Convenient Method for the Synthesis of Chloro-Bridged Methyl- and Acetylpalladium(II) Dimers

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A series of chloro-bridged methylpalladium(II) dimers of the type $[Pd_2(\mu\text{-}Cl)_2Me_2L_2]$ (**1a–h**; L = PEt_3, $PMePh_2$, PPh_3, $P(CH_2Ph)_3$, $P(OMe)_3$, $AsPh_3$, $CNBu^t$, 2,6-lutidine) has been prepared from [PdClMe(cod)] and 1 equiv of the appropriate ligand. Cis and trans isomers may be identified where L = PEt_3 or $CNBu^t$. Addition of a second equivalent of PEt_3 results in a bridge-splitting reaction to give *trans*-$[PdClMe(PEt_3)_2]$ (**2a**), but this process may be reversed by addition of further [PdClMe(cod)]. Carbonylation of [PdClMe(cod)] yields the corresponding acetyl complex, and treatment of the latter with PEt_3, $AsPh_3$, or $CNBu^t$ leads to the acetylpalladium dimers $[Pd_2(\mu\text{-}Cl)_2(COMe)_2L_2]$ (**3a,f,g**). Reaction of **3a** with PEt_3 produces *trans*-$[PdCl(COMe)(PEt_3)_2]$ (**4a**), but this may also be reversed by addition of further [PdCl(COMe)(cod)]. Addition of excess $CNBu^t$ to [PdClMe(cod)] generates the iminoacyl complex *trans*-$[PdCl\{C(=NBu^t)Me\}(CNBu^t)_2]$ (**6g**).

Introduction

Halide-bridged complexes of palladium(II) and platinum(II) are used extensively as starting materials in the syntheses of organometallic and coordination compounds.[1] Complexes of the type $[Pt_2(\mu\text{-}Cl)_2R_2L_2]$ (R = aryl; L = PR_3) have been prepared, and their chemistry has been investigated.[2,3] Only a few, isolated examples of halide-bridged organopalladium(II) complexes, including $[Pd_2(\mu\text{-}Cl)_2(CH_2Ph)_2(PPh_3)_2]$[4] and $[Pd_2(\mu'\text{-}Cl)_2R_2L_2]$ (R = C_6F_5, C_6Cl_5),[5-7] had been reported, however, until a general route to halide-bridged organopalladium(II) complexes was discovered in our laboratory.[8] This method involved treating $[Pd_2(\mu\text{-}Cl)_2Cl_2L_2]$ with HgR_2 to yield $[Pd_2(\mu\text{-}Cl)_2R_2L_2]$ (R = Ph, C_6H_4Me-4, CH_2Ph; L = PPh_3, $PMePh_2$, PBu_3). The difficulties of product separation, however, resulted in only moderate isolated yields. Recently, Nakamura and colleagues[9] have reported a high-yield (79–96%) route to halide-bridged methylpalladium(II) complexes, $[Pd_2(\mu\text{-}Cl)_2Me_2L_2]$ (L = PEt_3, PBu_3, PMe_2Ph). They prepared the complexes by treating $[Pd_2(\mu\text{-}Cl)_2Cl_2L_2]$ (L = PEt_3, PBu_3, PMe_2Ph) with 2 equiv of $AlMe_3$ at low temperatures. While this work was in progress, a modification of the method of Nakamura was reported by Singhal and Jain.[10] The halide-bridged methylpalladium(II) complexes $[Pd_2(\mu\text{-}Cl)_2Me_2L_2]$ (L = PEt_3, PBu_3, PMe_2Ph, $PMePh_2$, PPh_3) were prepared in 35–73% yield by reaction of $[Pd_2(\mu\text{-}Cl)_2Cl_2L_2]$ with tetramethyltin in benzene solution at ambient temperature.

We recently reported the synthesis of platinum dimers bridged by (diphenylphosphino)cyclopentadienyl ligands.[11] In the course of extending this chemistry to palladium,[12] we have developed a new, convenient, and high-yield approach to the preparation of halide-bridged methyl- and acetylpalladium(II) complexes. This method is more general than any reported to date. This paper describes our synthetic approach using [PdClMe(cod)][13,14] or the novel acetyl compound [PdCl(COMe)(cod)] as starting materials.

Results and Discussion

Reaction of [PdClMe(cod)] with 1 equiv of PEt_3 in $CDCl_3$ solution at ambient temperature results in the formation of the chloro-bridged methylpalladium(II) complexes $[Pd_2(\mu\text{-}Cl)_2Me_2(PEt_3)_2]$ (**1a**) in quantitative yield by NMR spectroscopy. The reaction is general for a variety of ligands (eq 1). The compounds are white or

$$[PdClMe(cod)] + L \xrightarrow{-cod} \underset{\mathbf{1a-h}}{[Pd_2(\mu\text{-}Cl)_2Me_2L_2]} \quad (1)$$

1a, L = PEt_3; **1b**, L = $PMePh_2$; **1c**, L = PPh_3; **1d**, L = $P(CH_2Ph)_3$; **1e**, L = $P(OMe)_3$; **1f**, L = $AsPh_3$; **1g**, L = $CNBu^t$; **1h**, L = 2,6-lutidine

off-white solids, with the exception of **1g,h**, which are obtained as purple and yellow solids, respectively. The

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Table 1. ^1H, ^{13}C, and ^{31}P NMR Data for the Complexes $[Pd_2(\mu\text{-}Cl)_2Me_2L_2]$ (1a–h)[a]

	L	^1H NMR, δ_H	^{13}C NMR, δ_C	^{31}P NMR, δ_P
1a	PEt_3	0.51 d (2.1) (Pd*Me*)[b]	–0.5 br (Pd*Me*)[b]	32.5
		1.20 dt (17.1, 7.6) (PCH_2CH_3)	9.5 (PCH_2CH_3)	32.0
		1.79 dq (10.1, 7.6) (PCH_2CH_3)	16.3 d (PCH_2CH_3)	
1b	$PMePh_2$	1.03 br (Pd*Me*)	5.5 br (Pd*Me*)[c]	24.3
		1.68 br (P*Me*)	14.9 d (33) (P*Me*)	
		6.9–7.5 m	128.3 d (11), 130.3 s, 132.8 d (12)	
1c	PPh_3[d]	0.63 s (Pd*Me*)		39.9
1d	$P(CH_2Ph)_3$[d]	0.57 s (Pd*Me*)	3.1 br (Pd*Me*)[c]	25.4
		3.16 br (PCH_2)	30.5 d (25) (PCH_2)	
			126.8 s, 128.4 s, 130.1 d (6), 133.4 d (5)	
1e	$P(OMe)_3$	1.38 s (Pd*Me*)	1.7 s (Pd*Me*)	120.2
		3.34 d (5.2) ($P(OMe)_3$)	52.3 ($P(OMe)_3$)	
1f	$AsPh_3$	0.67 s (Pd*Me*)		
1g	$CNBu^t$[c]	2.25 s (Pd*Me*), 1.54 s (Bu^t)	62.4 (Pd*Me*), 32.1 s (Bu^t)	
		2.27 s (PdMe), 1.53 s (Bu^t)	62.6 (Pd*Me*), 34.0 s (Bu^t)	
1h	$NC_5H_3Me_2$[c]	0.64 s (Pd*Me*)	–6.2 s (Pd*Me*), 28.5 s (*Me*)	
		3.36 br (*Me*)	122.0 s, 137.3 s, 159.9 s	
		7.0–7.6 m		

[a] Recorded in C_6D_6 solution at ambient temperature unless otherwise stated. Coupling constants (in parentheses) are in hertz. [b] Signals for cis and trans isomers are coincident. [c] Recorded in $CDCl_3$ solution at ambient temperature. [d] Recorded in acetone-d_6 solution at ambient temperature.

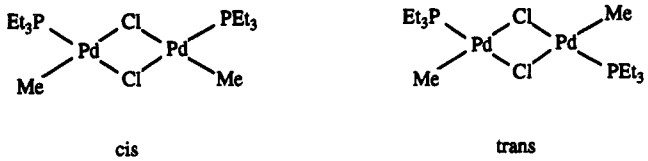
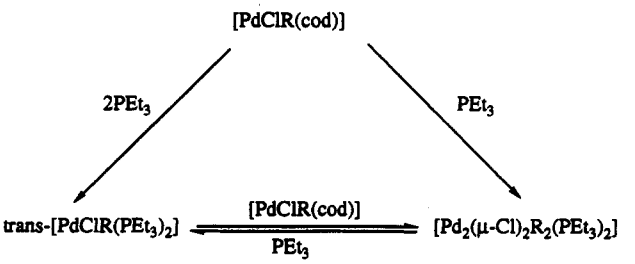


Figure 1.

Scheme 1



R = Me or COMe

compounds are air-stable as solids and can be stored under common atmosphere for several months. Compounds **1a–c,g** are soluble in benzene, whereas **1d–f,h** are only slightly soluble in this solvent. All of the compounds are soluble in chloroform or dichloromethane.

The dimeric compounds **1a–h** have been characterized by ^1H, ^{13}C, and ^{31}P (where applicable) NMR spectroscopy, infrared spectroscopy (where appropriate), and elemental analysis. The characterization data are presented in Table 1. In each case, with the exceptions of **1a,g** (L = PEt_3, $CNBu^t$, respectively), one set of resonances is observed in the ^1H NMR spectrum and a single resonance is observed in the ^{31}P NMR spectrum for the phosphorus-containing complexes at ambient temperature.

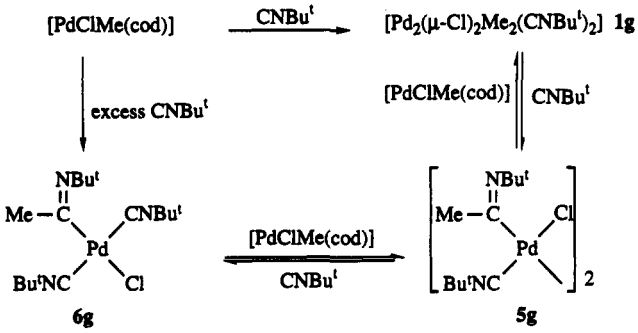
In the case of **1a** two ^{31}P resonances in ~4:1 ratio are observed in the spectrum obtained in benzene solution at ambient temperature. This is due to the presence of cis and trans isomers (Figure 1). When the spectrum is recorded for an acetone solution at ambient temperature, a broad singlet is observed at 34.5 ppm. When the sample is cooled to –60 °C, two sharp singlets in ~1:1 ratio are observed. The cis isomer should be favored in polar solvents due to increased dipole–dipole interactions;[15] therefore, we conclude that the predominant species in benzene is the trans isomer. In acetone the isomers exist in approximately equal ratio due to the increased ability of acetone to support the cis isomer. Similarly, in the case of **1g** two sets of two singlet resonances for the *tert*-butyl and methyl hydrogens (~1:1) are observed in the ^1H NMR spectrum obtained in benzene at ambient temperature. When the spectrum is recorded in acetone at ambient temperature, two sets of two singlet resonances in ~4:1 ratio are observed. Presumably, the more intense resonance in acetone is representative of the cis isomer for the reasons stated above.

Whereas [PdClMe(cod)] reacts cleanly with 1 equiv of any of the above ligands to produce the chloro-bridged methylpalladium(II) dimers in quantitative yield, the presence of a slight excess of ligand results in a bridge-splitting reaction. For example, both the dimeric complex **1a** and the monomeric complex *trans*-$[PdClMe(PEt_3)_2]$[9] (**2a**) are formed when 1.2 equiv of PEt_3 is introduced into an acetone solution of [PdClMe(cod)]. Subsequent addition of 0.2 equiv of [PdClMe(cod)] to the solution results in the formation of the dimeric complex **1a** exclusively.

In fact, addition of 1 equiv of [PdClMe(cod)] to an acetone solution of the monomeric complex *trans*-$[PdClMe(PEt_3)_2]$ (**2a**) gives the dimeric complex **1a** as the sole product (Scheme 1). Apparently, an equilibrium exists between **1a**, PEt_3, and **2a**. When excess PEt_3 (>1 equiv) is present in solution, the equilibrium is driven toward **2a**. When ≤1 equiv of PEt_3 per palladium is present in solution, the equilibrium is shifted in favor of the chloro-bridged dimer **1a**.

In the case where the ligand is $CNBu^t$, however, the chemistry is more complex, as shown in Scheme 2. As indicated above, [PdClMe(cod)] reacts cleanly with 1 equiv of $CNBu^t$ to produce **1g**, but addition of a further 3 equiv of isonitrile results in formation of the dimeric iminoacyl complex $[Pd_2(\mu\text{-}Cl)_2\{C{=}NBu^t)Me\}_2(CNBu^t)_2]$ (**5g**: δ_H 0.90 s ($CNBu^t$), 1.53 s (C=NBu^t), 2.25 s (Me)) as a minor product, and the monomeric iminoacyl species *trans*-$[PdCl\{C(=NBu^t)Me\}(CNBu^t)_2]$ (**6g**) as the major product. Complex **5g** has not been isolated, but it was identified in solution by comparison of its ^1H NMR resonances with those of the iodo analogue, which had been reported previously.[16] Complex **6g** was isolated and characterized by spectroscopy and by elemental analysis. Thus, addition of excess $CNBu^t$ to **1g** results first in insertion of the isonitrile into the Pd–Me bond, followed by splitting of

Scheme 2



the chloride bridges to generate **6g**. Indeed, addition of further $CNBu^t$ to a solution containing **5g** and **6g** results in exclusive formation of **6g**. Even the iminoacyl complexes **5g** and **6g** react with an appropriate amount of [PdClMe(cod)], by deinsertion of the isonitrile, to regenerate **1g**.

Bubbling carbon monoxide through a CH_2Cl_2 solution of [PdClMe(cod)] at −78 °C, with gradual warming to 0 °C over 30 min, results in formation of the corresponding acetyl complex [PdCl(COMe)(cod)], which is isolated in 66% yield after workup. The creamy white solid can be stored at 0 °C under argon for several months. This compound has been characterized by ^1H NMR and infrared spectroscopy and by elemental analysis. That the ^1H NMR resonance observed at 2.53 ppm is due to the acetyl protons was ascertained by preparing the carbon-13-labeled analogue, [PdCl(^{13}COMe)(cod)]. The observation of a doublet centered at 2.53 ppm ($^2J_{CH}$ = 6.4 Hz) confirms the assignment.

The acetylpalladium complex [PdCl(COMe)(cod)] reacts with 1 equiv of PEt_3, $AsPh_3$, or $CNBu^t$ to yield the corresponding chloro-bridged acetylpalladium(II) complexes [$Pd_2(\mu\text{-}Cl)_2(COMe)_2L_2$] (**3a**,**f**,**g**, respectively; eq 2).

$$[PdCl(COMe)(cod)] + L \rightarrow \underset{\mathbf{3a,f,g}}{[Pd_2(\mu\text{-}Cl)_2(COMe)_2L_2]} \quad (2)$$

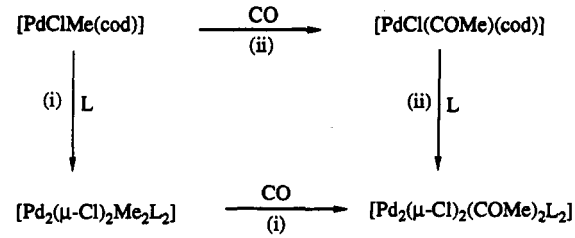
3a, L = PEt_3; **3f**, L = $AsPh_3$; **3g**, L = $CNBu^t$

These compounds have been characterized by NMR spectroscopy, infrared spectroscopy, and elemental analysis. They are white solids, which can be stored for several months at 0 °C under argon. Each one decomposes in solution at ambient temperature, **3g** decomposing quite rapidly under these conditions.

In the case of **3a** one broad singlet is observed at 28.9 ppm in the ^{31}P NMR spectrum obtained in acetone at room temperature. When the temperature is lowered to −78 °C, two sharp singlets in a 2:1 ratio are observed, indicating the presence of cis and trans isomers. When the spectrum is recorded in benzene at ambient temperature, one singlet is observed at 25.5 ppm, indicating that, in this solvent, **3a** either exists in one isomeric form or the chemical shifts of the two isomers are coincident.

[PdCl(COMe)(cod)] reacts with 1 equiv of PEt_3, $AsPh_3$, or $CNBu^t$ at ambient temperature to produce the chloride-bridged species exclusively, indicating that this is the thermodynamically favored product in each case. At −78 °C, however, the reaction with 1 equiv of $AsPh_3$ yields a 1:1 mixture of *trans*-[PdCl(COMe)($AsPh_3$)$_2$] (**4f**: δ_H 1.47 s (COMe)) and unreacted [PdCl(COMe)(cod)]. The reaction with PEt_3 produces a 1:4 ratio of **3a** and *trans*-[PdCl(COMe)(PEt_3)$_2$] (**4a**: δ_H 2.32 s (COMe); δ_P 14.5), an appropriate amount of unreacted [PdCl(COMe)(cod)] remaining. In contrast, **3g** is still the only product with $CNBu^t$. This suggests there is a fine balance between kinetic and thermodynamic effects in the low-temperature reactions, which is affected by the nature of the added ligand.

Scheme 3



As with the methylpalladium dimers **1a**–**h**, the chloro-bridged acetylpalladium dimers **3a**,**f**,**g** are formed in quantitative yield by NMR spectroscopy. Similarly, bridge-splitting reactions are observed when a slight excess of ligand is present in solution. For example, the reaction of [PdCl(COMe)(cod)] with 1.2 equiv of PEt_3 at ambient temperature results in the formation of both **3a** and the monomeric complex *trans*-[PdCl(COMe)(PEt_3)$_2$] (**4a**). Addition of the appropriate amount of [PdCl(COMe)(cod)] yields **3a** exclusively. Therefore, an equilibrium also exists between **3a** and **4a**, similar to the one between **1a** and **2a** (Scheme 1).

Carbonylation of chloro-bridged methylpalladium(II) complexes may also result in the formation of chloro-bridged acetylpalladium(II) complexes.[9] Indeed, we have found that [$Pd_2(\mu\text{-}Cl)_2Me_2(CNBu^t)_2$] (**1g**), for example, reacts with carbon monoxide to form **3g**. Therefore, chloro-bridged acetylpalladium(II) complexes can be prepared with [PdClMe(cod)] as starting material by (i) reaction with the neutral ligand followed by CO or (ii) reaction with CO to yield [PdCl(COMe)(cod)], followed by reaction with the ligand (Scheme 3).

Experimental Section

All reactions were carried out under an atmosphere of argon. Solvents were dried and distilled immediately prior to use. Ligands were obtained commercially and used without purification. NMR spectra were recorded on a Varian XL-300 spectrometer. ^1H and ^{13}C chemical shifts are relative to the residual solvent resonance, and ^{31}P shifts are relative to external 85% H_3PO_4, positive shifts representing deshielding. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Preparation of [PdClMe(cod)].[13,14] [$PdCl_2$(cod)] (2.97 g, 10.4 mmol) was charged into a 500-mL flask, and CH_2Cl_2 (200 mL) was introduced. The mixture was stirred, and Me_4Sn (1.86 mL, 1.29 equiv) was added by syringe. The mixture was refluxed until the yellow color was discharged (some decomposition to palladium metal was observed). The solution was cooled and filtered through Hyflosupercel; then the solvent was evaporated to leave a white solid. The solid was washed with ether (3 × 10 mL) and dried *in vacuo* (2.61 g, 95%). Anal. Calcd for $C_9H_{15}ClPd$: C, 40.78; H, 5.70. Found: C, 40.50; H, 5.66.

Preparation of [$Pd_2(\mu\text{-}Cl)_2Me_2(PEt_3)_2$] (1a). [PdClMe(cod)] (0.114 g, 0.431 mmol) was dissolved in benzene (8 mL), and PEt_3 (64 μL, 1.05 equiv) was introduced via syringe. The solution was stirred for 4 h; then the solvent was evaporated to

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leave a viscous, light green oil. Pentane (5 mL) was added to the oil, and the mixture was stirred. An off-white solid precipitated, which was filtered and washed with another 5 mL of pentane and dried *in vacuo* (0.075 g, 63%). Anal. Calcd for $C_{14}H_{36}Cl_2P_2Pd_2$: C, 30.57; H, 6.54. Found: C, 30.47; H, 6.56.

Preparation of $[Pd_2(\mu\text{-}Cl)_2Me_2(PMePh_2)_2]$ (1b). This complex was prepared similarly from [PdClMe(cod)] (0.117 g, 0.439 mmol) and $PMePh_2$ (82 μL, 1.0 equiv) and obtained as a white solid in 76% yield. Anal. Calcd for $C_{30}H_{36}Cl_2P_2Pd_2$: C, 47.09; H, 4.51. Found: C, 47.03; H, 4.56.

Preparation of $[Pd_2(\mu\text{-}Cl)_2Me_2(PPh_3)_2]$ (1c). This was prepared from [PdClMe(cod)] (0.108 g, 0.409 mmol) and PPh_3 (0.114 g, 1.0 equiv) and isolated as a white solid in 85% yield. Anal. Calcd for $C_{38}H_{36}Cl_2P_2Pd_2$: C, 54.40; H, 4.32. Found: C, 54.38; H, 4.36.

Preparation of $[Pd_2(\mu\text{-}Cl)_2Me_2\{P(CH_2Ph)_3\}_2]$ (1d). This was prepared from [PdClMe(cod)] (0.099 g, 0.374 mmol) and $P(CH_2Ph)_3$ (0.115 g, 1.0 equiv) and obtained as a white solid in 92% yield. Anal. Calcd for $C_{44}H_{48}Cl_2P_2Pd_2$: C, 57.29; H, 5.21. Found: C, 57.14; H, 5.21.

Preparation of $[Pd_2(\mu\text{-}Cl)_2Me_2\{P(OMe)_3\}_2]$ (1e). [PdClMe(cod)] (0.102 g, 0.385 mmol) was charged into a 25-mL one-necked, side-armed flask. Benzene (8 mL) was then introduced followed by $P(OMe)_3$ (45 μL, 1.0 equiv). The initially clear, colorless solution turned yellow immediately. After it was stirred for 5 h, the solution was concentrated and the resulting off-white solid was washed with pentane and dried *in vacuo* (0.083 g, 77%). Anal. Calcd for $C_8H_{24}Cl_2O_2P_2Pd_2$: C, 17.10; H, 4.27. Found: C, 17.18; H, 4.28.

Preparation of $[Pd_2(\mu\text{-}Cl)_2Me_2(AsPh_3)_2]$ (1f). This was prepared from [PdClMe(cod)] (0.138 g, 0.521 mmol) and $AsPh_3$ (0.161 g, 1.0 equiv) and isolated in 96% yield. Anal. Calcd for $C_{38}H_{36}As_2Cl_2Pd_2$: C, 49.23; H, 3.93. Found: C, 49.20; H, 3.94.

Preparation of $[Pd_2(\mu\text{-}Cl)_2Me_2(CNBu^t)_2]$ (1g). [PdClMe(cod)] (0.130 g, 0.489 mmol) was dissolved in benzene (12 mL). *tert*-Butyl isocyanide (55 μL, 1.0 equiv) was introduced, and the solution turned purple immediately. After 5 h, the solution was evaporated to dryness and the solid was washed with pentane. After it was dried *in vacuo*, the product was obtained as a fine purple powder (0.091 g, 78%): ν(CN) 2208 cm^{-1}. Anal. Calcd for $C_{12}H_{24}Cl_2N_2Pd_2$: C, 30.02; H, 5.00. Found: C, 30.28; H, 5.01.

Preparation of $[Pd_2(\mu\text{-}Cl)_2Me_2(2,6\text{-lutidine})_2]$ (1h). [PdClMe(cod)] (0.541 g, 2.04 mmol) was dissolved in benzene (20 mL), and 2,6-lutidine (0.285 mL, 1.2 equiv) was introduced. A yellow color was observed immediately, followed by precipitation of a solid. After 5 h, the mixture was concentrated to 10 mL and filtered. The solid obtained was washed with pentane and then dried *in vacuo*, leaving the product as a yellow powder (0.496 g, 92%). Anal. Calcd for $C_{16}H_{24}Cl_2N_2Pd_2$: C, 36.39; H, 4.54. Found: C, 36.64; H, 4.62.

Preparation of [PdCl(COMe)(cod)]. [PdClMe(cod)] (0.457 g, 1.72 mmol) was dissolved in 20 mL of dry dichloromethane, and the solution was cooled to −78 °C. Carbon monoxide was introduced to the system and then bubbled through the solution as the temperature was raised gradually from −78 to 0 °C. Some palladium metal was deposited. The bubbling was continued until the initially faint yellow solution had turned an intense yellow (~30 min). The solution was filtered through Hyflosupercel and stripped under vacuum below 0 °C. The resulting off-white solid was protected from light and dried *in vacuo* at ambient temperature for 2 h (0.333 g, 66%): ν(CO) 1732 cm^{-1}. Anal. Calcd for $C_{10}H_{15}ClOPd$: C, 40.99; H, 5.12. Found: C, 40.31; H, 5.19. ^1H NMR ($CDCl_3$, −50 °C): δ_H 2.4–2.8 (m, 8H, CH_2), 2.60 (s, 3H, $COCH_3$), 5.18 (br t, 2H, CH=), 5.79 (br t, 2H, CH=). $^{13}C\{^1H\}$ NMR ($CDCl_3$, −50 °C): δ_C 27.1 s, 30.4 s (CH_2), 37.0 s (CO*Me*), 105.3 s, 125.1 s (CH=), 216.0 s (COMe). The compound decomposes slowly even in the solid state of 0 °C.

Preparation of $[Pd_2(\mu\text{-}Cl)_2(COMe)_2(PEt_3)_2]$ (3a). [PdCl(COMe)(cod)] (0.124 g, 0.422 mmol) was dissolved in acetone (15 mL). The solution was cooled to −78 °C, and triethylphosphine (63 μL, 1.0 equiv) was introduced via syringe. The solution was warmed to ambient temperature over 20 min and stirred for another 20 min. The light green solution was filtered through Hyflosupercel. The filtrate was concentrated, and pentane (5 mL) was added to give a thick, greenish oil. Ether (2 mL) was introduced, and a solid formed. The solids were separated by filtration and dried *in vacuo* at 0 °C for 5 h. The product was obtained as a white solid (0.101 g, 79%): ν(CO) 1696 cm^{-1}. Anal. Calcd for $C_{16}H_{36}Cl_2O_2P_2Pd_2$: C, 31.71; H, 5.99. Found: C, 31.80; H, 6.02. ^1H NMR (C_6D_6): δ_H 2.49 s (CO*Me*). $^{13}C\{^1H\}$ NMR (acetone-d_6, −50 °C): δ_C 38.6 d, J_{PC} = 23 Hz (CO*Me*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P 25.5.

Preparation of $[Pd_2(\mu\text{-}Cl)_2(COMe)_2(AsPh_3)_2]$ (3f). [PdCl(COMe)(cod)] (0.123 g, 0.421 mmol) and triphenylarsine (0.131 g, 1.0 equiv) were charged into a 25-mL flask. Dry chloroform (5 mL) was introduced to give a homogeneous solution. The solution was stirred for 10 min and gradually turned into a suspension containing a white precipitate. Pentane (7 mL) was introduced to precipitate further solid. The chloroform/pentane solution was filtered, and the solid was washed once with pentane. The white solid obtained was dried *in vacuo* (0.145 g, 70%): ν(CO) 1714 cm^{-1}. Anal. Calcd for $C_{40}H_{36}As_2Cl_2O_2Pd_2$: C, 48.91; H, 3.66. Found: C, 48.74; H, 3.72. ^1H NMR ($CDCl_3$): δ_H 2.07 s (CO*Me*), 7.2–7.6 m (*Ph*).

Preparation of $[Pd_2(\mu\text{-}Cl)_2(COMe)_2(CNBu^t)_2]$ (3g). [PdCl(COMe)(cod)] (0.199 g, 0.678 mmol) was dissolved in acetone (10 mL). The solution was cooled to −78 °C, and *tert*-butyl isocyanide (77 μL, 1.0 equiv) was introduced via syringe. The solution was stirred at −78 °C for 50 min and then evaporated under vacuum while the temperature was gradually raised from −78 to 0 °C, leaving a white solid. The product was washed with copious amounts of pentane and dried *in vacuo* at 0 °C for 5 h (0.120 g, 66%): ν(CO) 1731, ν(CN) 2199 cm^{-1}. Anal. Calcd for $C_{14}H_{24}Cl_2N_2O_2Pd_2$: C, 31.37; H, 4.51. Found: C, 31.44; H, 4.46. ^1H NMR (C_6D_6): δ_H 1.54 s (CMe_3), 2.07 s (CO*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, −50 °C): δ_C 29.7 s (CMe_3), 38.1 s (CO*Me*).

Preparation of *trans*-$[PdCl\{C(=NBu^t)Me\}(CNBu^t)_2]$ (6g). [PdClMe(cod)] (0.185 g, 0.701 mmol) was dissolved in benzene (10 mL), and *tert*-butyl isocyanide (0.457 mL, 6.0 equiv) was introduced. The solution turned yellow. After 0.5 h, the solution was evaporated to 0.5 mL, and diethyl ether (10 mL) was added to precipitate a white solid, which was dried *in vacuo* (0.170 g, 60%): ν(CN) 2197, 1654 cm^{-1}. Anal. Calcd for $C_{16}H_{30}ClN_3Pd$: C, 47.30; H, 7.44. Found: C, 47.23; H, 7.40. ^1H NMR (C_6D_6): δ_H 0.77 br s ($CNCMe_3$), 1.71 s ($C{=}NCMe_3$), 2.52 s (*Me*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ_C 29.5 s($CNCMe_3$), 32.1 s ($C{=}NCMe_3$), 35.6 s (*Me*).

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