1526(3)	26(1)
C(27)	−3472(5)	4555(3)	707(4)	35(1)
C(28)	−2833(6)	4641(3)	−27(3)	38(2)
C(29)	−1536(9)	4496(3)	72(3)	37(2)
C(30)	−873(5)	4255(2)	904(3)	28(1)
C(31)	−1572(4)	4007(2)	3548(3)	19(1)
C(32)	−2539(4)	3584(2)	3732(3)	25(1)
C(33)	−3253(5)	3752(3)	4405(3)	32(1)
C(34)	−2976(5)	4346(3)	4893(3)	33(1)
C(35)	−2009(5)	4766(3)	4734(3)	30(1)
C(36)	−1291(4)	4596(2)	4056(3)	25(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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Supplementary Material Available: Tables of bond lengths and bond angles, anisotropic displacement coefficients for non-hydrogen atoms, calculated hydrogen atom coordinates, and isotropic displacement coefficients (5 pages). Ordering information is given on any current masthead page.

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