Nucleophilic Attack on Cyclooctadiene Complexes of Palladium: Stereochemistry of the Resulting Cyclooctenylpalladium Derivatives

Gretchen R. Hoel, Robert A. Stockland, Jr., Gordon K. Anderson,* Folami T. Ladipo, Janet Braddock-Wilking, Nigam P. Rath, and Juan C. Mareque-Rivas

Department of Chemistry, University of Missouri−St. Louis, 8001 Natural Bridge Road, St. Louis, Missouri 63121

Received September 23, 1997

Reaction of [PdClMe(cod)] with $MeO_2CC{\equiv}CCO_2Me$ occurs in two steps, namely, insertion of the alkyne into the Pd−Me bond followed by migratory insertion of one of the double bonds of the coordinated cyclooctadiene into the Pd−alkenyl bond thus formed. The resulting chloride-bridged, cyclooctenyl complex was converted to [Pd(acac){η^1,η^2-$C_8H_{12}C(CO_2Me){=}CMe(CO_2Me)$}], **2a**, which was characterized crystallographically. The molecular structure revealed that each insertion took place in a cis manner. Reactions of [$PdCl_2$(cod)] with a range of nucleophiles were performed, which gave analogous chloride-bridged, cyclooctenylpalladium dimers, **1**, which could be converted to their acetylacetonate derivatives, **2**. The solid-state structure of the methoxy complex [Pd(acac)(η^1,η^2-C_8H_{12}OMe)], **2b**, obtained by reaction of [$PdCl_2$(cod)] with NaOMe followed by Ag(acac), was determined. This showed that exo attack of the OMe group occurred. In contrast, the structure of the phenyl derivative [Pd(acac)(η^1,η^2-C_8H_{12}Ph)], **2e**, produced by treatment of [$PdCl_2$(cod)] with Ph_4Sn followed by Ag(acac), indicated that the phenyl group added in an endo fashion, presumably via a phenylpalladium intermediate of the type [PdClPh(cod)]. With the larger mesityl group, the complex [PdCl($C_6H_2Me_3$)(cod)] could be isolated. Each of the complexes was fully characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and the appearance of the C*H*Pd signal was used to distinguish between the exo and endo isomers. On the basis of the crystallographic and NMR data, it was deduced that the organometallic reagents ArMgX (Ar = Ph, 2-MeC_6H_4, 2,4,6-$Me_3C_6H_2$), Ph_4Sn, and (4-$MeC_6H_4)_2$Hg generate the endo products by initial attack at the metal. In contrast, reactions with NaOR (R = Me, Et), $NaCH(CO_2Me)_2$, AgOAc, and Et_2NH proceed by direct attack of the nucleophile at the coordinated double bond to give the exo products.

Introduction

During the course of our investigations[1] of the chemistry of [PdClMe(cod)] (cod = 1,5-cyclooctadiene)[2] and related complexes,[3] we found that reaction with carbon monoxide generates the acetylpalladium species [PdCl(COMe)(cod)].[1] In contrast, we have found that reaction with dimethylacetylene dicarboxylate (DMAD) produces a compound derived from formal insertion of the alkyne into the Pd−C bond followed by migration of the resulting alkenyl group to one of the double bonds of the cyclooctadiene ligand. This observation led us to carry out a detailed study of the stereochemistry of the products obtained by nucleophilic attack on [$PdCl_2$(cod)], where attack on the coordinated double bond may take place in an endo (attack at the metal followed by migratory insertion of the double bond) or exo (direct attack from the face opposite the metal) fashion.

Reactions of palladium diene complexes with a range of nucleophiles have been described previously. Reactions with hydroxide, alkoxides, carboxylates, malonate, azide, or amines[4−10] have been reported, and they all were supposed to occur by direct, exo attack of the nucleophile on the coordinated diene. In contrast, the reaction of [$PdCl_2$(nbd)] (nbd = norbornadiene) with diphenylmercury produced an endo-substituted species, which was characterized crystallographically.[11] More recently, the monomeric species [PdCl(C_6F_5)(cod)], formed

(1) Ladipo, F. T.; Anderson, G. K. *Organometallics* **1994**, *13*, 303.
(2) Rulke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769.
(3) Stockland, R. J., Jr.; Anderson, G. K.; Rath, N. P.; Braddock-Wilking, J.; Ellegood, J. C. *Can. J. Chem.* **1996**, *74*, 1990.
(4) Stille, J. K.; James, D. E. *J. Organomet. Chem.* **1976**, *108*, 401. Rotondo, E.; Cusmano Priolo, F.; Donato, A.; Pietropaolo, R. *J. Organomet. Chem.* **1983**, *251*, 273.
(5) Stille, J. K.; Morgan, R. A.; Whitehurst, D. D.; Doyle, J. R. *J. Am. Chem. Soc.* **1965**, *87*, 3282. Schultz, R. G. *J. Organomet. Chem.* **1966**, *6*, 435. Pietropaolo, R.; Cusmano, F.; Rotondo, E.; Spadaro, A. *J. Organomet. Chem.* **1978**, *155*, 117.
(6) Anderson, C. B.; Burreson, B. J. *J. Organomet. Chem.* **1967**, *7*, 181. Akbarzadeh, M.; Anderson, C. B. *J. Organomet. Chem.* **1980**, *197*, C5.
(7) Tsuji, J.; Takahashi, H. *J. Am. Chem. Soc.* **1965**, *87*, 3275.
(8) Tada, M.; Kuroda, Y.; Sato, T. *Tetrahedron Lett.* **1969**, 2871.
(9) Palumbo, R.; De Renzi, A.; Panunzi, A.; Paiaro, G. *J. Am. Chem. Soc.* **1969**, *91*, 3874.
(10) Evans, D. J.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1986**, *312*, C24.

S0276-7333(97)00836-4 CCC: $15.00
Publication on Web 02/26/1998

by reaction of $[PdCl_2(cod)]$ with C_6F_5Li, was shown to rearrange slowly in solution to generate $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{12}C_6F_5)_2]$, the latter being converted to $[Pd(acac\text{-}F_6)(\eta^1,\eta^2\text{-}C_8H_{12}C_6F_5)]$ by treatment with thallium(I) hexafluoroacetylacetonate. The crystal structure of $[Pd(acac\text{-}F_6)(\eta^1,\eta^2\text{-}C_8H_{12}C_6F_5)]$ revealed that the product had been formed, as might be expected, by endo attack of the pentafluorophenyl group on the coordinated double bond.[12]

In this paper, we report the syntheses of a number of cyclooctenylpalladium derivatives, first as their chloride-bridged dimers and subsequently as acetylacetonate derivatives. We also describe the crystal structures of three complexes, one formed by exo attack and two formed by endo attack on coordinated cyclooctadiene. In addition, we present NMR studies of these complexes and the use of the magnitudes of $^3J(H,H)$ coupling constants to determine the stereochemistry of addition to the coordinated double bond.

Experimental Section

All reactions were carried out under an atmosphere of argon. Solvents were dried and distilled immediately prior to use. $[PdCl_2(cod)]$ was prepared according to the method of Chatt.[13] Silver(I) acetylacetonate was purchased from Aldrich. Solutions of NaOMe and NaOEt were prepared by addition of sodium metal to the appropriate alcohol. $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{13})_2]$, **1g**, was prepared as described previously.[3] The complexes $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{12}R)_2]$ (R = OMe (**1b**),[14] $CH(CO_2Me)_2$ (**1d**),[7] NEt_2 (**1j**),[9] OAc (**1k**)[6]) were prepared according to literature methods. NMR spectra were recorded on a Varian XL-300, Varian Unity plus 300, or Bruker ARX-500 spectrometer. ^1H and ^{13}C chemical shifts were measured relative to the residual solvent signal, positive shifts representing deshielding; coupling constants are given in hertz. Microanalyses were performed by Atlantic Microlab Inc. (Norcross, Georgia).

Preparation of $[Pd_2(\mu\text{-}Cl)_2\{\eta^1,\eta^2\text{-}C_8H_{12}C(CO_2Me)\text{=}CMe(CO_2Me)\}_2]$, 1a. $[PdClMe(cod)]$ (0.22 g, 0.83 mmol) was dissolved in toluene (8 mL). Dimethylacetylene dicarboxylate (0.12 mL, 0.95 mmol) was introduced by syringe. The yellow solution was stirred at ambient temperature for 20 h, during which time a white solid precipitated. Ether (15 mL) was added to complete precipitation, and the solid was filtered off. After washing with ether (3 mL), the solid was dried in vacuo (0.30 g, 89%). Anal. Calcd for $C_{30}H_{42}Cl_2O_8Pd_2$: C, 44.25; H, 5.16. Found: C, 44.16; H, 5.19.

Preparation of $[Pd(acac)\{\eta^1,\eta^2\text{-}C_8H_{12}C(CO_2Me)\text{=}CMe(CO_2Me)\}]$, 2a. To a CH_2Cl_2 solution (20 mL) of $[Pd_2(\mu\text{-}Cl)_2\{\eta^1,\eta^2\text{-}C_8H_{12}C(CO_2Me)\text{=}CMe(CO_2Me)\}_2]$ (0.10 g, 0.12 mmol) was added Ag(acac) (0.051 g, 0.25 mmol), and the mixture was stirred in the dark for 1 h. The solvent was removed, and the residue was extracted with ether and passed down a Hyflo Supercel/Florosil column, eluting with ether. The ether was removed in vacuo. The resulting solid was crystallized by slow evaporation of an ether/hexane solution, giving the product as colorless crystals (0.94 g, 81%). Anal. Calcd for $C_{20}H_{28}O_6Pd$: C, 51.02; H, 5.95. Found: C, 51.02; H, 6.01.

Preparation of $[Pd(acac)(\eta^1,\eta^2\text{-}C_8H_{12}OMe)]$, 2b. To a CH_2Cl_2 solution (20 mL) of $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{12}OMe)_2]$ (0.10 g, 0.18 mmol) was added Ag(acac) (0.078 g, 0.38 mmol). The mixture was stirred in the dark at ambient temperature for 35 min, then the solvent was removed in vacuo. The solid was dissolved in ether (5 mL) and passed down a short Florosil column, eluting with ether (40 mL). The ether was removed, and the residue was extracted with hexane. After filtration, the solvent was removed in vacuo to leave the product as a colorless solid (0.114 g, 93%). Anal. Calcd for $C_{14}H_{22}O_3Pd$: C, 48.81; H, 6.39. Found: C, 48.82; H, 6.39. A portion of the product was dissolved in hexane (1.5 mL), and the solution was cooled to −40 °C. Colorless crystals were obtained after 1 week.

Preparation of $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{12}OEt)_2]$, 1c. To an ethanol suspension of $[PdCl_2(cod)]$ (0.10 g, 0.35 mmol) was slowly added an ethanol solution of NaOEt (0.35 mL of a 1.0 M solution). The solution became lighter in color. The mixture was stirred for 30 min, and a white precipitate formed. The solution was filtered through a Hyflo Supercel column, which was washed with CH_2Cl_2 (100 mL). The resulting solution was evaporated, and the residue was dried in vacuo, leaving the product as a pale yellow solid (65%).

Preparation of $[Pd(acac)(\eta^1,\eta^2\text{-}C_8H_{12}OEt)]$, 2c. To a CH_2Cl_2 solution (50 mL) of $[Pd_2(\mu\text{-}Cl)_2(C_8H_{12}OEt)_2]$ (0.050 g, 0.085 mmol) was added Ag(acac) (0.037 g, 0.18 mmol). The solution was stirred in the dark for 1 h at ambient temperature. The resulting mixture was passed through a Hyflo Supercel/Florosil column, washing with CH_2Cl_2 (100 mL). The solvent was removed in vacuo, leaving the product as a colorless solid (0.052 g, 85%). Anal. Calcd for $C_{15}H_{24}O_3Pd$: C, 50.22; H, 6.70. Found: C, 50.14; H, 6.34.

Preparation of $[Pd(acac)\{\eta^1,\eta^2\text{-}C_8H_{12}CH(CO_2Me)_2\}]$, 2d. Ag(acac) (0.054 g, 0.26 mmol) was added to $[Pd_2(\mu\text{-}Cl)_2\{C_8H_{12}CH(CO_2Me)_2\}_2]$ (0.10 g, 0.13 mmol) in CH_2Cl_2 solution (50 mL). The solution was stirred in the dark at ambient temperature for 1 h. The solution was passed down a Hyflo Supercel/Florosil column, and the solvents were removed. The residue was extracted with ether (50 mL). After filtration, the solvent was removed in vacuo, leaving the product as a colorless solid (0.098 g, 84%). Anal. Calcd for $C_{18}H_{26}O_6Pd$: C, 48.60; H, 5.85. Found: C, 49.16; H, 6.13.

Preparation of $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{12}C_6H_5)_2]$, 1e. Method A. To a CH_2Cl_2 solution (100 mL) of $[PdCl_2(cod)]$ (0.82 g, 2.9 mmol) was added tetraphenyltin (1.38 g, 3.2 mmol). The solution was stirred at ambient temperature for 15 h, and then it was evaporated to leave a light gray solid. The latter was subjected to a Soxhlet extraction with ether for 12 h to remove Ph_3SnCl and unreacted Ph_4Sn. The remaining solid was extracted with CH_2Cl_2, and the solution was evaporated to leave the product as an off-white solid (0.782 g, 84%). Anal. Calcd for $C_{28}H_{34}Pd_2Cl_2$: C, 51.39; H, 5.21. Found: C, 51.41; H, 5.17.

Method B. To a CH_2Cl_2 solution (50 mL) of $[PdCl_2(cod)]$ (0.10 g, 0.35 mmol) at 0 °C was introduced phenylmagnesium bromide (0.18 mL of a 3.0 M solution in ether). The solution darkened and was stirred for 5 min. The reaction was quenched with water (0.1 mL), then the solvents were evaporated, leaving a black solid. The solid was dissolved in CH_2Cl_2 and filtered. The solvent was evaporated, leaving the product as a colorless solid (0.010 g, 9%).

Preparation of $[Pd(acac)(\eta^1,\eta^2\text{-}C_8H_{12}C_6H_5)]$, 2e. To a CH_2Cl_2 solution (20 mL) of $[Pd_2(\mu\text{-}Cl)_2(C_8H_{12}C_6H_5)_2]$ (0.10 g, 0.15 mmol) was added Ag(acac) (0.063 g, 0.31 mmol). The mixture was stirred for 2 h at ambient temperature, and then it was passed down a Hyflo Supercel/Florosil column, eluting with CH_2Cl_2 (50 mL). The solvent was removed in vacuo, leaving the product as a colorless solid (0.11 g, 89%). The solid was crystallized from hexane solution at −40 °C.

Preparation of $[Pd_2(\mu\text{-}Br)_2(\eta^1,\eta^2\text{-}C_8H_{12}C_6H_2Me_3)_2]$, 1f. $[PdCl_2(cod)]$ (0.35 g, 1.2 mmol) was dissolved in CH_2Cl_2 (50 mL). 2-Mesitylmagnesium bromide (1.8 mL of a 1.0 M diethyl ether solution) was added by syringe. The mixture was allowed to stir at ambient temperature for 10 min. Water (0.1 mL) was added to quench any remaining Grignard reagent.

(11) Segnitz, A.; Kelly, E.; Taylor, S. H.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *124*, 113.
(12) Albeniz, A. C.; Espinet, P.; Jeannin, Y.; Philoche-Levisalles, M.; Mann, B. E. *J. Am. Chem. Soc.* **1990**, *112*, 6594.
(13) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413.
(14) Bailey, C. T.; Lisensky, G. C. *J. Chem. Educ.* **1985**, *62*, 896.

Table 1. Data Collection, Structure Solution, and Refinement Parameters for [Pd(acac){η^1,η^2-$C_8H_{12}C(CO_2Me)$=CMe(CO_2Me)}], 2a, [Pd(acac)(η^1,η^2-C_8H_{12}OMe)], 2b, and [Pd(acac)(η^1,η^2-$C_8H_{12}C_6H_5$)], 2e

	2a	2b	2e
cryst syst	monoclinic	monoclinic	orthorhombic
space group, Z	$P2_1/c$, 4	$P2_1/n$, 8	$Pna2_1$, 4
a (Å)	22.0367(2)	14.3942(2)	34.43(2)
b (Å)	7.1271(1)	13.4702(1)	7.100(4)
c (Å)	13.8417(1)	14.8865(2)	7.078(5)
β (deg)	106.922(1)	104.596(1)	
V (Å^3)	2079.82(4)	2793.23(8)	1730(2)
density (g/cm^{-3}) (calcd)	1.504	1.639	1.500
temp (K)	223(2)	298(2)	293(2)
abs coeff (mm^{-1})	0.924	1.327	5.598
diffractometer	Siemens R3m/V	Siemens R3m/V	Siemens R3m/V
range (deg)	1.93−28.00	2.07−25.00	2.93−23.99
no. of reflns colld	43 988	25 464	1903
no. of indep reflns (R_{int})	5029 (0.051)	4914 (0.1523)	1413 (0.0206)
least-squares params	244	325	208
$R(F)$, $R_w(F^2)$ ($F^2 > 2.0\sigma(F^2)$)	0.0294, 0.0657	0.0733, 0.1683	0.0304, 0.0598
$R(F)$, $R_w(F^2)$ (all data)	0.0392, 0.0701	0.1527, 0.2315	0.0563, 0.1253
$S(F^2)$	1.082	1.003	1.333

The solvents were evaporated, and the dark residue was dissolved in CH_2Cl_2 (5 mL) and passed down a Hyflo Supercel column, eluting with CH_2Cl_2 (100 mL). The eluant was collected at −78 °C, and the solvent was removed below 0 °C. The residue was washed with ether (100 mL), and then it was dissolved in benzene (80 mL). The benzene solution was passed down a Hyflo Supercel column; then the benzene was removed to leave the product as a white solid (0.39 g, 77%).

Preparation of [Pd(acac)(η^1,η^2-$C_8H_{12}C_6H_2Me_3$)], 2f. [Pd(cod)Cl_2] (0.35 g, 1.2 mmol) was dissolved in CH_2Cl_2 (50 mL). 2-Mesitylmagnesium bromide (1.8 mL of a 1.0 M diethyl ether solution) was added by syringe. The mixture was allowed to stir at ambient temperature for 10 min; then water was added to quench the Grignard reagent. The solvents were evaporated, and the residue was washed with ether (100 mL) and then dissolved in CH_2Cl_2 (50 mL). Ag(acac) (0.25 g, 1.2 mmol) was added, and the mixture was stirred at ambient temperature for 30 min. The solvent was removed, and the residue was dissolved in ether (5 mL) and passed down a Hyflo Supercel/Florosil column, eluting with ether (100 mL). The ether was removed, and the solid was extracted with hexane at −78 °C. The hexane was removed, and the solid was dried in vacuo to leave the product as a colorless solid (0.35 g, 65%). Anal. Calcd for $C_{22}H_{30}O_2Pd$: C, 61.05; H, 6.94. Found: C, 61.16; H, 6.99.

Preparation of [$Pd_2(\mu$-Cl)$_2(\eta^1,\eta^2$-$C_8H_{12}C_6H_4$Me-2)$_2$], 1h. To a CH_2Cl_2 solution (30 mL) of [$PdCl_2$(cod)] (0.10 g, 0.35 mmol) at 0 °C was added 2-tolylmagnesium chloride (0.50 mL of a 1.0 M ether solution). The solution was stirred for 10 min, then the solvent was removed, and the residue was washed with ether and hexane. The solid was extracted with benzene and filtered. The benzene was removed in vacuo to leave the product as a pale yellow solid (0.058 g, 49%).

Preparation of [$Pd_2(\mu$-Cl)$_2(\eta^1,\eta^2$-$C_8H_{12}C_6H_4$Me-4)$_2$], 1i.[15] To a CH_2Cl_2 solution (30 mL) of [$PdCl_2$(cod)] (0.10 g, 0.35 mmol) at ambient temperature was added (4-MeC_6H_4)$_2$Hg (0.20 g, 0.52 mmol). The mixture was stirred in the dark for 1 h, then the solvents were removed, and the residue was washed with ether and THF. The solid was then dissolved in CH_2Cl_2 and passed down a Florosil column, eluting with CH_2Cl_2. The solvent was evaporated, and the product was left as a pale yellow solid (0.85 g, 71%).

Preparation of [$Pd_2(\mu$-Cl)$_2(\eta^1,\eta^2$-$C_8H_{12}NO_2$)$_2$], 1l.[16] [$PdCl_2$(cod)] (0.10 g, 0.35 mmol) was dissolved in CH_3CN (30 mL). $AgNO_2$ (0.054 g, 0.35 mmol) was added, and the mixture was stirred in the dark at ambient temperature overnight. The solution was filtered to remove the silver salts. The solvent was removed in vacuo, leaving the product as a pale yellow powder (0.093 g, 95%). ^{1}H NMR ($CDCl_3$): 1.48 (dd, 1H, 14.1, 8.0, CH_2), 2.1 (m, 1H, CH_2), 2.26 (m, 1H, CH_2), 2.37 (m, 1H, CH_2), 2.46 (m, 1H, CH_2), 2.64 (qd, 1H, 8.9, 4.6, CH_2), 2.72 (m, 1H, CH_2), 2.81 (m, 1H, CH_2), 3.71 (dd, 1H, C*H*Pd), 4.86 (dt, 1H, C*H* NO_2), 5.63 (m, 1H, =C*H*), 6.17 (m, 1H, =C*H*).

Table 2. Selected Bond Distances and Angles for [Pd(acac){η^1,η^2-$C_8H_{12}C(CO_2Me)$=CMe(CO_2Me)}], 2a

Bond Distances (Å)			
Pd−C1	2.024(2)	Pd−C5	2.151(2)
Pd−C6	2.154(2)	Pd−O5	2.129(2)
Pd−O6	2.046(2)	C1−C2	1.554(3)
C2−C9	1.519(3)	C5−C6	1.380(4)
C9−C10	1.338(3)	C9−C14	1.504(3)
C10−C11	1.502(4)	C10−C13	1.510(4)
Bond Angles (deg)			
C1−Pd−O5	177.32(8)	C1−Pd−O6	89.03(8)
O5−Pd−O6	91.11(7)	Pd−C1−C2	115.18(14)
Pd−C1−C8	104.3(2)	C1−C2−C3	114.9(2)
C1−C2−C9	110.6(2)	C2−C9−C10	124.8(2)
C2−C9−C14	114.7(2)	C10−C9−C14	120.5(2)
C9−C10−C11	119.0(2)	C9−C10−C13	124.7(3)
C11−C10−C13	116.3(2)		

X-ray Structure Determinations. In each case, a crystal was mounted on a glass fiber in random orientation. Preliminary examination and data collection were performed using a Siemens SMART CCD detector system single-crystal X-ray diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) equipped with a sealed-tube X-ray source (50 kV × 40 mA), as described elsewhere.[17] The SMART software package was used for data collection, and SAINT was used for frame integration. Structure solution and refinement were carried out using the SHELXTL-PLUS (5.03) software package.[18] Data collection, structure solution, and refinement parameters are given in Table 1. Selected bond distances and bond angles are presented in Tables 2−4.

Results and Discussion

Reaction of [PdClMe(cod)] with MeO_2CC≡CCO_2Me (DMAD). When [PdClMe(cod)] was allowed to react with 1.15 mol equiv of MeO_2CC≡CCO_2Me (DMAD), a

(15) Tamaru, Y.; Yoshida, Z. *J. Org. Chem.* **1979**, *44*, 1188.
(16) Andrews, M. A.; Chang, T. C.-T.; Cheng, C.-W. F.; Kapustay, L. V.; Kelly, K. P.; Zweifel, M. J. *Organometallics* **1984**, *3*, 1479.
(17) Stockland, R. A., Jr.; Anderson, G. K.; Rath, N. P. *Inorg. Chim. Acta*, in press.
(18) Siemens Analytical X-Ray Division, Madison, WI, 1995.

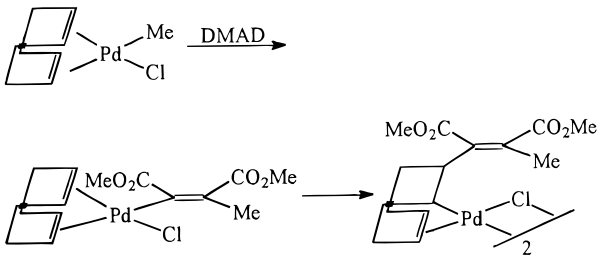
Table 3. Selected Bond Distances and Angles for [Pd(acac)(η^1,η^2-C_8H_{12}OMe)], 2b

	molecule 1	molecule 2		molecule 1	molecule 2
		Bond Distances (Å)			
Pd−C1	2.015(11)	2.017(10)	Pd−C5	2.128(10)	2.108(10)
Pd−C6	2.118(11)	2.130(10)	Pd−O2	2.042(7)	2.032(8)
Pd−O3	2.113(7)	2.121(8)	C1−C2	1.502(14)	1.527(14)
C2−O1	1.417(12)	1.450(12)	C5−C6	1.38(2)	1.41(2)
O1−C9	1.391(13)	1.391(13)			
		Bond Angles (deg)			
C1−Pd−O2	89.4(4)	89.8(4)	C1−Pd−O3	177.4(4)	177.9(4)
O2−Pd−O3	91.3(3)	91.4(3)	Pd−C1−C2	112.8(7)	110.2(7)
Pd−C1−C8	106.7(8)	108.2(7)	C1−C2−C3	114.4(9)	115.3(9)
C1−C2−O1	108.0(9)	105.7(9)	C2−O1−C9	114.3(9)	114.5(9)

Table 4. Selected Bond Distances and Angles for [Pd(acac)(η^1,η^2-$C_8H_{12}C_6H_5$)], 2e

	Bond Distances (Å)		
Pd−C1	2.018(8)	Pd−C5	2.162(10)
Pd−C6	2.152(10)	Pd−O1	2.054(6)
Pd−O2	2.125(5)	C1−C2	1.537(11)
C2−C9	1.505(13)	C5−C6	1.35(2)
	Bond Angles (deg)		
C1−Pd−O1	89.2(3)	C1−Pd−O2	179.0(3)
O1−Pd−O2	90.3(2)	Pd−C1−C2	113.9(6)
Pd−C1−C8	105.3(6)	C1−C2−C3	115.6(7)
C1−C2−C9	110.2(6)		

well-defined two-step reaction occurred, namely, insertion of DMAD into the Pd−Me bond followed by migratory insertion of a double bond of the diene into the alkenylpalladium linkage thus formed (eq 1). When the

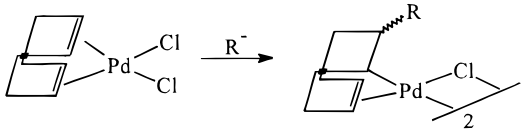


(1)

reaction was monitored by ^{1}H NMR spectroscopy, a major new species was observed after 1.5 h, whose NMR parameters were consistent with a species of the form [PdCl{C(CO_2Me)═Me(CO_2Me)}(cod)] (δ(*H*) 2.37 (s, CH_3), 2.4−2.7 (m, CH_2), 3.64, 3.78 (s, CO_2CH_3), 5.50, 6.15 (m, C*H*═)), but this converted to the chloride-bridged complex [$Pd_2(\mu$-Cl)$_2${η^1,η^2-C_8H_{12}C(CO_2Me)═CMe(CO_2Me)}$_2$], **1a**, on standing. The final product was characterized by elemental analysis and by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (Tables 5 and 6), including ^{1}H−^{1}H and ^{13}C−^{1}H correlation experiments. Although the observation of an intermediate of the type [PdClR(cod)] would suggest that the final product was formed by cis addition of palladium and the alkenyl group on the coordinated double bond, we were unable to confirm this because attempts to grow crystals of the chloride-bridged complex suitable for an X-ray diffraction study were unsuccessful. Conversion to the acetylacetonate derivative did allow the isolation of X-ray-quality crystals, however, and the structure of this complex is discussed below.

As mentioned above, [PdCl(C_6F_5)(cod)] was shown to rearrange to [$Pd_2(\mu$-Cl)$_2$(η^1,η^2-$C_8H_{12}C_6F_5$)$_2$], which was converted to its hexafluoroacetylacetonate analogue. The molecular structure of the latter revealed that cis addition of the Pd and C_6F_5 moieties had indeed occurred.[11] The molecular structure of [$Pd_2(\mu$-Cl)$_2$(η^1,η^2-$C_7H_8C_6H_5$)$_2$], formed by reaction of [$PdCl_2$(nbd)] with Ph_2Hg, also indicated that the product was formed by endo attack of the phenyl group on one of the double bonds.[10] A number of other reactions of palladium diene complexes with nucleophiles have been assumed to proceed by exo attack on a coordinated double bond, but unambiguous structural information is lacking. Thus, we decided to prepare a number of η^1,η^2-cyclooctenyl complexes to determine the solid-state structures of both the exo and endo isomers and to show how NMR spectroscopy can be used to determine the stereochemistry of addition when solid-state structural data are unavailable.

Reactions of [$PdCl_2$(cod)] with Nucleophiles. With the exception of the case discussed above, each of the complexes of the type [$Pd_2(\mu$-Cl)$_2$(η^1,η^2-$C_8H_{12}R$)$_2$] was prepared using [$PdCl_2$(cod)] as a precursor (eq 2). The



(2)

alkoxy derivatives **1b,c** were prepared by reaction with NaOMe[14] or NaOEt in the appropriate alcohol solution, whereas the malonate complex **1d** was generated by reaction of [$PdCl_2$(cod)] with dimethyl malonate in the presence of Na_2CO_3 in ether solution.[7] Each complex was isolated as an air-stable, pale yellow solid. The aryl-substituted species were prepared by reaction of [$PdCl_2$(cod)] with the appropriate Grignard reagent in CH_2Cl_2 solution or more conveniently in the phenyl case, by reaction with Ph_4Sn. The previously reported 4-tolyl derivative[15] was prepared in good yield using the diarylmercury reagent. In the case of the mesityl-substituted complex **1f**, the product obtained was the bromide-bridged derivative, since a bromide-containing Grignard reagent was employed in the synthesis. In each case, the product was obtained as a colorless or pale yellow solid. Complexes **1j,k** (R = NEt_2, OAc) were prepared by literature methods,[6,9] by reaction of [$PdCl_2$-(cod)] with diethylamine or sodium acetate, respectively. The nitro derivative **1l** was prepared by the reaction of [PdCl(NO_2)(CH_3CN)$_2$] with 1,5-cyclooctadiene[16] and by treatment of [$PdCl_2$(cod)] with $AgNO_2$ in CH_3CN solution. ^{1}H NMR spectroscopy indicated that the same product was formed in each case.

When the reaction of [$PdCl_2$(cod)] with 2-mesitylmagnesium bromide was performed at −78 °C, the solution turned red immediately; an impure solid was isolated

Table 5. ^{1}H NMR Data for the Complexes $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{12}R)_2]$, 1a−h[a]

	1a, R = CX=CMeX (X = CO_2Me)	**1b**, R = OMe	**1c**, R = OEt	**1d**, R = $CH(CO_2Me)_2$	**1e**, R = Ph	**1f**, R = $C_6H_2Me_3$[b]	**1g**, R = H[c]	**1h**, R = 2-C_6H_4Me	**1i**, R = 4-C_6H_4Me
H1	3.70	3.58	3.53	3.36	3.85	3.98	3.90	3.84	3.80
H2	2.05	3.58	3.66	2.62	1.91	2.75	0.40, 1.70	2.25	1.87
H3, H3′	2.05, 2.60	1.96 (2)	1.95 (2)	1.73, 1.76	2.19, 2.72	1.89, 2.89	1.45 (2)	2.07, 2.65	2.15, 2.66
H4, H4′	1.80, 2.35	2.54, 2.67	2.52, 2.65	2.49, 2.56	1.98, 2.39	1.89, 2.37	1.70, 1.92	1.97, 2.35	1.96, 2.34
H5	5.95	5.57	5.44	5.49	6.07	6.02	5.60	6.05	6.02
H6	6.45	5.90	5.86	5.96	6.46	6.75	5.88	6.46	6.41
H7, H7′	2.05 (2)	2.13, 2.23	2.14, 2.21	2.13, 2.22	2.08 (2)	2.14, 2.26	1.55 (2)	2.13 (2)	2.10 (2)
H8, H8′	1.10, 2.60	1.42, 2.23	1.43, 2.21	1.15, 2.31	1.20, 2.62	1.17, 2.66	0.60, 2.13	1.14, 2.61	1.14, 2.55
R	1.90 (CH_3), 3.67, 3.77 (OCH_3)	3.24 (OCH_3)	3.33, 3.46 (OCH_2), 1.08 (CH_3)	3.35 (CH), 3.69, 3.70 (OCH_3)	7.16 (*p*-CH), 7.27 (*m*-CH), 7.37 (*o*-CH)	2.20, 2.29, 2.60 (CH_3), 6.75, 6.81 (CH)		2.28 (CH_3), 7.03 (2), 7.18, 7.65 (CH)	2.28 (CH_3), 7.07 (2), 7.25 (2) (CH)

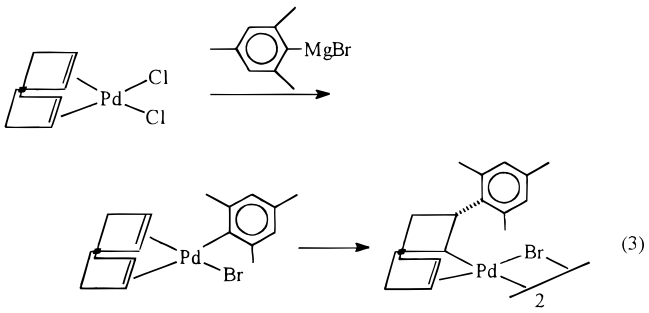
[a] Recorded in $CDCl_3$ solution unless stated. [b] Bromide-bridged complex. [c] Recorded in C_6D_6 solution.

Table 6. ^{13}C NMR Data for the Complexes $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{12}R)_2]$, 1a−h[a]

	1a, R = CX=CMeX (X = CO_2Me)	**1b**, R = OMe	**1c**, R = OEt	**1d**, R = $CH(CO_2Me)_2$	**1e**, R = Ph	**1f**, R = $C_6H_2Me_3$[c]	**1g**, R = H[b]	**1h**, R = 2-C_6H_4Me	**1i**, R = 4-C_6H_4Me
C1	59.4	52.2	53.3	53.5	66.6	67.5	56.0	67.0	66.9
C2	48.5	81.4	79.9	43.4	55.6	49.1	35.7	49.8	55.2
C3	40.0	30.9	31.6	29.0	44.9	40.1	27.0	44.5	44.8
C4	26.1	28.1	28.6	29.7	26.6	28.4	28.7	26.9	26.6
C5	103.6	101.9	102.1	100.5	105.0	104.5	100.7	105.2	104.9
C6	111.2	106.4	106.5	105.9	111.2	114.5	105.2	111.7	111.1
C7	24.0	26.5	26.9	27.1	24.3	24.4	26.3	24.4	24.3
C8	43.0	34.5	35.1	36.1	43.2	43.2	40.2	43.9	43.2
R	14.7 (CH_3), 52.2, 52.4 (OCH_3), 126.6, 145.1 (C=C), 168.3, 168.9 (CO)	56.6 (OCH_3)	64.6 (OCH_2), 16.1 (CH_3)	54.5 (CH). 52.8, 53.0 (OCH_3), 168.6, 168.8 (CO)	125.9 (*p*-CH), 127.2 (*o*-CH), 128.5 (*m*-CH), 146.9 (quat C)	21.0, 22.4, 23.9 (CH_3), 129.2, 131.4 (CH), 135.3, 135.6, 137.1, 139.5 (quat C)	14.7 (CH_3), 52.2, 52.4 (OCH_3), 168.3, 168.9 (CO)	20.4 (CH_3), 126.0, 127.1, 127.8, 130.2 (CH); 134.0, 145.6 (quat C)	21.4 (CH_3), 127.4, 129.5 (CH), 135.8, 144.3 (quat C)

[a] Recorded in $CDCl_3$ solution unless stated. [b] Recorded in C_6D_6 solution. [c] Bromide-bridged complex.

after solvent removal at 0 °C and washing of the residue with water. The ^{1}H NMR spectrum of the solid was consistent with [PdBr($C_6H_2Me_3$-2,4,6)(cod)] (δ(H) 2.20 (s, 3H, 4-CH_3), 2.58 (s, 6H, 2-CH_3), 2.55−2.79 (m, 8H, CH_2), 5.18 (m, 2H, =C*H* cis to Br), 6.03 (m, 2H, =C*H*, trans to Br), 6.69 (s, 2H, C*H*)). Attempts to purify this material, however, always resulted in some rearrangement (10−20%) to **1f**. When a solution of [PdBr(C_6H_2-Me_3)(cod)], generated at low temperature, was allowed to warm to ambient temperature, the complex converted cleanly to **1f**. The observation of the monomeric intermediate indicates that, in this instance, the reaction proceeds by initial transfer of the organic group to the metal, followed by migratory insertion of one of the C=C double bonds (eq 3). A similar observation was made

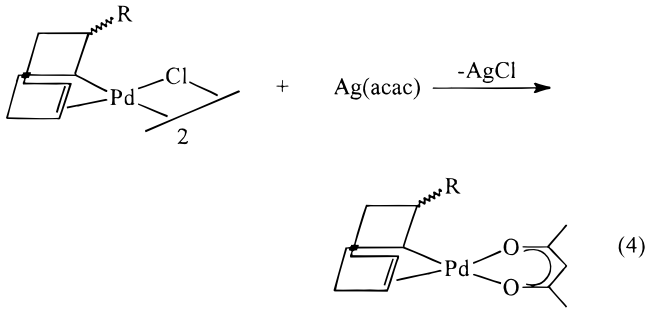


(3)

by Espinet and co-workers, who isolated the monomeric intermediate in the reaction of [$PdCl_2$(cod)] with C_6F_5-Li.[12] In that case, they were able to obtain a crystal structure of the intermediate as well as observe its conversion to [$Pd_2(\mu$-Cl)$_2(\eta^1,\eta^2$-$C_8H_{12}C_6F_5)_2$] on standing in solution.

The large size of the mesityl group is no doubt responsible for our being able to observe an intermediate of the type [PdClR(cod)]. The 2-tolyl complex **1h** was prepared in reasonable yield from [$PdCl_2$(cod)] and 2-tolylmagnesium chloride, but the monomeric intermediate was not detected. In contrast, reactions with PhMgBr or 4-MeC_6H_4MgBr led predominantly to reductive elimination of the diaryl. Reductive elimination was observed in the reaction of [$PdCl_2$(nbd)] with PhMgBr,[19] and we have found that reactions of [$PdCl_2$-(dppm)] with aryl Grignard reagents also result in diaryl formation.[20]

Preparation of the Complexes [Pd(acac)(η^1,η^2-C_8H_{12}R)], 2a−f. The chloride-bridged complexes [$Pd_2(\mu$-Cl)$_2(\eta^1,\eta^2$-C_8H_{12}R)$_2$] were of limited solubility in some cases, and for the more soluble examples, repeated attempts to obtain crystals suitable for X-ray diffraction studies were unsuccessful. Thus, several of the complexes (**1a**−**f**, R = C(CO_2Me)=CMe(CO_2Me), OMe, OEt, CH($CO_2Me)_2$, Ph, $C_6H_2Me_3$) were converted to their corresponding acac derivatives **2a**−**f** by reaction with silver(I) acetylacetonate (eq 4). The reactions were performed in CH_2Cl_2 solution, and the products were isolated as colorless solids. The acac complexes are considerably more soluble than their dimeric precursors, being quite soluble in benzene and hexane as well as in more polar organic solvents. Crystals of **2a**, **2b**, and



(4)

2e were grown from hexane solution, and their solid-state structures were determined by X-ray crystallography.

Molecular Structures of [Pd(acac)(η^1,η^2-C_8H_{12}R)] (R = C(CO_2Me)=CMe(CO_2Me), OMe, Ph). The complex [Pd(acac){η^1,η^2-C_8H_{12}C(CO_2Me)=CMe(CO_2Me)}], **2a**, obtained by reaction of [PdClMe(cod)] with DMAD followed by metathesis with Ag(acac), crystallizes in the monoclinic space group $P2_1/c$, with four molecules per unit cell. The molecular structure is shown in Figure 1 and shows the approximate square-planar geometry at palladium. Two cis positions are occupied by the O,O-bonded acac ligand, and the other positions are occupied by C1 and the remaining double bond (C5, C6). The C=C bond lies perpendicular to the coordination plane, which is typical of palladium(II) complexes. Selected bond distances and angles are given in Table 2. The structure reveals that the Pd−Me bond has added in a cis fashion to the C≡C bond of DMAD, and subsequently, the palladium and the alkenyl group have added cis to one of the coordinated double bonds of the cyclooctadiene.

The C9−C10 distance of 1.338(3) Å indicates that the triple bond of DMAD has been reduced to a double bond. The sums of the three bond angles about C9 and C10 are exactly 360°, indicating planarity at these atoms, as expected for sp^2 hybridization. The coordinated C=C distance (C5−C6) of 1.380(4) Å is slightly longer than expected for a free double bond, whereas the C1−C2 distance of 1.554(3) Å indicates a reduction in bond order from two to one. The Pd−O5 distance (2.129(2) Å) trans to the Pd−C σ-bond is significantly longer than Pd−O6 (2.046(2) Å), consistent with the relative trans-influences of σ- and π-bonded carbon ligands.[21] The Pd−C1 distance of 2.024(2) Å is within the expected range for a Pd−C single bond,[22] and the Pd−C5 and Pd−C6 distances are normal for coordinated double bonds. The Pd−C1−C2−C9 torsion angle of 121.9° suggests that cis-addition across the C=C bond has taken place, but rotation about the C1−C2 bond has occurred in order to minimize the steric strain caused by the substituted alkenyl group. This rotation necessitates some distortion of the eight-membered ring, as may be seen in Figure 1.

The methoxy derivative, **2b**, crystallizes in the monoclinic space group $P2_1/n$, with eight molecules per unit cell. There are two unique molecules per unit cell, and the structure of one of the unique molecules is shown in Figure 2. The molecular structure reveals almost

(19) Segnitz, A.; Kelly, E.; Taylor, S. H.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *124*, 113.
(20) Stockland, R. A., Jr.; Anderson, G. K.; Rath, N. P. *Organometallics* **1997**, *16*, 5096.
(21) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.
(22) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

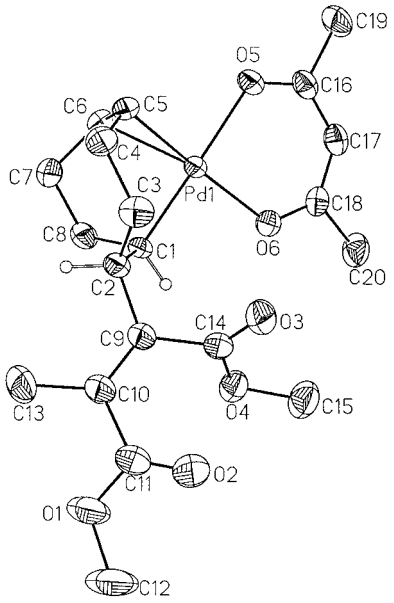


Figure 1. Molecular structure of [Pd(acac){η^1,η^2-C_8H_{12}C-(CO_2Me)=CMe(CO_2Me}], **2a**, showing the atom-labeling scheme.

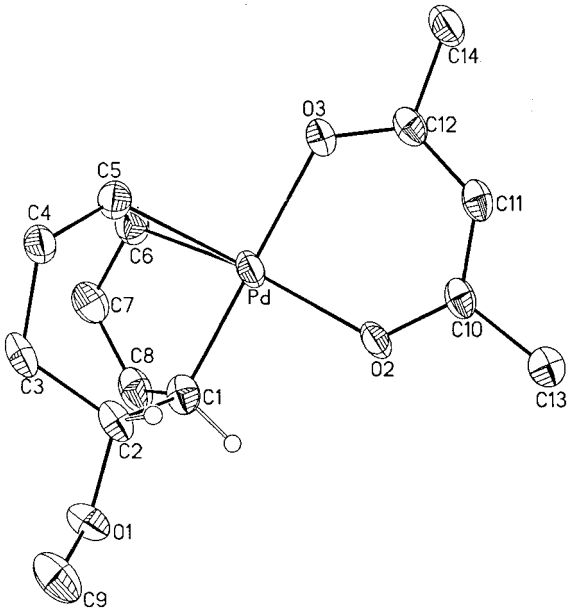


Figure 2. Molecular structure of [Pd(acac)(η^1,η^2-C_8H_{12}-OMe)], **2b**, showing the atom-labeling scheme.

square-planar geometry about palladium. The acetylacetonate ligand is again O,O-bonded, and the remaining coordination sites contain the Pd−C σ-bond and the C=C double bond of the chelated cyclooctenyl group, the latter lying perpendicular to the square plane. Selected bond distances and angles are presented in Table 3. The C=C bond distance (1.38(2) Å) is again slightly longer than expected for a free double bond, whereas the C1−C2 distance is lengthened to 1.50(1) Å, indicating a single bond. The Pd−O3 distance trans to the Pd−C σ-bond (2.113(7) Å) is again longer than that opposite the coordinated double bond (2.042(7) Å). The Pd−C1 distance of 2.015(11) Å is within the expected range for a Pd−C single bond, and the Pd−C5 and Pd−C6 distances are slightly shorter than normal. The structure reveals that the palladium and the methoxy group have added across one of the C=C double bonds, and

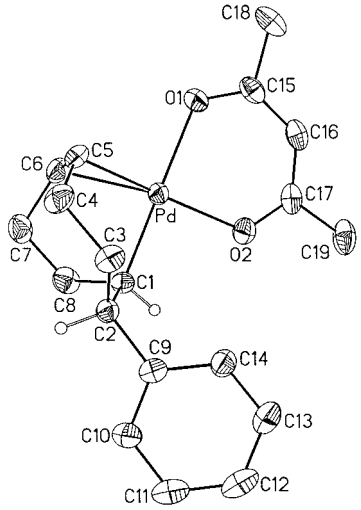


Figure 3. Molecular structure of [Pd(acac)(η^1,η^2-C_8H_{12}Ph)], **2e**, showing the atom-labeling scheme.

the Pd−C1−C2−O1 torsion angle of 167.1° shows that the addition occurred in a trans manner. The eight-membered ring shows little distortion from the shape it adopts in cyclooctadiene complexes, such as [$PdCl_2$-(cod)].[23]

The phenyl complex, **2e**, crystallizes in the orthorhombic space group $Pna2_1$, with four molecules per unit cell. Again, the molecule adopts approximate square-planar geometry about palladium (Figure 3). Selected bond distances and angles are given in Table 4. The C=C bond distance is 1.35(2) Å, close to what would be expected for an uncoordinated double bond, suggesting that there is little π-back-bonding from the metal. The C1−C2 distance is 1.54(1) Å, similar to that in **2a** but slightly longer than that in **2b**. The Pd−O2 distance trans to the Pd−C σ-bond of 2.125(5) Å is again longer than the Pd−O1 bond trans to the C=C double bond (2.054(6) Å). The Pd−C1 distance of 2.018(8) Å is typical of a Pd−C single bond, and the Pd−C5 and Pd−C6 distances are again slightly shorter than normal. In this case, the Pd−C1−C2−Ph torsion angle is 114.6°, similar to that in **2a**, suggesting that addition occurred in a cis fashion, but rotation about the C1−C2 bond again took place to reduce the steric interactions, resulting in distortion of the eight-membered ring (Figure 3).

It may be seen from Figures 1−3 that **2a** and **2e** exist as the same diastereomer (C1 and C2 being chiral centers), whereas the exo isomer has the opposite stereochemistry. Using the priority schemes Pd > C2 > C8 and C1 > C9 > C3, the structures depicted in Figures 1 and 3 are each of the (*R*,*R*) form. There should be no regioselectivity associated with addition across the double bond, and addition of Pd and the R group to opposite ends of the double bond would yield the (*S*,*S*) form. Since the molecule crystallizes in an achiral space group, the two forms are, of course, present. Using the same sequence of substituents for **2b** (replacing C9 by O1), the two unique molecules are observed to be of (*R*,*S*) and (*S*,*R*) stereochemistry. This is exactly what should be expected when the substituent at C2 and the metal have added from the same or the opposite face of the double bond, respectively.

(23) Benchekroun, L.; Herpin, P.; Julia, M.; Saussine, L. *J. Organomet. Chem.* **1977**, *128*, 275.

Table 7. ^{1}H NMR Data for the Complexes [Pd(acac)(η^1,η^2-$C_8H_{12}R$)], 2a−f[a]

	2a, R = CX=CMeX (X = CO_2Me)	**2b**, R = OMe	**2c**, R = OEt	**2d**, R = $CH(CO_2Me)_2$	**2e**, R = Ph	**2f**, R = $C_6H_2Me_3$
H1	3.17	3.18	3.18	2.90	3.33	3.29
H2	2.09	3.63	3.75	2.65	1.98	2.70
H3, H3′	1.96, 2.56	1.94 (2)	1.92 (2)	1.72, 1.78	2.17, 2.47	1.80, 2.83
H4, H4′	1.82, 2.31	2.59 (2)	2.60 (2)	2.54 (2)	1.98, 2.29	1.88, 2.34
H5	5.62	5.21	5.28	5.25	5.75	5.66
H6	6.18	5.67	5.71	5.74	6.18	6.29
H7, H7′	2.02, 2.09	2.15, 2.24	2.25 (2)	2.16, 2.23	2.11 (2)	2.14 (2)
H8, H8′	1.21, 2.47	1.52, 2.15	1.54, 2.18	1.28, 2.23	1.27, 2.47	1.25, 2.48
R	1.95 (CH_3), 3.70, 3.73 (OCH_3)	3.27 (OCH_3)	3.37, 3.58 (OCH_2), 1.18 (CH_3)	3.45 (CH), 3.70, 3.73 (OCH_3)	7.15 (*p*-CH), 7.26 (*m*-CH), 7.39 (*o*-CH)	2.20, 2.31, 2.48 (CH_3), 6.76, 6.81 (CH)
acac CH	5.23	5.24	5.28	5.24	5.28	5.26
acac CH_3	1.85, 1.96	1.84, 1.97	1.86, 1.99	1.81, 1.95	1.92, 2.04	1.88, 1.94

[a] Recorded in $CDCl_3$ solution unless stated.

Table 8. ^{13}C NMR Data for the Complexes [Pd(acac)(η^1,η^2-$C_8H_{12}R$)], 2a−f[a]

	2a, R = CX=CMeX (X = CO_2Me)	**2b**, R = OMe	**2c**, R = OEt	**2d**, R = $CH(CO_2Me)_2$	**2e**, R = Ph	**2f**, R = $C_6H_2Me_3$
C1	54.5	45.5	46.3	47.7	60.2	60.2
C2	49.0	82.6	81.3	44.2	55.4	48.7
C3	39.5	30.9	31.6	29.3	45.1	40.0
C4	26.2	28.1	28.7	29.8	26.3	27.7
C5	97.5	96.0	96.4	95.0	99.5	97.7
C6	106.3	100.3	101.0	99.9	105.4	106.7
C7	25.1	27.2	27.7	27.9	25.6	24.8
C8	42.3	32.5	33.1	34.3	42.2	42.5
R	15.3 (CH_3), 52.4, 52.5 (OCH_3), 127.3, 146.6 (C=C), 169.0, 170.0 (CO)	56.1 (OCH_3)	64.1 (OCH_2), 16.3 (CH_3)	54.9 (CH), 52.8, 52.9 (OCH_3), 169.0, 169.3 (CO)	126.0 (*p*-CH), 127.9 (*o*-CH), 128.7 (*m*-CH), 137.9 (quat C)	21.0, 22.5, 22.0 (CH_3), 129.0, 131.3 (CH), 135.1, 135.2, 137.3, 140.8 (quat C)
acac CH_3	28.2, 28.9	27.8, 28.2	28.5, 29.2	28.2, 28.9	28.7, 29.4	27.8, 28.7
acac CH	99.7	99.5	100.4	99.8	100.2	99.8
acac CO	186.5, 189.0	186.2, 188.7	186.9, 189.4	186.7, 189.2	186.8, 189.9	185.9, 189.1

[a] Recorded in $CDCl_3$ solution unless stated.

NMR Studies of [$Pd_2(\mu$-Cl)$_2$(η^1,η^2-$C_8H_{12}R)_2$], 1a−l, and [Pd(η^1,η^2-$C_8H_{12}R$)(acac)], 2a−f. These complexes have been characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and in a number of cases, complete assignments have been made using a combination of ^{1}H−^{1}H and ^{13}C−^{1}H correlation methods. Complete listings of ^{1}H and ^{13}C NMR parameters for the chloride-bridged complexes **1a**−**i** are presented in Tables 5 and 6, and those for the acetylacetonate species **2a**−**f** are collected in Tables 7 and 8.

The ^{1}H NMR spectra of the chloride-bridged complexes **1a**−**i** each exhibit two well-defined resonances for the olefinic hydrogens H5 and H6, that for H6 always lying at higher frequency. (The numbering scheme is that shown in Figures 1−3.) The signal due to H1, α to palladium, is shifted to high frequency and lies in the range 3.3−4.0 ppm, whereas the position of the H2 resonance depends on the nature of the substituent on C2. The other ring hydrogens give rise to a series of multiplets in the range 1.7−2.9 ppm, with the exception of the resonance associated with one of the hydrogens attached to C8, which appears as a doublet of doublets to lower frequency of the others. In the case of the unsubstituted cyclooctenyl complex **1g** (R = H), one hydrogen on each of the β-carbons C2 and C8 produces a particularly low-frequency resonance (vide infra). All of the signals are shifted to low frequency in aromatic solvents compared to their positions in $CDCl_3$ solution. Signals due to the β-substituents appear as expected in **1a**−**e**. In **1f**, there are three methyl signals (2.20, 2.29, and 2.60 ppm) and two aromatic CH signals due to the mesityl group, indicating that there is restricted rotation about the C2−$C_6H_2Me_3$ bond at ambient temperature. This is perhaps unsurprising, owing to the large size of the mesityl moiety. When a toluene solution of **1f** was heated to 360 K, the methyl signals at 2.29 and 2.60 ppm broadened considerably (indicating that slow exchange was occurring) whereas the lowest frequency resonance remained sharp. The signal at 2.20 ppm is due to the CH_3 group in the 4-position, and therefore, the other two signals are due to the 2-methyl groups. These are separated by 0.3 ppm, suggesting that the groups occupy quite different environments in the static structure.

The ^{1}H NMR spectra of the acetylacetonate derivatives **2a**−**f** are qualitatively similar but contain additional signals due to the acac ligand. In each case, the CH resonance appears as a sharp singlet around 5.25 ppm whereas the methyls are nonequivalent and produce two broad singlets in the range 1.8−2.05 ppm. The signal due to H1 is shifted to lower frequency by 0.4−0.7 ppm when the bridging chlorides are replaced by the acac ligand, and the H5 and H6 resonances are also more shielded by 0.2−0.4 ppm, whereas the signals due to the other ring hydrogens are largely unaffected. Thus, only the hydrogens closest to the site of coordination are affected, and the shifts to lower frequency suggest there is greater electron density associated with the palladium center in the acac complexes. Again, there is restricted rotation of the mesityl group in **2f**.

The $^{13}C\{^1H\}$ NMR spectra of **1a**−**i** each exhibit the expected number of signals, and these have been assigned from their $^{13}C-^1H$ correlated spectra. Each complex gives rise to two olefinic signals due to C5 and C6 between 100 and 115 ppm, the resonance for C6 always exhibiting the higher frequency of the two. The resonance due to C1 appears at quite high frequency (52−67 ppm), paralleling the observations for H1 in the ^1H spectra, and again illustrating the deshielding nature of the palladium center. The location of the signal due to C2 depends on the nature of the substituent at C2, and the resonances due to the ring methylene carbons lie in the range 24−45 ppm. The expected signals are observed for the R substituents; three methyl and six aromatic resonances are detected for the mesityl group, again indicating that it is not free to rotate about the C2−$C_6H_2Me_3$ bond.

A comparison of the $^{13}C\{^1H\}$ NMR spectra for **1a**−**f** and the acetylacetonate complexes **2a**−**f** reveals a trend similar to that found in the ^1H NMR spectra. The signals due to C1 are shifted by about 7 ppm to lower frequency in the acac complexes, and analogous shifts are observed for the resonances due to C5 and C6. The signals due to C2−C4, C7, and C8 show much smaller variations, again suggesting that the palladium center affords greater shielding of the coordinated carbon atoms in the acac derivatives. The expected number of signals are observed for the R groups, and the acac ligands also produce the expected five resonances. In each case, the central carbon gives rise to a peak at ca. 100 ppm, the two carbonyl signals are detected in the range 186−190 ppm, and the two methyl carbon signals appear around 28 ppm.

When a $CDCl_3$ solution of **1a** was cooled, the olefinic signals in the ^1H NMR spectrum broadened and, on further cooling to 220 K, split into six resonances. Throughout this process the other signals remained relatively sharp, although splitting of the methyl signals also occurred. The $^{13}C\{^1H\}$ NMR spectrum at 220 K also exhibited six olefinic resonances, in addition to those associated with the C(CO_2Me)═CMe(CO_2Me) moiety. A $^1H-^1H$ EXSY spectrum for **1a** at 235 K showed cross-peaks for three pairs of olefinic resonances but no off-diagonal peaks relating the olefinic signals to those in other parts of the spectrum. This suggests that the fluxional process involves no change of the cyclooctenyl group itself but may involve rearrangement between dimers of cis or trans geometry and between species with the R groups syn or anti with respect to the Pd_2Cl_2 plane. Such interconversions may occur associatively or dissociatively via a three-coordinate [PdCl(η^1,η^2-C_8H_{12}R)] intermediate. The fact that the acac derivative **2a** does not exhibit this behavior supports such an interpretation. Similar variable-temperature NMR phenomena were observed for the other chloride-bridged complexes of type **1**.

A key question which prompted this study was whether it would be possible to use NMR spectroscopy to distinguish between the products of exo and endo addition of the R group to the coordinated cyclooctadiene. Having shown, unequivocally, by X-ray crystallography that the methoxy derivative **2b** exhibits exo geometry, whereas **2a** and **2e** have endo configurations, we should begin with a comparison of the spectra of these complexes and their chloride-bridged precursors. A consideration of the signals due to H1 should be informative, where we would expect to see couplings to H2, H8, and H8′. In the solid-state structure of **2b**, the dihedral angles between H1 and these three hydrogens are 67.5, 35.4, and 81.0°, respectively. If a conformation similar to this is maintained in solution, the Garbisch equations[24] suggest that one larger and two smaller couplings should be observed. In contrast, the structures of **2a** and **2e** provide H1−C−C−H dihedral angles of 116.5°, 68.8°, and 50.1°, and 111.5°, 71.3°, and 47.0°, respectively, which should lead to three couplings of comparable size. It may be that there is some distortion of the structures in solution, but we observe only two nonnegligible H−H couplings for H1; **2b** exhibits a doublet of doublets with couplings of 6.6 and 3.7 Hz, whereas for **2a** and **2e**, apparent triplets are observed with $^3J_{HH}$ = 4.4 and 4.0 Hz, respectively. In the chloride-bridged complex **1b,** the signals due to H1 and H2 overlap in $CDCl_3$ solution but in C_6D_6 the resonances are separated and the H1 resonance appears as a doublet of doublets of doublets with $^3J_{HH}$ values of 5.7, 3.3, and 1.7 Hz. The H1 signal for **1e** appears as an apparent triplet with a coupling of 4.1 Hz. Thus, it appears that, qualitatively at least, we may be able to differentiate between the products of exo and endo attack on the basis of the appearance of their H1 signals. A listing of the couplings to H1 in each of the complexes is given in Table 9. It may be seen that the aryl-substituted complexes **1e,f**, **1h,i**, and **2e,f**, as well as **1a** and **2a**, each produce apparent triplets for H1, with couplings of 4−5 Hz, whereas all of the other compounds show one larger coupling (6−7 Hz) and one or two smaller ones (Figure 4). This would indicate that the aryl- or alkenyl-substituted compounds are formed by endo attack of the organic group on the coordinated cyclooctadiene, whereas the others are produced by external attack on the C═C bond. The pentafluorophenyl-substituted complex [$Pd_2(\mu$-Cl)$_2(\eta^1,\eta^2$-$C_8H_{12}C_6F_5)_2$] exhibits two couplings of 3.6 Hz for H1.[12]

With these assignments in mind, we note the following additional differences between the ^1H and ^{13}C NMR resonances of the exo and endo isomers. The H1 resonances for the endo complexes appear at higher

Table 9. Couplings to H1 in the ^1H NMR Spectra of 1a−l and 2a−f[a]

	complex **1**	complex **2**
a, R = C(CO_2Me)═C(CO_2Me)Me	*b*	4.4, 4.4
b, R = OMe	5.7, 3.3, 1.7[c]	6.6, 3.7
c, R = OEt	broad	7.1, 3.4, 1.8
d, R = CH(CO_2Me)$_2$	*d*	6.6, 2.2, 2.2
e, R = Ph	4.1, 4.1	4.0, 4.0
f, R = $C_6H_2Me_3$	broad	4.8, 4.8
h, R = C_6H_4Me-2	4.1, 4.1[e]	
i, R = C_6H_4Me-4	4.1, 4.1	
j, R = NEt_2	11.5, 4.1, 4.1	
k, R = OAc	7.0, 3.5	
l, R = NO_2	5.6, 3.4	

[a] Recorded in $CDCl_3$ solution unless stated. Coupling constants are in hertz. The FID was resolution-enhanced using a Gaussian weighting function in each case. [b] Obscured by OC*H*$_3$ resonance. [c] In C_6D_6 solution. [d] Obscured by malonate C*H* resonance. [e] In toluene-d_8 solution.

(24) Garbisch, E. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 5561.

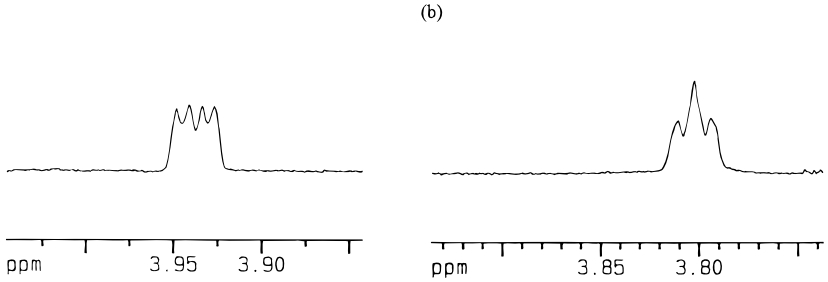


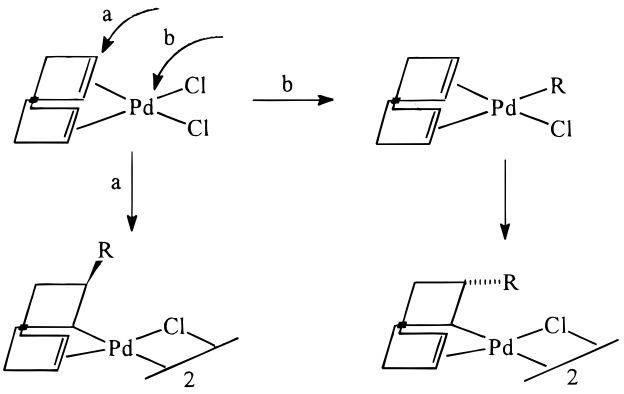
Figure 4. H1 resonances for (a) $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{12}OMe)_2)]$, **1b**, in C_6D_6, and (b) $[Pd_2(\mu\text{-}Cl)_2\ (\eta^1,\eta^2\text{-}C_8H_{12}C_6H_4Me\text{-}4)_2]$, **1i**, in $CDCl_3$ solution.

frequency (3.70−3.98 ppm for **1**) than their exo analogues (δ(H) 3.36−3.58). The olefinic signals are also shifted to higher frequencies in the endo species, as are the signals due to H3 and H3′ and one of the hydrogens attached to C8. In contrast, the signals due to both H4 and H4′ appear at high frequency (2.49−2.67 ppm) in the exo derivatives, whereas one of them is consistently found at lower frequencies (1.80−1.98 ppm) in the endo complexes. Similar observations can be made for the acac complexes **2a**−**f**. Analogously, in their ^{13}C NMR spectra, the signals due to C1 are found at higher frequencies (59.4−67.0 ppm) for the endo complexes compared to their exo counterparts (δ(C) 52.2−53.5). The olefinic carbon signals are also shifted to high frequency in the endo derivatives, and the signals due to C3 and C8 are also noticeably deshielded. Again, parallels are found among the acac derivatives **2a**−**f**. Thus, it appears that there are a number of NMR parameters which may be used together to differentiate between the cyclooctenyl complexes that are formed by endo or exo attack on $[PdCl_2(cod)]$ or related precursors.

Finally, we also observe that for the two endo isomers characterized crystallographically, H8 appears at particularly low frequency in the ^1H NMR spectrum whereas H8′ and H3′ give rise to the highest frequency signals observed for the methylene hydrogens. From the solid-state structures, we find that these last two exhibit the shortest nonbonded distances to palladium (2.81−2.99 Å), and this may be responsible for the deshielding of these hydrogens. In contrast, H8 is directed away from the metal, and this hydrogen apparently exhibits the greatest shielding. In the case of the exo isomer **2b**, however, H8′ and H3′ are not deshielded significantly and the shortest nonbonded distance is 3.15 Å. Again, H8, which is the most shielded hydrogen, is directed away from palladium.

Mechanism of Attack on the Coordinated Double Bond. It is reasonable to expect that when nucleophilic attack occurs directly at one of the double bond carbons, the exo product would be formed, whereas if the nucleophile reacts first at the metal center, the endo complex would be formed upon migratory insertion of the C═C bond (Scheme 1). The oxygen and nitrogen nucleophiles, as well as the malonate anion, therefore, react directly with the coordinated double bond, as has been supposed. It is interesting to note that the exo product is formed in the case of **1l**, either by reaction of $[PdCl_2(cod)]$ with $AgNO_2$ or when $[PdCl(NO_2)(MeCN)_2]$ (containing a metal-bound NO_2 group) is allowed to react with free cyclooctadiene. In the latter case, displacement of NO_2^- by cyclooctadiene must occur, allowing external attack on the coordinated diene.

Scheme 1



When organometallic reagents are employed (Grignards, Ph_4Sn, $(4\text{-}MeC_6H_4)_2Hg$, or C_6F_5Li[12]), substitution of one of the coordinated chlorides occurs first to generate a species of the form [PdClR(cod)]. When R = $C_6H_2Me_3$ or C_6F_5,[12] this species may be isolated, although migratory insertion occurs on standing. With PhMgBr or $4\text{-}MeC_6H_4MgBr$, the organopalladium intermediate may react by migratory insertion but substitution of the second chloride to produce $[PdAr_2(cod)]$ and subsequent reductive elimination of the diaryl is a competing process, even when low Grignard-to-Pd ratios are used. We have not detected the diarylpalladium intermediates in this case, but in the corresponding reactions of $[PdCl_2(dppm)]$ with ArMgX, we have observed $[PdAr_2(dppm)]$ by NMR spectroscopy at low temperatures.[20] With 2-tolylmagnesium chloride, the intermediate $[PdCl(C_6H_4Me\text{-}2)(cod)]$ could not be isolated, but migratory insertion occurred to give the cyclooctenyl derivative in a modest yield. Thus, it appears that the larger aryls, 2-tolyl and mesityl, as well as those containing electron-withdrawing groups (C_6F_5) inhibit attack of a second equivalent of Grignard and allow greater yields of the cyclooctenyl derivatives to be achieved. Organotin or -mercury reagents such as Ph_4Sn or $(4\text{-}MeC_6H_4)_2Hg$, being less reactive, allow the cyclooctenyl complexes to be formed more cleanly. With tetraalkyltin reagents (R = Me, Et, CH_2Ph), however, the [PdClR(cod)] compounds do not undergo migratory insertion.[1−3]

It is curious to find that the reaction of [PdClMe(cod)] with DMAD proceeds cleanly by alkyne insertion, followed by migratory insertion of a C═C bond of cyclooctadiene. Analogous reactions with $HC{\equiv}CCO_2Me$ or $PhC{\equiv}CH$ were slow and gave complex mixtures of products. We have noted previously that [PdClMe(cod)] reacts with CO to generate the corresponding acetyl complex,[1] but despite the tendency of acylpalladium

species to undergo migratory insertion of alkenes,[25] insertion into the Pd−acetyl bond was not observed. [PdCl(COMe)(cod)] does decompose above 0 °C, however, so it may be that the relatively rapid decomposition precludes observation of any insertion. Thus, we find the following relative rates of migratory insertion in complexes of the type [PdClR(cod)]: Ph, 4-MeC_6H_4 > 2-MeC_6H_4 > 2,4,6-$Me_3C_6H_2$ > $C(CO_2Me)$═$C(CO_2Me)$-Me ≫ Me, Et, CH_2Ph (COMe). The decreasing reactivity of the aryl groups is presumably a reflection of their increasing size, whereas the lack of reactivity of the alkyl groups may be due to the strength of the Pd−$C(sp^3)$ bond.

Acknowledgment. Thanks are expressed to the National Science Foundation (Grant Nos. CHE-9508228 and CHE-9530085) for support of this work, to Johnson Matthey Aesar/Alfa for a generous loan of palladium salts, and to the National Science Foundation (Grant Nos. CHE-9318696 and 9309690), the U.S. Department of Energy (Grant No. DE-FG02-92CH10499), and the University of Missouri Research Board for instrumentation grants.

Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, complete bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **2a**, **2b**, and **2e** (16 pages). Ordering information is given on any current masthead page.

OM970836J

(25) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663.