

Insertion of Olefins into Palladium(II)-Acyl Bonds. Mechanistic and Structural Studies

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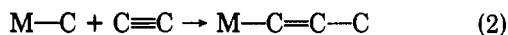
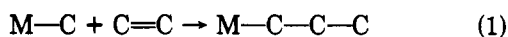
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The reaction of norbornylene with $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})(\text{COR})]\text{BF}_4$ (2) produced $[\text{Pd}(\text{PPh}_3)_2(\text{C}_7\text{H}_{10}\text{COR})](\text{BF}_4)$ (3). The crystal structure of 3a (R = Me) revealed a square-planar coordination around the palladium atom. The two triphenylphosphine ligands occupied cis positions, and the 2-acetylnorborn-1-yl residue acted as a chelating ligand by coordinating through the norbornyl carbon and the carbonyl oxygen. The two palladium-phosphorus distances, 2.238 (2) and 2.434 (2) Å, were dramatically different. Crystallographic data: space group $P2_1/n$; $a = 11.430$ (10), $b = 23.042$ (3), $c = 16.338$ (3) Å; $\beta = 99.90$ (2)°; $V = 4238.7$ Å³; $Z = 4$; $R = 0.0673$, $R_w = 0.0894$. The reaction mechanism, determined by studying the analogous reaction of 2 with norbornadiene, involved insertion from a four-coordinate intermediate formed by olefin displacement of the acetonitrile ligand. The reaction of $\text{Pd}(\text{PPh}_3)_2(\text{Cl})(\text{COR})$ (1) with norbornylene produced $\text{Pd}(\text{PPh}_3)(\text{Cl})(\text{C}_7\text{H}_{10}\text{COR})$ (6). For this reaction a mechanism involving insertion from a four-coordinate intermediate formed by olefin displacement of a triphenylphosphine ligand was consistent with the experimental results. The reaction of 1 with olefin was significantly accelerated in the presence of a "phosphine sponge" (e.g., $\text{Pd}(\text{PhCN})_2\text{Cl}_2$, CH_3I , or S).

Introduction

The insertion of unsaturated hydrocarbons into metal-carbon bonds is a critical step in many catalytic reactions, including the transition-metal-catalyzed oligomerization, polymerization, and alkylation of both olefins and acetylenes.² The insertion of an olefin into a metal-acyl bond also constitutes one of the two propagation steps in the palladium(II)-³ and rhodium(I)-catalyzed⁴ copolymerization of olefins with carbon monoxide. Thus, considering both the academic and industrial significance of these reactions, an investigation into the mechanism of the insertion process is important with regard to both developing new catalytic systems and improving those already established.

From a thermodynamic perspective, the insertion of an olefin (eq 1) or an acetylene (eq 2) into a metal-carbon bond represents a downhill process. When 83, 146, and

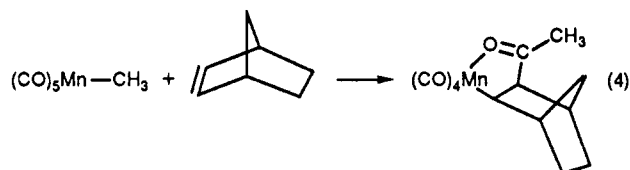
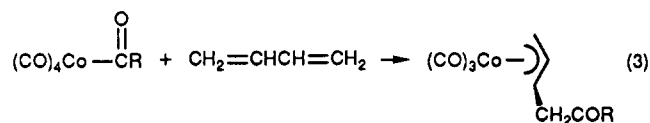


200 kcal/mol are used as the average carbon-carbon single-, double-, and triple-bond energies,⁵ respectively, the enthalpy changes associated with eqs 1 and 2 are -20 and -29 kcal/mol, respectively. It is unlikely that these large favorable enthalpies could be offset by the unfavorable entropic contributions (two particles forming one), except in the case of gaseous olefins at very high temperatures.

Despite the favorable thermodynamics, the direct observation of an olefin or acetylene insertion into a metal-carbon bond has rarely been reported, primarily due to three factors.² First, the inserted complexes decompose to secondary products (e.g., by β -hydride elimination). Second, products derived from multiple insertions are

formed. Third, kinetic barriers prevent the reaction from taking place. It is with regard to this last factor that an understanding of the process is so important.

A few direct observations of insertions in stoichiometric reactions have been reported,⁶ particularly with acetylenes. In addition to unactivated monoolefins and -acetylenes, stable insertion products have also been reported with conjugated dienes.^{6c,7} In the specific case of *intermolecular* olefin insertion into a metal-acyl complex, only one example of a direct insertion to form a stable, nonisomerized, and undecomposed product has been reported. In this reaction, a π -allyl complex was formed from the insertion of butadiene into the metal-acyl bond of a cobalt reagent (eq 3).⁷ In another closely related reaction, Booth,



Gardner, and Haszeldine⁸ and later DeShong et al.^{6a} re-

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Table I. Physical and Spectral Properties^a for Complexes of the General Formula Pd(PR₃)₂(X)(COR')

compd	R	X	R'	% yield ^b	color	IR (ν _{CO}), ^c cm ⁻¹	³¹ P NMR, ^d ppm
1a	Ph	Cl	CH ₃	95	white	1688	18.65
1b	Ph	Cl	Et	97	white	1685	18.76
1o	Ph	Cl	Ph	93	pale yellow	1638	18.83
1o*	<i>p</i> -tolyl	Cl	Ph	94	pale yellow	1665	17.03
1p	Ph	Cl	<i>p</i> -tolyl	96	pale yellow	1643	18.72
						1668	
1q	Ph	I	<i>p</i> -tolyl	83	yellow	1641	18.37
						1671	
1r	Ph	Cl	OEt	96	white	1634	19.11
						1652	

^a Excluding ¹H NMR data. ^b Isolated yield, based on palladium. ^c Nujol. ^d All resonances are singlets in CDCl₃; referenced to 85% H₃PO₄.

Table II. ¹H NMR Spectral Data for Complexes of the General Formula Pd(PR₃)₂(X)(COR')

compd	R	X	R'	¹ H NMR, ^a ppm
1a	Ph	Cl	CH ₃	1.40 (s, 3 H), 7.38 (m, 18 H), 7.72 (m, 12 H)
1b	Ph	Cl	Et	-0.32 (t, <i>J</i> = 7 Hz, 3 H), 1.98 (q, <i>J</i> = 7 Hz, 2 H), 7.41 (m, 18 H), 7.77 (m, 12 H)
1o	Ph	Cl	Ph	7.2-7.7 (m, 35 H)
1o*	<i>p</i> -tolyl	Cl	Ph	2.29 (s, 18 H), 7.0 (m, 15 H), 7.5 (m, 14 H)
1p	Ph	Cl	<i>p</i> -tolyl	2.19 (s, 3 H), 6.76 (d, <i>J</i> = 8 Hz, 2 H), 7.30 (m, 18 H), 7.44 (d, <i>J</i> = 8 Hz, 2 H), 7.67 (m, 12 H)
1q	Ph	I	<i>p</i> -tolyl	2.23 (s, 3 H), 6.82 (d, <i>J</i> = 8 Hz, 2 H), 7.27 (m, 18 H), 7.48 (d, <i>J</i> = 8 Hz, 2 H), 7.65 (m, 12 H)
1r	Ph	Cl	OEt	0.52 (t, <i>J</i> = 7 Hz, 3 H), 2.98 (q, <i>J</i> = 7 Hz, 2 H), 7.34 (m, 18 H), 7.72 (m, 12 H)

^a CDCl₃. Multiplicity abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

ported the insertion of olefins into a manganese-acyl intermediate, which was formed in situ via carbon monoxide insertion into the manganese-alkyl reactant (eq 4). In addition to these reports, Samsel and Norton have examined in detail the *intramolecular* insertion of both olefins and acetylenes into Pd-acyl bonds.^{6b}

Our interest in the process by which olefins insert into metal-acyl complexes stems from its role as one of the propagation steps in the rhodium-⁴ and, especially, palladium-catalyzed³ olefin-carbon monoxide copolymerization reaction. By using a rational model of the palladium-acyl copolymerization intermediate and by employing olefins already demonstrated to undergo copolymerization with carbon monoxide, we were able to successfully observe the insertion reaction. Because the products resulting from the insertion of norbornylene and norbornadiene do not contain β-hydrogens that are accessible to the metal center, subsequent decomposition of the inserted product does not take place. Furthermore, presumably because of the formation of a stable five-membered cyclic ring, multiple insertions are not observed. Presented herein are the results of our investigation of this and related reactions. These studies also led to a better understanding of why cationic palladium compounds were efficient catalysts for the copolymerization reaction while their neutral analogues were inactive under the same conditions.

Experimental Procedure

A. General Considerations. All reactions were conducted in a glovebox, where all reagents were stored. All solvents, including NMR solvents, were dried over calcium hydride, except for benzene, which was dried over sodium benzophenone ketyl. Once dry and deoxygenated, the solvents were stored in brown bottles in the glovebox.

All olefins and acetylenes, including norbornylene and norbornadiene, were used as received without purification. Ethylene (Matheson-CP Grade) was used directly from the cylinder. The acid chlorides used in the synthesis of starting materials were distilled prior to use. Silver tetrafluoroborate was used as received.

Routine ¹H NMR spectra were recorded in CDCl₃ or CD₃CN on Varian EM-360 (60 MHz), Bruker WP-200 (200 MHz), or Bruker WM-360 (360 MHz) spectrometers. ¹³C NMR spectra were

recorded on the Bruker WP-200 spectrometer. For both nuclei, chemical shifts are reported as δ values relative to tetramethylsilane at 0.00 ppm. ³¹P NMR spectra were run on a Varian CFT-20 (32.2 MHz for phosphorus) spectrometer. ³¹P chemical shifts are reported as δ values relative to 85% H₃PO₄ at 0.00 ppm, with resonances downfield from H₃PO₄ being taken as positive. Infrared spectra were recorded on a Perkin-Elmer Model 580 grating spectrometer as Nujol mulls. Gas chromatography was carried out with a Varian 3700 gas chromatograph, equipped with a flame ionization detector. A 10 ft × 1/8 in. stainless steel column having a 10% SP-2100 packing on 80/100 Supelcoport was employed. Peak areas were determined by the method of cutting and weighing. Gas chromatograph-mass spectrometry was performed on a system composed of a Finnigan 9500 gas chromatograph, a Finnigan 3200 mass spectrometer, and a Finnigan 6000 mass spectral data system. Impact energy was imparted at 70 eV. In the case of chemical ionization, methane was used as reagent gas. Minimum detection limits were 35 and 60 amu for electron impact and chemical ionization, respectively.

B. Preparation of Palladium Complexes. All the palladium complexes used in this investigation were ultimately synthesized from PdCl₂, which was used as received from Johnson-Matthey, Inc. Pd(PPh₃)₄ and Pd[P(*p*-tolyl)₃]₄ were prepared via hydrazine reduction of PdCl₂, as described by Coulson.⁹

Complexes of the general formulas Pd(PPh₃)₂(Cl)(COR) and Pd[P(*p*-tolyl)₃]₂(Cl)(COR) were prepared via the well-known oxidative addition of carboxylic acid chlorides to Ph(PPh₃)₄ and Pd[P(*p*-tolyl)₃]₄, respectively, as reported in the literature.¹⁰ Pd(PPh₃)₂(I)(COR), where R = *p*-tolyl, was prepared by insertion of carbon monoxide¹¹ into Pd(PPh₃)₂(I)(*p*-tolyl), which was synthesized from Pd(PPh₃)₄ and *p*-tolyl iodide.¹² Percentage yields, as well as ³¹P NMR and IR spectral data, are presented for these complexes in Table I, while ¹H NMR spectral data are presented in Table II.

Metathesis of the corresponding neutral complexes with AgBF₄ in the presence of acetonitrile generated the cationic complexes [Pd(PPh₃)₂(CH₃CN)(COR)](BF₄) and [Pd[P(*p*-tolyl)₃]₂(CH₃CN)(COR)](BF₄) in high yields. Typically, 1.0 g of Pd(PPh₃)₂(Cl)(COR) was dissolved in a minimum volume (~20 mL) of a 10:1 (v/v) solution of CH₂Cl₂ and CH₃CN. To the rapidly stirred solution was added dropwise exactly 1 equiv of AgBF₄

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Table III. Physical and Spectral Properties^a for Complexes of the General Formula [Pd(PR₃)₂(CH₃CN)(COR)](BF₄)

compd	R	R'	% yield ^b	color	IR (ν _{CO}), ^c cm ⁻¹	IR (ν _{CN}), ^c cm ⁻¹	³¹ P NMR, ^d ppm
2a	Ph	Me	95	white	1693	2243 2272	19.43
2b	Ph	Et	97	white	1689	2245 2272	19.80
2o	Ph	Ph	93	white	1660	2240 2267	19.98
2o*	<i>p</i> -tolyl	Ph	88	pale yellow	1658	2242 2265	18.30
2p	Ph	<i>p</i> -tolyl	85	pale yellow	1653 1676	2248 2272	19.85
2r	Ph	OEt	92	white	1640 1667	2258 2282	19.16

^a Excluding ¹H NMR data. ^b Isolated yield, based on palladium. ^c Nujol. ^d All resonances are singlets in CDCl₃; referenced to 85% H₃PO₄.

Table IV. ¹H NMR Spectral Data for Complexes of the General Formula [Pd(PR₃)₂(CH₃CN)(COR)](BF₄)

compd	R	R'	¹ H NMR, ^a ppm
2a	Ph	Me	1.42 (bs, 3 H), 1.50 (t, ³ J _{P-H} = 1.6 Hz, 3 H), 7.56 (m, 30 H)
2b	Ph	Et	0.10 (t, <i>J</i> = 7 Hz, 3 H), 1.50 (bs, 3 H), 2.05 (q, <i>J</i> = 7 Hz, 2 H), 7.55 (m, 30 H)
2o	Ph	Ph	1.52 (s, 3 H), 7.04 (t, <i>J</i> = 7 Hz, 2 H), 7.18 (d, <i>J</i> = 7 Hz, 1 H), 7.40 (m, 32 H)
2o*	<i>p</i> -tolyl	Ph	1.54 (s, 3 H), 2.33 (s, 18 H), 7.01 (t, <i>J</i> = 7 Hz, 2 H), 7.15 (d, <i>J</i> = 8 Hz, 13 H), 7.33 (m, 12 H), 7.46 (d, <i>J</i> = 7 Hz, 2 H)
2r	Ph	OEt	3.33 (t, <i>J</i> = 7 Hz, 3 H), 1.45 (bs, 3 H), 2.83 (q, <i>J</i> = 7 Hz, 2 H), 7.46 (m, 30 H)

^a CDCl₃; referenced to TMS. Multiplicity abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad singlet.

dissolved in 1–2 mL of CH₃CN. The resulting heterogeneous solution was then filtered, yielding a white precipitate (AgCl) and a pale yellow filtrate. The filtrate was immediately added dropwise to a rapidly stirred diethyl ether solution at 0 °C, instantaneously precipitating the cationic complex as a white or off-white solid, which was isolated by filtration. The product was then successively washed with ether and pentane, after which it was dried under vacuum. Percentage yields, as well as ³¹P NMR and IR spectral data, are presented for these complexes in Table III, while ¹H NMR data are presented in Table IV.

Pd(PHCN)₂Cl₂ was prepared from PdCl₂ according to the method of Kharasch.¹³ Addition of 2.2 equiv of PPh₃ to this complex generated Pd(PPh₃)₂Cl₂ as yellow crystals, which were isolated in 95% yield by filtration.

C. Reaction of [Pd(PPh₃)₂(CH₃CN)(COR)](BF₄) with Olefins. 1. [Pd(PPh₃)₂(CH₃CN)(COMe)](BF₄) + Norbornylene. Norbornylene (0.50 g, 5.3 mmol) was added to a stirred solution of 2a (1.00 g, 1.25 mmol) in 20 mL of CH₂Cl₂. After 6 h the initially homogeneous pale yellow solution had not changed in physical appearance. At this time the solution was triturated with 100 mL of diethyl ether, after which the resulting heterogeneous solution was filtered. A white solid was collected on the frit and was successively washed with ether and pentane. Finally, the product, 3a, was dried overnight under vacuum; yield 1.00 g (94%). ¹H NMR (CDCl₃): δ -0.06 (m, 1 H), 0.89 (m, 1 H), 1.15 (m, 1 H), 1.26 (d, *J* = 9.9 Hz, 1 H), 1.42 (m, 1 H), 1.76 (d, *J* = 9.9 Hz, 1 H), 2.02 (m, 1 H), 2.20 (m, 1 H), 2.25 (s, 3 H), 2.49 (m, 1 H), 3.22 (m, 1 H), 7.01–7.61 (m, 30 H). ³¹P{¹H} NMR (CDCl₃): δ 15.3 (d, *J* = 42.6 Hz, 1 P), 39.7 (d, *J* = 42.6 Hz, 1 P). ¹³C{¹H} NMR (CDCl₃): δ 26.9 (s, 1 C), 28.2 (s, 1 C), 30.2 (t, *J* = 9.3 Hz, 1 C), 36.3 (s, 1 C), 43.3 (s, 1 C), 43.7 (s, 1 C), 65.6 (dd, *J* = 79.3, 5.4 Hz, 1 C), 72.1 (d, *J* = 5.1 Hz, 1 C), 128.3–134.2 (phenyl carbons), 238.9 (d, *J* = 16.8 Hz, 1 C). IR (Nujol): ν_{CO} = 1620 cm⁻¹. Anal. Calcd for C₄₅H₄₃OP₂BF₄Pd: C, 63.22; H, 5.07. Found: C, 62.03; H, 5.42.

2. [Pd(PPh₃)₂(CH₃CN)(COMe)](BF₄) + Norbornadiene. The reaction was carried out exactly as described for norbornylene

above, except that 0.60 mL (5.6 mmol) of norbornadiene was substituted for norbornylene. A white solid, 4a, was isolated in 96% yield (1.02 g). ¹H NMR (CDCl₃): δ 1.39 (d, *J* = 8.9 Hz, 1 H), 1.66 (d, *J* = 8.9 Hz, 1 H), 1.73 (m, 1 H), 2.36 (s, 3 H), 2.54 (m, 1 H), 2.97 (dd, *J* = 5.2, 4.1 Hz, 1 H), 3.11 (bs, 1 H), 4.99 (dd, *J* = 5.3, 3.0 Hz, 1 H), 5.84 (dd, *J* = 5.3, 2.9 Hz, 1 H), 7.06–7.61 (m, 30 H). ³¹P{¹H} NMR (CDCl₃): δ 16.0 (d, *J* = 41.9 Hz, 1 P), 40.1 (d, *J* = 41.9 Hz, 1 P). ¹³C{¹H} NMR (CDCl₃): δ 27.1 (s, 1 C), 44.7 (s, 1 C), 47.9 (s, 1 C), 49.0 (s, 1 C), 58.7 (dd, *J* = 78.5, 3.0 Hz, 1 C), 64.2 (s, 1 C), 128.2–134.3 (phenyl carbons), 132.9 (s, 1 C), 136.9 (t, *J* = 7.2 Hz, 1 C), 237.3 (d, *J* = 12.9 Hz, 1 C). IR (Nujol): ν_{CO} = 1620 cm⁻¹. Anal. Calcd for C₄₅H₄₁OP₂BF₄Pd: C, 63.36; H, 4.85. Found: C, 61.65; H, 4.99.

3. [Pd(PPh₃)₂(CH₃CN)(COMe)](BF₄) + Dicyclopentadiene. The reaction was carried out exactly as described above for norbornylene, except that 0.50 mL (3.5 mmol) of dicyclopentadiene was substituted for norbornylene; 0.94 g (90%) of a pale yellow solid was isolated. Due to a poor signal-to-noise ratio and an overwhelming number of resonances, the ¹H NMR and ¹³C NMR spectra were uninterpretable. ³¹P{¹H} NMR (CDCl₃): δ 15.60 (d, *J* = 42.8 Hz, 0.7 P), 15.90 (d, *J* = 43.7 Hz, 1 P), 39.43 (d, *J* = 43.7 Hz, 1 P), 39.95 (d, *J* = 42.8 Hz, 0.7 P). IR (Nujol): ν_{CO} = 1620 cm⁻¹. Anal. Calcd for C₄₈H₄₆OP₂BF₄Pd: C, 64.55; H, 5.08. Found: C, 63.70; H, 5.19.

4. [Pd(PPh₃)₂(CH₃CN)[CO(*p*-tolyl)]](BF₄) + Ethylene. To a 25-mL round-bottom flask equipped with a side arm and stopcock were added 0.280 g of 2p and 5 mL of CH₂Cl₂. The resulting homogeneous yellow solution was frozen under liquid nitrogen and placed under vacuum. One atmosphere of ethylene was added to the system through the side arm, after which the mixture was warmed to room temperature. Occasionally, the system was quickly vented via the stopcock to prevent an explosion from the warming gas. After it was stirred for 1 day at room temperature, the solution remained homogeneous but had become dark red. A volatile portion was then collected by distillation at reduced pressure (0.01 mmHg) and room temperature. The organic products were extracted from the nonvolatile layer by addition of diethyl ether, followed by filtration. The reaction products, which were not quantified, were determined to be ethyl vinyl ketone and tolyl vinyl ketone on the basis of mass spectral molecular weight measurements. GC-MS (CI, methane, in amu): ethyl vinyl ketone, 84 (M), 85 (P, M + 1), 113 (M + 29), 125 (M + 41); *p*-tolyl vinyl ketone, 91 (M - 55), 119 (M - 27), 146 (M), 147 (P, M + 1), 175 (M + 29), 187 (M + 41).

5. [Pd(PPh₃)₂(CH₃CN)(COMe)](BF₄) + Cyclopentene. Cyclopentene (0.275 mL, 3.12 mmol) was added to a solution of 2a (0.250 g, 0.312 mmol) in 2 mL of CH₂Cl₂. The initially homogeneous yellow solution remained homogeneous after 24 h at room temperature but had become dark red. Diethyl ether (20 mL) was then added dropwise, and the resulting heterogeneous solution was filtered. The organic products in the filtrate were determined by GC-MS to be methyl cyclopentenyl ketone and cyclopentyl cyclopentenyl ketone, in a ratio of approximately 1:3. GC-MS (CI, methane, in amu): methyl cyclopentenyl ketone, 95 (M - 15), 110 (M), 111 (P, M + 1), 139 (M + 29); cyclopentyl cyclopentenyl ketone, 67 (M - 97), 69 (M - 95), 95 (M - 69), 97 (M - 67), 164 (M), 165 (P, M + 1), 193 (M + 29).

D. Reaction of Pd(PPh₃)₂(Cl)(COMe) with Olefins. 1. Norbornylene. Norbornylene (1.33 g, 14.1 mmol) was added to

(13) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* 1938, 60, 882.

a stirred solution of **1a** (1.00 g, 1.41 mmol) in 25 mL of CH_2Cl_2 . After 8 h the homogeneous pale yellow solution did not change in physical appearance and was thus triturated with 100 mL of pentane. The resulting heterogeneous solution was filtered, and the white precipitate, **6a**, was successively washed with diethyl ether and pentane before being dried overnight under vacuum; yield 0.72 g (94%). ^1H NMR (CDCl_3): δ -0.02 (m, 1 H), 0.81 (m, 1 H), 1.01 (m, 1 H), 1.07 (d, $J = 11$ Hz, 1 H), 1.38 (m, 1 H), 1.73 (m, 2 H), 1.88 (d, $J = 10.1$ Hz, 1 H), 2.39 (m, 1 H), 2.69 (d, $J = 6.6$ Hz, 1 H), 7.27–7.46 (m, 9 H), 7.70–7.85 (m, 6 H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 37.8 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 26.8 (s, 1 C), 28.8 (s, 1 C), 29.9 (d, $J = 6.8$ Hz, 1 C), 36.0 (s, 1 C), 43.1 (s, 1 C), 43.3 (s, 1 C), 54.5 (d, $J = 2.5$ Hz, 1 C), 72.0 (s, 1 C), 128.0–135.1 (phenyl carbons), 233.4 (s, 1 C). IR (Nujol): $\nu_{\text{CO}} = 1628$ cm^{-1} .

2. Norbornadiene. The reaction was carried out exactly as described above for norbornylene, except that 1.50 mL (13.9 mmol) of norbornadiene was substituted for norbornylene. A white solid, **7a**, was isolated in 93% yield (0.71 g). ^1H NMR (CDCl_3): δ 1.21 (d, $J = 8.9$ Hz, 1 H), 1.34 (ddd, $J_{\text{P-H}} = 8.4$ Hz, $J_{\text{H-H}} = 6.2$ Hz, $J_{\text{H-H}} = 2.4$ Hz, 1 H), 1.77 (d, $J = 9.0$ Hz, 1 H), 2.24 (bs, 1 H), 2.42 (s, 3 H), 2.47 (d, $J = 6.2$ Hz, 1 H), 2.98 (bs, 1 H), 5.05 (dd, $J = 5.3$, 3.0 Hz, 1 H), 5.76 (dd, $J = 5.4$, 2.9 Hz, 1 H), 7.27–7.47 (m, 9 H), 7.78–7.85 (m, 6 H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 37.9 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 26.9 (d, $J = 1$ Hz, 1 C), 44.8 (s, 1 C), 47.8 (s, 1 C), 48.4 (s, 1 C), 48.5 (s, 1 C), 64.3 (s, 1 C), 128.1–135.0 (phenyl carbons), 132.0 (s, 1 C), 137.6 (d, $J = 5.5$ Hz, 1 C), 232.0 (s, 1 C). IR (Nujol): $\nu_{\text{CO}} = 1627$ cm^{-1} .

E. Kinetics. Unless stated otherwise, all reactions were monitored by ^{31}P NMR spectroscopy under pseudo-first-order conditions. When the data were fit to a straight line, a linear regression from a least-squares analysis was performed.

1. $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})(\text{COPh})](\text{BF}_4) + \text{Norbornadiene}$. All reactions were monitored by observing the disappearance of **2o**.

a. Reaction Order in Palladium–Acyl Complex. Norbornadiene (0.200 mL) was syringed into 1.30 mL of a solution containing **2o** (0.0863 g), acetonitrile (0.010 mL), and chloroform, thus making the initial concentrations of **2o**, olefin, and acetonitrile equal to 0.0667, 1.24, and 0.125 M, respectively. The resulting homogeneous yellow solution was immediately placed into the probe of the spectrometer (temperature 29 (± 1) $^\circ\text{C}$), at which time data collection was initiated.

b. Olefin Dependence. Solutions (total volume 1.50 mL) of **2o** (0.0821 g, 0.0634 M), acetonitrile (0.032 mL, 0.40 M), and the appropriate concentrations of norbornadiene were prepared in CDCl_3 . The resulting homogeneous yellow solutions were immediately placed into the probe of the spectrometer, which was maintained at 28 (± 1) $^\circ\text{C}$. Data points were then taken at intervals determined by the reaction rates.

The olefin dependence was also determined in a 5.0 M acetonitrile solution by using **2o** (initially 0.0667 M) and in a 0.50 M acetonitrile solution by using **2p** (also initially 0.0667 M).

c. Acetonitrile Dependence. Solutions (total volume 1.50 mL) of **2o** (0.0863 g, 0.0667 M), norbornadiene (0.200 mL, 1.24 M), and the appropriate concentrations of acetonitrile were prepared in CDCl_3 . The resulting homogeneous yellow solutions were immediately placed into the spectrometer probe, which was maintained at 29 (± 1) $^\circ\text{C}$. Data points were taken at intervals determined by the reaction rates.

d. Phosphine Dependence. Solutions (total volume 1.50 mL) of **2o** (0.0800 g, 0.062 M), norbornadiene (0.100 mL, 0.62 M), and the appropriate weight of triphenylphosphine were prepared in CDCl_3 . Data points were taken every 10 or 15 min through at least 2 half-lives. The reaction temperature was maintained at 14 (± 1) $^\circ\text{C}$ by cooling the probe with ice water.

2. $\text{Pd}(\text{PPh}_3)_2(\text{Cl})[\text{CO}(p\text{-tolyl})] + \text{Norbornadiene}$. All reactions were monitored by observing the disappearance of **1p**.

a. No Additives. A solution (total volume 1.50 mL) of **1p** (0.100 g, 0.0849 M) and norbornadiene (0.150 mL, 0.927 M) in CDCl_3 was prepared. The reaction was initiated when the olefin was added via syringe. The temperature was maintained at 25 (± 1) $^\circ\text{C}$ in the NMR probe. Data points were initially collected every 1 h, but after 8 h, they were taken at much larger intervals, typically 8–24 h. The initially homogeneous pale yellow solution did not change in physical appearance, but after 5 days $\text{Ph}_3\text{P}=\text{O}$, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and other decomposition products were observed

spectroscopically.¹⁴ At this time data collection was terminated.

b. Presence of Sulfur. A solution exactly as described above was prepared, except that sulfur (0.040 g, 0.83 M) was also present. Again, the reaction was initiated by addition of olefin. The temperature was maintained at 25 (± 1) $^\circ\text{C}$ in the NMR probe. Only two data points were collected. After the second, which was complete after 20 min, only the inserted product and $\text{Ph}_3\text{P}=\text{S}^{14}$ were present in equal molar quantities.

c. Presence of $\text{Pd}(\text{PhCN})_2\text{Cl}_2$. A solution exactly as described above for the reaction with no additives was prepared, except that $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ (0.024 g, 0.042 M) was also present. Before the reaction was initiated by adding the olefin, the solution was heterogeneous and yellow-orange, due to the formation of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and, presumably, the chloro-bridged acyl dimer $[\text{Pd}(\text{PPh}_3)(\mu\text{-Cl})[\text{CO}(p\text{-tolyl})]]_2$. The reaction reached completion within 5 min of olefin addition.

d. Presence of Methyl Iodide. A solution exactly as described above for the reaction containing no additives was prepared, except that methyl iodide (0.050 mL, 0.54 M) was also present. Concomitant with the expected formation of **7p** was the formation of both **1q** and **7q**. The reaction reached completion after about 2 h, when only **7p** and **7q**, in addition to $(\text{Ph}_3\text{P}-\text{CH}_3)\text{I}$ and, presumably,¹⁵ $(\text{Ph}_3\text{P}-\text{CH}_3)\text{Cl}$, were observed in solution.

3. $\text{Pd}(\text{PPh}_3)_2(\text{I})[\text{CO}(p\text{-tolyl})] + \text{Norbornadiene}$. Since these reactions were very rapid at room temperature, it was not possible to collect a sufficient number of data points in order to make quantitative rate calculations. Therefore, the kinetics were studied in a crude and qualitative manner.

a. Absence of Methyl Iodide. A solution (total volume 1.50 mL) of **1q** (0.040 g, 0.030 M) and norbornadiene (0.100 mL, 0.62 M) in CDCl_3 was prepared. The reaction was initiated via introduction of the olefin and had reached completion after approximately 2 h. The temperature was maintained at 26 (± 1) $^\circ\text{C}$ in the NMR probe.

b. Presence of Methyl Iodide. A solution was prepared exactly as described above, except that 0.025 mL (0.27 M) of methyl iodide was also added. This reaction was complete after approximately 75 min. Another solution identical with that above, except containing 0.050 mL (0.54 M) methyl iodide, was observed to be completely reacted after 45 min.

F. Phosphine Exchange Reactions. 1. $\text{Pd}(\text{PPh}_3)_2(\text{Cl})(\text{COPh}) + \text{Pd}[\text{P}(p\text{-tolyl})_3]_2(\text{Cl})(\text{COPh})$. **1o** (0.050 g, 0.065 mmol) in 1.30 mL of CDCl_3 was added to **1o*** (0.056 g, 0.065 mmol) in 1.30 mL of CDCl_3 , forming a homogeneous yellow solution. A ^{31}P NMR spectrum was then run within 5 min, showing, in addition to the starting materials, resonances at 17.91 and 17.96 ppm, which were assigned to the new complex $\text{Pd}(\text{PPh}_3)[\text{P}(p\text{-tolyl})_3]_2(\text{Cl})(\text{COPh})$.

2. $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})(\text{COPh})](\text{BF}_4) + [\text{Pd}[\text{P}(p\text{-tolyl})_3]_2(\text{CH}_3\text{CN})(\text{COPh})](\text{BF}_4)$. **2o** (0.053 g, 0.061 mmol) in 1.30 mL of CDCl_3 was added to **2o*** (0.058 g, 0.061 mmol) in 1.30 mL of CDCl_3 , forming a homogeneous yellow solution. A ^{31}P NMR spectrum was then run within 5 min, showing in addition to starting materials resonances at 19.10 and 19.18 ppm that were assigned to the new complex $[\text{Pd}(\text{PPh}_3)[\text{P}(p\text{-tolyl})_3]_2(\text{CH}_3\text{CN})(\text{COPh})](\text{BF}_4)$.

G. Halide Exchange Reactions. 1. $\text{Pd}(\text{PPh}_3)_2(\text{Cl})[\text{CO}(p\text{-tolyl})] + (\text{Ph}_3\text{P}-\text{CH}_3)\text{I}$. **1p** (0.050 g, 0.065 mmol) and $(\text{Ph}_3\text{P}-\text{CH}_3)\text{I}$ (0.026 g, 0.065 mmol) were dissolved in 1.40 mL of CDCl_3 , forming a homogeneous yellow solution. A ^{31}P NMR spectrum collected within 10 min indicated the presence of $\text{Pd}(\text{PPh}_3)_2(\text{I})[\text{CO}(p\text{-tolyl})]$, in addition to the starting materials. The ratio of **1p** to its iodo analogue, **1q**, was crudely determined to be 2:1 by integration and did not change, even after 24 h. No new resonance was observed for $(\text{Ph}_3\text{P}-\text{CH}_3)\text{Cl}$, since the ^{31}P NMR chemical shift of the phosphonium salt is independent of its halide counterion.¹⁵

2. $\text{Pd}(\text{PPh}_3)_2(\text{Cl})(\text{COPh}) + \text{Pd}(\text{PPh}_3)_2(\text{I})[\text{CO}(p\text{-tolyl})]$. **1o** (0.025 g, 0.032 mmol) and **1q** (0.028 g, 0.032 mmol) were dissolved in 1.50 mL of CDCl_3 , forming a homogeneous pale yellow solution. After 24 h, both the physical appearance and ^{31}P NMR spectrum

(14) ^{31}P NMR (CDCl_3): Ph_3PO , 29.0; $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 23.2; Ph_3PS , 43.4 ppm.

(15) These are indistinguishable by ^{31}P NMR spectroscopy.

Table V. Crystal Data and Data Collection Summary

compd	3a·0.5Et ₂ O
formula	C ₄₅ H ₄₃ OP ₂ PdBF ₄ ·0.5C ₄ H ₁₀ O
formula weight	892.05
space group	P2 ₁ /n
cryst syst	monoclinic
a, Å	11.430 (10)
b, Å	23.042 (3)
c, Å	16.338 (3)
β, deg	99.90 (2)
V, Å ³	4238.7
Z	4
density (calcd), g cm ⁻³	1.398
F(000)	1836
temp, K	293
radiation	Mo Kα
μ, cm ⁻¹	5.57
λ, Å	0.71073
2θ range, deg	3–43
scan methods	ω/2θ
ω-scan width, deg	1.40 + 0.35 tan θ
cryst decay, %	2.1
empirical abs corr factors: min, max	0.8825, 0.9993
no. of unique data measd	4007
no. of data used [I > 3σ(I)]	3044
data:param ratio	6.9
R	0.0673
R _w	0.0894
(Δ/σ) _{max} in last cycle	0.09
Δρ in final ΔF map, e Å ⁻³	0.9 (H's)
final ρ param in weighting scheme	0.060
error in weights	2.12

of the solution were identical with those observed initially.

H. IR and ¹H NMR Spectral Investigations of [Pd-(PPh₃)₂(CH₃CN)(COR)](BF₄) in the Presence of Added Acetonitrile. 1. **IR Spectroscopy.** A solution 0.0667 M in [Pd(PPh₃)₂(CH₃CN)(COPh)](BF₄) was prepared by dissolving 0.1439 g of 2o in 2.50 mL of CHCl₃. The resulting solution was divided into five equal portions of 0.50 mL each. Acetonitrile concentrations were then made equal to 0.0, 0.10, 0.20, 0.50, and 1.00 M by addition of 0, 2.6, 5.2, 13, and 26 μL of acetonitrile, respectively.

By use of a CHCl₃ reference cell, an infrared spectrum was run for each solution in the region 2000–2500 cm⁻¹. The infrared spectrum of a sixth solution, containing 5.2 μL of acetonitrile in 0.50 mL of CHCl₃, was also taken in this region.

2. **Proton NMR Spectroscopy.** A 0.0123-g sample of [Pd-(PPh₃)₂(CH₃CN)(COMe)](BF₄) was dissolved into 1.20 mL of CDCl₃, and the resulting solution was divided into two equal portions, which were immediately placed into 7-mm ¹H NMR tubes. Into one portion were successively added 1.0, 1.0, 3.0, and 28 μL of acetonitrile, corresponding to 0.3, 0.6, 1.5, and 10 total equiv (relative to palladium), respectively. ¹H NMR spectra were run before and after each addition of acetonitrile, from which the chemical shifts of the CH₃CN resonance were determined. The process was repeated for the second portion by successively adding 3.3, 3.3, and 60 μL of acetonitrile, corresponding in this case to 1.0, 2.0, and 20 total equiv, respectively.

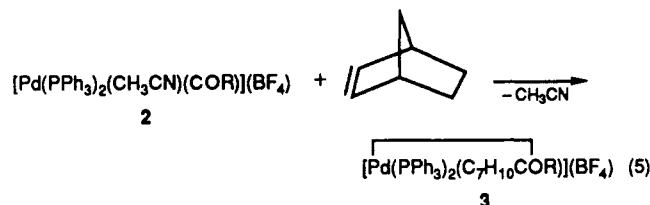
I. X-ray Crystallography. Crystals suitable for X-ray diffraction were prepared at -15 °C by slow diffusion of diethyl ether into a saturated solution of 3a in CH₂Cl₂. Data were collected with an Enraf-Nonius CAD4 diffractometer. Crystal data and a summary of the data collection are presented in Table V.

Accurate cell dimensions and a crystal orientation matrix were determined by a least-squares refinement of the setting angles of 25 reflections with θ in the range 10–15°. Intensity data were collected by the ω/2θ scan method with use of monochromatized radiation in the range 3 < 2θ < 43°. The intensities of three reflections, chosen as standards, were monitored at regular intervals and decreased by 2.1% over the course of the data collection; this decay was corrected for by appropriate scaling. Intensities of 4007 unique reflections were measured, of which 3044 had I > 3σ(I), and were used in the structure solution and refinement. Data were corrected for Lorentz and polarization factors and for empirical absorption (minimum and maximum correction factors are 0.8825 and 0.9993, respectively).

The structure was solved by the heavy-atom method.¹⁶ Refinement of the structure was by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic temperature factors for the non-hydrogen atoms of the cationic palladium complex; the tetrafluoroborate anion and the solvent molecule were refined isotropically. Refinement converged with R = 0.067 and R_w = (ΣwΔ²/ΣF²)^{1/2} = 0.089. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Mann,¹⁷ and allowance was made for anomalous dispersion.¹⁸ A difference map calculated at the conclusion of refinement had peaks corresponding to most of the hydrogen atoms, but these were not included in the refinement.

Results

A. Stoichiometric Insertion Reactions and Characterization of Products. The reaction of 2 with excess norbornylene at room temperature generated 3 in quantitative yield after 2 h (eq 5). As a solid, 3 was stable for



at least 1 year, even in air. However, when R was electron-withdrawing (phenyl, *p*-nitrophenyl), 3 decomposed to unidentified products in chloroform after less than 1 day. With electron-donating R groups (methyl, ethyl, etc.), 3 was stable in chloroform for several days.

The ³¹P NMR spectrum of 3a (R = Me) consists of a pair of doublets centered at 15.3 and 39.7 ppm (²J_{P-P} = 42.6 Hz), indicating the presence of nonequivalent *cis* phosphine ligands. The infrared spectrum contains stretches at both 1620 cm⁻¹ (ν_{CO}) and 1010–1075 cm⁻¹ (ν_{BF}), while no absorbances are present between 2000 and 2500 cm⁻¹ (ν_{CN}). Thus, tetrafluoroborate remains in the product as a counteranion, while acetonitrile is no longer present. The unusually low carbonyl stretching frequency is consistent with coordination of the carbonyl oxygen to the metal center.

Therefore, it is apparent from the ³¹P NMR and IR spectra that norbornylene inserted into the palladium-acyl bond of 2a, forming a product with *cis* triphenylphosphine ligands and a carbonyl oxygen coordinated to the metal. Because acetonitrile is no longer present, it can be further concluded that the remaining ligands adopt a square-planar geometry about the d⁸ palladium(II) atom. However, the stereochemistry of the now-substituted norbornane unit remained uncertain, as three possible structures (i–iii) can be envisioned.

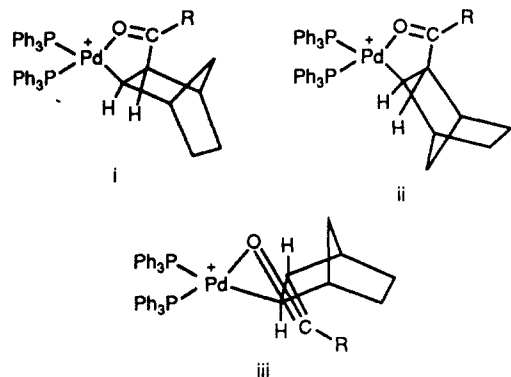
These isomers can in principle be distinguished by using the magnitudes of the coupling constants between the two labeled hydrogens. Values of 6–7, 9–10, and 2.5–5 Hz are predicted for i, ii, and iii, respectively.¹⁹ Unfortunately, due to extensive long-range coupling, the aliphatic resonances in the ¹H NMR (360 MHz) spectrum of 3a are too broad and complex to be of any diagnostic value. This problem persists even after selective decoupling. There-

(16) All computer programs were part of the Enraf-Nonius Structure Determination Package: SDP Plus, Version 1.0; Enraf-Nonius: Delft, Holland, 1982.

(17) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* 1968, A24, 321.

(18) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* 1970, 53, 1891.

(19) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; p 274.



fore, ^1H NMR spectroscopy cannot distinguish between the three possibilities.

Fortunately, **3a** is easily crystallized, allowing for an X-ray structural determination. The crystal structure consists of discrete molecules of the cationic palladium species and disordered molecules of anionic tetrafluoroborate and diethyl ether solvent. The inner coordination sphere of the molecule, including the entire chelating 2-acetylnorborn-1-yl ligand, is shown in Figure 1. Selected bond distances and bond angles are given in Tables VI and VII, respectively.

The coordination around the palladium atom is square-planar, with the two triphenylphosphine ligands occupying cis positions and the 2-acetylnorborn-1-yl residue acting as a chelating ligand by complexing through the norbornyl carbon and the carbonyl oxygen. There exists a small but significant tetragonal distortion of the square plane, as evidenced by (1) the mean (0.073 Å) and maximum (0.100 Å) deviations of atoms from the best plane and (2) the P(1)–Pd–C(1) and P(2)–Pd–C(1) bond angles of 170.6 (2) and 171.2 (2)°, respectively. The primary cause of this distortion is probably relief of steric congestion associated with the bulky cis triphenylphosphine ligands. Similar distortions have been observed in other square-planar complexes containing bulky and/or chelating ligands.²⁰

The Pd–C(1) bond distance (2.103 (8) Å) is typical of other Pd–C(sp³) bonds (sum of the covalent radii equals 2.05 Å²¹). The Pd–O(1) bond distance (2.114 (6) Å) is also normal (sum of the covalent radii equals 1.94 Å²¹). The two palladium–phosphorus bond distances are very unique, however. Pd–P(1) is 2.238 (2) Å, while Pd–P(2) is 2.434 (2) Å—a difference of 0.196 Å or 98 σ! Typical bond lengths range from 2.23 to 2.35 Å²² and rarely exceed the sum of the covalent radii (2.38 Å²¹). Thus, Pd–P(1) represents one of the shortest palladium–phosphorus bonds known. Moreover, to the best of our knowledge, Pd–P(2) constitutes the longest palladium–phosphorus bond ever observed.

The C(8)–O(1) bond distance (1.240 (10) Å) is slightly longer than the average carbon–oxygen double bond (1.23 Å²³) but does not even remotely resemble a single bond (1.43 Å²³). Although the corresponding carbonyl stretch in the infrared spectrum (1620 cm⁻¹) suggests more single-bond character than does the crystallographic bond

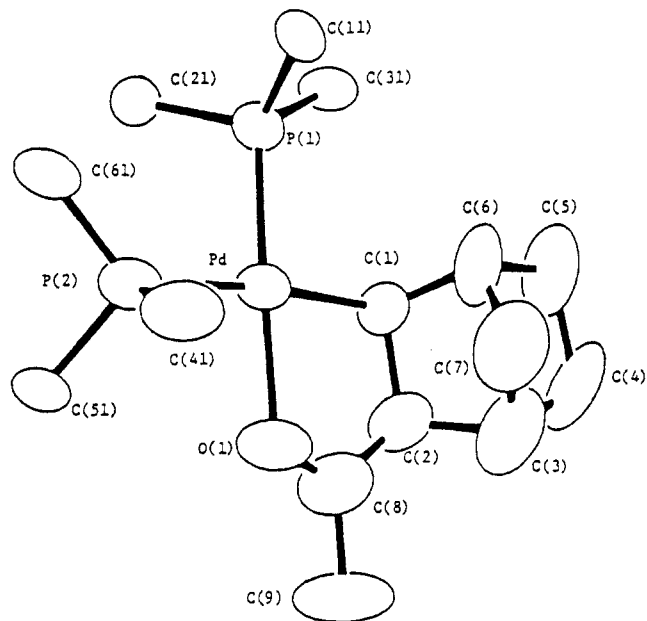


Figure 1. View of the inner coordination sphere of **3a**, including the entire chelating 2-acetylnorborn-1-yl ligand.

Table VI. Selected Bond Distances (Å) from the Crystal Structure of **3a**

Pd–P(1)	2.238 (2)	C(2)–C(3)	1.585 (15)
Pd–P(2)	2.434 (2)	C(3)–C(4)	1.53 (2)
Pd–O(1)	2.114 (6)	C(3)–C(7)	1.62 (2)
Pd–C(1)	2.103 (8)	C(4)–C(5)	1.60 (2)
C(1)–C(2)	1.550 (12)	C(5)–C(6)	1.60 (2)
C(2)–C(8)	1.487 (13)	C(6)–C(7)	1.53 (2)
O(1)–C(8)	1.240 (10)	P–C _{Ph}	<1.825> ^a
C(8)–C(9)	1.523 (13)	C _{Ph} –C _{Ph}	<1.41> ^a
C(1)–C(6)	1.541 (13)	B–F	<1.270> ^a

^a Average bond distance.

Table VII. Selected Bond Angles (deg) from the Crystal Structure of **3a**

P(1)–Pd–P(2)	98.36 (8)	C(1)–C(6)–C(7)	103 (1)
P(1)–Pd–O(1)	170.6 (2)	C(3)–C(7)–C(6)	93 (1)
P(1)–Pd–C(1)	89.7 (2)	Pd–P(1)–C(31)	119.3 (3)
P(2)–Pd–O(1)	89.4 (2)	Pd–P(2)–C(61)	124.1 (3)
P(2)–Pd–C(1)	171.2 (2)	C(11)–P(1)–C(21)	110.7 (4)
O(1)–Pd–C(1)	82.8 (3)	C(11)–P(1)–C(31)	103.6 (4)
Pd–C(1)–C(2)	107.1 (6)	C(21)–P(1)–C(31)	102.3 (4)
C(1)–C(2)–C(8)	114.2 (8)	C(41)–P(2)–C(51)	105.3 (5)
C(1)–C(2)–C(3)	102.2 (9)	C(51)–P(2)–C(61)	103.2 (4)
C(2)–C(3)–C(7)	99.8 (9)	C _{Ph} –C _{Ph} –C _{Ph}	<120.0>
C(4)–C(5)–C(6)	100 (1)	F–B–F	<109>
C(1)–C(6)–C(5)	102 (1)		

distance, other crystal structure determinations²⁴ indicate that the differences in carbon–oxygen bond lengths between coordinated and noncoordinated carbonyls are generally less than 0.04 Å.

One particularly important feature of the norbornyl unit is the stereochemistry of the palladium and acetyl groups at the 1- and 2-positions, respectively. As can be most clearly seen in Figure 1, both substituents lie on the exo face of norbornane. It may therefore be deduced that this product was formed via syn insertion of norbornylene into the palladium–acyl bond of **2a**.

The insertion of norbornylene into the metal–acyl bond of an analogous platinum complex, [Pt(PPh₃)₂–

(20) (a) Anderson, O. P.; Packard, A. G. *Inorg. Chem.* **1979**, *18*, 1129. (b) Miki, K.; Kai, Y.; Yasuoka, N.; Kasai, N. *J. Organomet. Chem.* **1977**, *135*, 53. (c) Martin, L. L.; Jacobson, R. A. *Inorg. Chem.* **1971**, *10*, 1795. (d) Bailey, N. A.; Mason, R. *J. Chem. Soc. A* **1968**, 2594.

(21) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

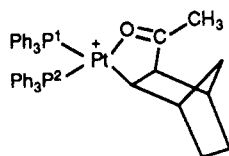
(22) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic: New York, 1971; Vol. 1, p 38.

(23) *CRC Handbook of Chemistry and Physics*; Weast, R. C., Astle, M. J., Beyer, W. H., Eds.; CRC Press: Boca Raton, FL, 1988; p F-166.

(24) (a) Brock, C. P.; Attig, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 1319.

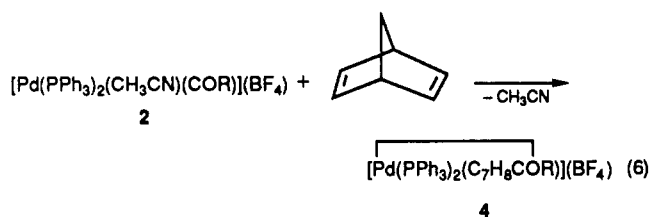
(b) Roe, D. M.; Calvo, C.; Krishnamachari, N.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1975**, 125.

$(\text{CH}_3\text{CN})(\text{COMe})(\text{BF}_4)$, has also been successfully demonstrated:²⁵

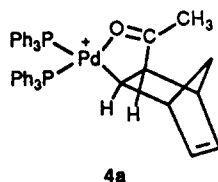


The structure of the product was determined to be exactly that formed with palladium, except that platinum now occupied the center of the square plane. From the platinum-phosphorus coupling constants, it was determined that P^1 ($^1J_{\text{Pt-P}} = 1634.7$ Hz) resonates at 28.1 ppm, while P^2 ($^1J_{\text{Pt-P}} = 5029.6$ Hz) resonates at 13.00 ppm. Assuming analogous chemical shift behavior for the palladium complex, the resonance at 15.3 ppm is thus assigned to the phosphorus trans to the carbonyl oxygen. Similarly, the resonance at 39.7 ppm is assigned to the phosphorus trans to the norbornyl carbon. The significance of these assignments will become more apparent when the stereochemistry must be determined for products containing only one phosphine ligand (*vide infra*).

The reaction of **2** with norbornadiene (eq 6) proceeded analogously to that with norbornylene. The ^{31}P NMR spectrum of the product, **4a** ($\text{R} = \text{Me}$), consists of a pair of doublets at 16.0 and 40.1 ppm ($^2J_{\text{P-P}} = 41.9$ Hz). Carbonyl (1620 cm^{-1}) and B-F ($1010\text{--}1075\text{ cm}^{-1}$), but no nitrile, stretches are present in the infrared spectrum.



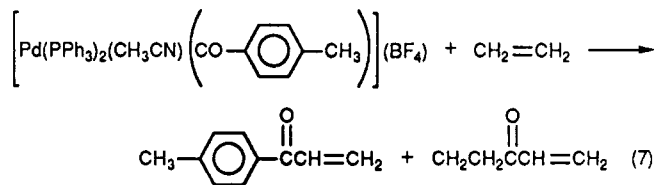
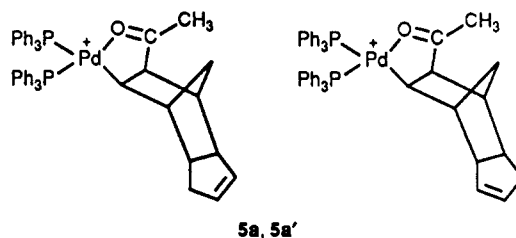
Both the above spectral data and the previous results from norbornylene insertion are consistent with the structure of **4a** shown. Because of the fewer number and



different types of protons on **4a**, the corresponding ^1H NMR spectrum is much simpler than that of **3a**. Thus, the coupling constant between the labeled protons was determined to be 5.2 Hz by selective decoupling. Although slightly lower than predicted¹⁹ (6–7 Hz), this value, coupled with the other spectra, confirms that the reaction of **2** with norbornadiene is analogous to that of **2** with norbornylene.

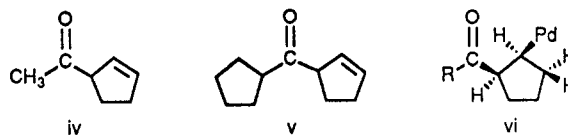
The reaction of **2a** with dicyclopentadiene generated two products. Although not well characterized, these products are assigned the isomeric structures **5a** and **5a'**, on the basis of both the appearance of two pairs of doublets in the ^{31}P NMR spectrum and the previously described reactions with norbornylene and norbornadiene.

Unlike the reactions previously described, the reaction of $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})[\text{CO}(p\text{-tolyl})]](\text{BF}_4)$ with ethylene did not yield a stable product. Rather, tolyl vinyl ketone and ethyl vinyl ketone were produced (eq 7). Concomitant



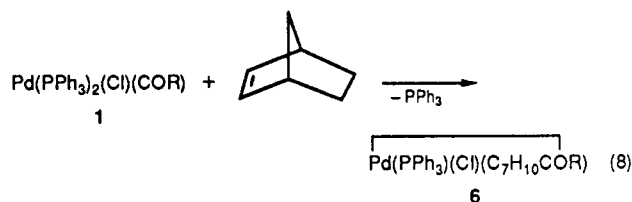
with the formation of these organic products was decomposition of the metal complex, as evidenced by (1) a solution color change from pale yellow to dark cherry red and (2) many unidentified resonances in the ^{31}P NMR spectrum of the final solution.

The reaction of **2a** with cyclopentene yielded methyl cyclopentenyl ketone and cyclopentyl cyclopentenyl ketone as the major organic products. Since these products were identified by mass spectrometry, the exact location of the double bond in the cyclopentenyl groups could not be determined. However, the structures of these products are tentatively assigned as **iv** and **v**. These assignments are



based on a mechanism involving β -hydride abstraction from the intermediate **vi**, which would be generated from the syn addition of cyclopentene across the palladium-acyl bond. Although **iv** is easily explained as olefin insertion into **2a**, the formation of **v** remains a curiosity, suggesting the reaction to be more complex than would be first be predicted.

After 2 h at room temperature, the reaction of **1** with a large excess of norbornylene generated **6** in quantitative yield (eq 8). The reaction was complicated by subsequent

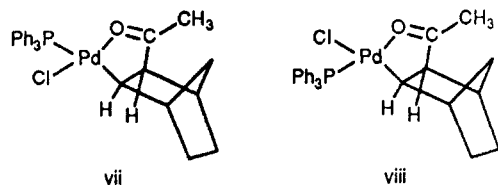


product decomposition to $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ plus unidentified organic products. The reaction byproduct, triphenylphosphine, appears to accelerate this decomposition, since addition of triphenylphosphine to a solution of **6** in CDCl_3 caused decomposition within 1 day, whereas no decomposition was observed in a similar solution not containing added phosphine. Since triphenylphosphine also inhibits the rate of reaction (*vide infra*), a large excess of norbornylene must be employed to accelerate product formation so that the reaction is complete before decomposition takes place. Once isolated as a solid, **6** was indefinitely stable, even in air.

The ^{31}P NMR spectrum of **6a** ($\text{R} = \text{Me}$) exhibits a single resonance at 37.8 ppm, attributable to a single phosphine ligand. The infrared spectrum contains a carbonyl stretch at 1628 cm^{-1} , consistent with coordination of the carbonyl

oxygen to the metal center. Finally, the ^1H NMR spectrum gives the proper integration for a norbornylene-inserted product. Although the individual resonances are too broad to be completely diagnosed, the coupling constant between the two labeled hydrogens was determined by selective decoupling to be 6.6 Hz, consistent with syn addition across the exo face of the olefin.¹⁹

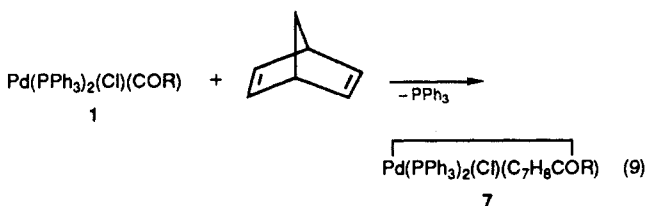
From the above spectroscopic data, there are two possible structures for **6a**: vii and viii. Isomer vii is supported by two additional spectroscopic observations.



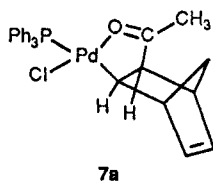
First, the carbonyl resonance in the ^{13}C NMR spectrum of **6a** is not coupled to a phosphorus atom, whereas coupling is observed in both **3a** and **4a**. Coupling in the latter complexes probably originates from the phosphorus trans to the carbonyl oxygen, since trans couplings are generally larger than cis.

Second, the ^{31}P NMR resonance at 15.3 ppm in **3a** has been assigned to the phosphine trans to the carbonyl oxygen, while that at 39.7 ppm has been assigned to the phosphine trans to the norbornyl carbon (*vide supra*). Assuming ^{31}P NMR chemical shifts to be consistent for similar complexes, the resonance at 37.8 ppm for **6a** is more consistent with a phosphine trans to the norbornyl carbon, as in the case for vii.

The reaction of **1** with norbornadiene (eq 9) proceeded analogously to that with norbornylene. The ^{31}P NMR spectrum of **7a** ($\text{R} = \text{Me}$) consists of a single resonance at 37.9 ppm, while a carbonyl stretch at 1627 cm^{-1} appears in the infrared spectrum.



Both the above spectral data and the previous results from norbornylene insertion are consistent with the structure of **7a** shown. As was previously the case for

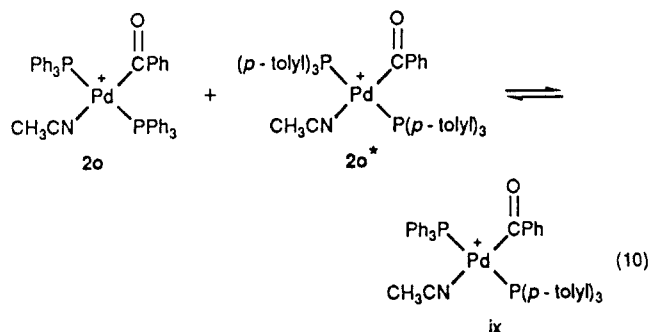


insertions into **2**, the ^1H NMR (360 MHz) spectrum of the norbornadiene-inserted product is much less complex than that of the norbornylene-inserted product. Thus, the coupling constant for the labeled protons was unambiguously established to be 6.2 Hz by selective decoupling. This value is completely consistent with that expected for these protons as a result of syn addition across the exo face of norbornadiene.¹⁹

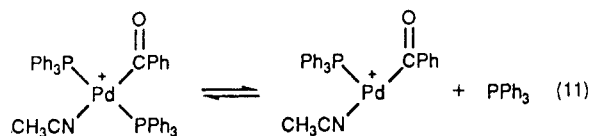
B. Mechanistic Aspects of Insertion into Cationic Complexes. For the mechanistic analyses described below, $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})(\text{COPh})](\text{BF}_4)$ (**2o**) was chosen as the cationic palladium-acyl complex to be studied for two reasons. First, olefins insert more slowly into this species

than its acetyl analogue, thus permitting a convenient monitoring of the reaction by ^{31}P NMR spectroscopy. Second, **2o** does not spontaneously isomerize in solution, as do several of the complexes studied.²⁶ The olefin selected for the study was norbornadiene.

1. Ligand Dissociation. A solution of **2o** was added to a solution of its tri-*p*-tolylphosphine analogue **2o*** (eq 10), after which a ^{31}P NMR spectrum of the resulting solution was run. In addition to the resonances for **2o** and



2o* at 19.98 and 18.30 ppm, respectively, two new "singlets" at 19.10 and 19.18 ppm were observed. These resonances were subsequently assigned to ix, in which the outermost peaks expected for the AX system were not observed because $\Delta\nu/J$ is very small.²⁷ On the basis of this experiment, the triphenylphosphine ligands on **2o** must be considered at least partly dissociated in solution, as shown in eq 11.



Because the insertion reaction is inhibited by added acetonitrile (*vide infra*), it is important to elucidate the nature of this dependency. Fortunately, an associative inhibition can be eliminated on the basis of observations in the nitrile region of the infrared spectrum. Although fast on the NMR time scale, exchange is slow on the IR time scale. Consequently, separate $\text{C}\equiv\text{N}$ stretches are observed for free and coordinated acetonitrile.

Free acetonitrile exhibits bands at 2285 and 2251 cm^{-1} , while acetonitrile coordinated to **2o** displays absorbances at 2305 and 2275 cm^{-1} . When the nitrile region of **2o** in chloroform was monitored as the concentration of free acetonitrile was systematically increased from 0 to 1.0 M, new nitrile bands were not observed. Furthermore, the intensities of those absorbances associated with coordinated acetonitrile did not increase, while those of free acetonitrile did. Therefore, the evidence indicates that **2o** remains four-coordinate in solutions up to 1.0 M in free acetonitrile, eliminating the possibility of an associative rate inhibition.

The conclusions from infrared spectroscopy were complemented by observations in the ^1H NMR spectrum of $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})(\text{COMe})](\text{BF}_4)$ in CDCl_3 . The bound CH_3CN resonance of **2a** appears at 1.42 ppm, shifted 0.58 ppm upfield from free acetonitrile at 2.00 ppm. Addition of acetonitrile to a solution of **2a** resulted not in two res-

(26) Brumbaugh, J. S.; Sen, A. *J. Am. Chem. Soc.* 1988, 110, 803.

(27) The 0.08 ppm difference between the inner peaks corresponds to 2.8 Hz. Hence, the assumption that $\Delta\nu/J$ is small is reasonable since trans phosphine coupling constants are generally several hundred hertz; see: (a) Goodfellow, R. J.; Taylor, B. F. *J. Chem. Soc., Dalton Trans.* 1974, 1676. (b) Verkade, J. G. *Coord. Chem. Rev.* 1972, 9, 1.

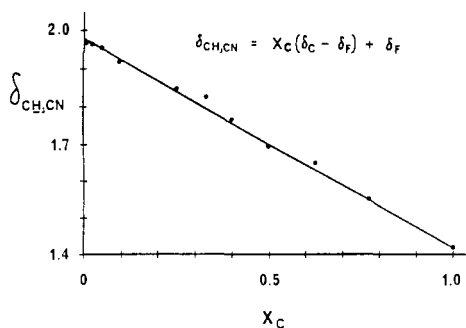


Figure 2. Plot of δ_{obs} versus X_C for solutions of **2a** containing different concentrations of added acetonitrile.

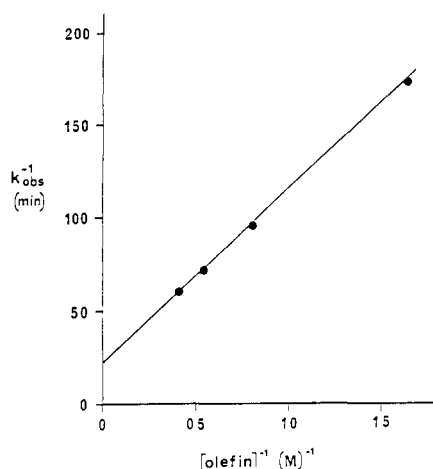


Figure 3. Plot of $1/k_{\text{obs}}$ versus $1/[\text{olefin}]$ in the reaction of **2o** with norbornadiene.

onances, but rather in a single time-averaged resonance, due to fast acetonitrile exchange on the NMR time scale. Increasing the concentration of free acetonitrile shifted the resonance progressively downfield, according to eq 12,

$$\delta_{\text{CH}_3\text{CN}} = X_C(\delta_C - \delta_F) + \delta_F \quad (12)$$

where X_C is the mole fraction of coordinated acetonitrile and δ_C and δ_F are the chemical shifts of coordinated and free acetonitrile, respectively. Figure 2 shows the linearity of a plot of δ_{obs} versus X_C , which is consistent only with a fast ligand exchange involving no (or negligible) formation of a five-coordinate species.

2. Kinetics. All kinetic analyses were performed by monitoring either the disappearance of **2o** (a singlet) or the appearance of **4o** (a pair of doublets). At no time were any species attributable to intermediates observed.

Since **2o** was a primary reactant and the kinetics were monitored by the disappearance of this species, it was first necessary to establish its order in the rate law. Under pseudo-first-order conditions (excess of both olefin and acetonitrile), the reaction was found to be first-order in the metal complex for at least 3 half-lives.

The rate of insertion was found to increase with increasing concentration of norbornadiene and decreasing concentration of added acetonitrile. Best straight lines were obtained for plots of $1/k_{\text{obs}}$ versus $1/[\text{olefin}]$ (Figure 3) and k_{obs} versus $1/[\text{CH}_3\text{CN}]$ (Figure 4).

The reaction was virtually independent of the concentration of added triphenylphosphine since a rate decrease of less than a factor of 2 was observed in the presence of 20 equiv of added phosphine. Therefore, a phosphine dissociative pathway can be ruled out.

C. Mechanistic Aspects of Insertion into Neutral Complexes. Although a rigorous kinetic analysis of the

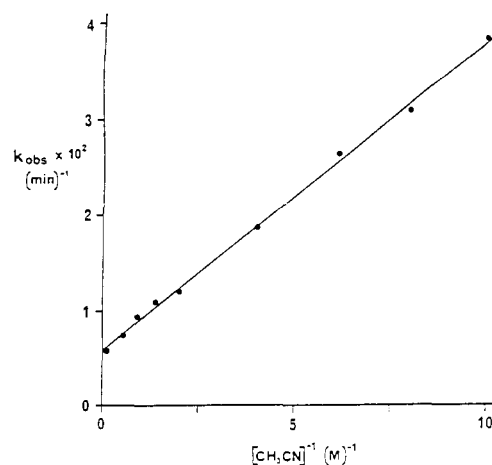
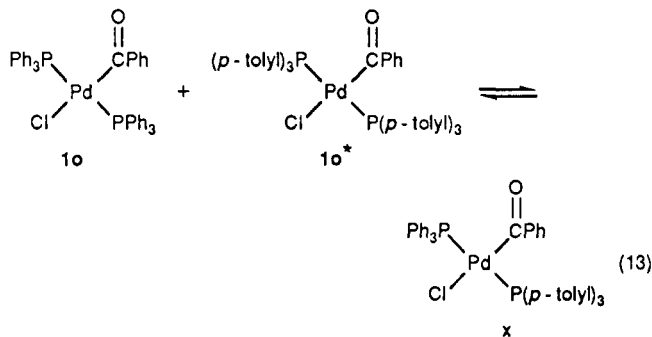


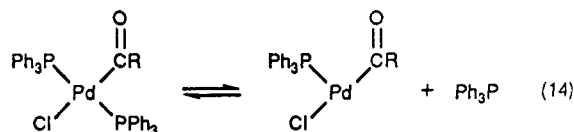
Figure 4. Plot of k_{obs} versus $1/[\text{CH}_3\text{CN}]$ in the reaction of **2o** with norbornadiene.

type described above was not undertaken, it is possible to draw several mechanistic conclusions from the available data. These are presented below.

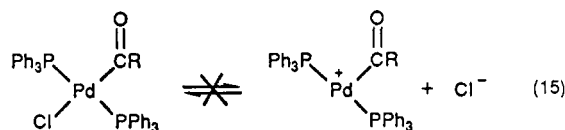
1. Ligand Dissociation. A chloroform solution of **1o** was added to a solution of its tri-*p*-tolylphosphine analogue **1o*** (eq 13), after which a ^{31}P NMR spectrum was run. In



addition to the resonances of **1o** and **1o*** at 18.8 and 17.0 ppm, respectively, two new resonances at 17.91 and 17.96 ppm were observed and subsequently assigned as **x**. For reasons previously stated,²⁷ the outermost peaks of the expected AX splitting pattern were not observed. On the basis of this experiment, the phosphine ligands on **1o** and related complexes must be at least partly dissociated in solution, as shown by eq 14.

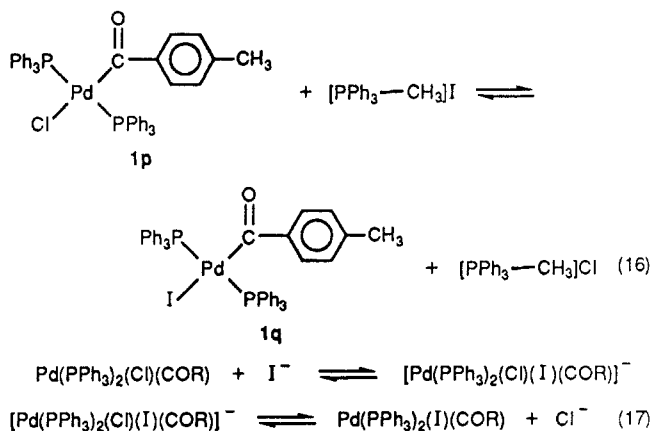


A solution of **1o** was added to a solution of $\text{Pd}(\text{PPh}_3)_2(\text{I})[\text{CO}(p\text{-tolyl})]$, after which a ^{31}P NMR spectrum was run. Only those resonances of the initial reactants were present. Even after 3 days, no evidence for halide exchange was observed. Thus, eq 15 apparently does not occur to an appreciable extent under the conditions of the insertion reactions.



These complexes do undergo an associative halide exchange process, however. When $[\text{Ph}_3\text{P}-\text{CH}_3]\text{I}$ was added to a chloroform solution of $\text{Pd}(\text{PPh}_3)_2(\text{Cl})[\text{CO}(p\text{-tolyl})]$

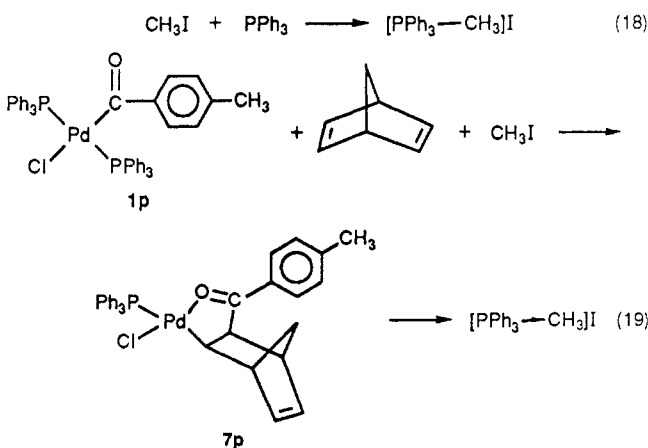
(**1p**), the subsequent ^{31}P NMR spectrum indicated the presence of both **1p** and its iodo analogue $\text{Pd}(\text{PPh}_3)_2(\text{I})[\text{CO}(p\text{-tolyl})]$. A single resonance was observed for the phosphonium salts, consistent with the halide acting as a noncoordinating counteranion.²⁸ Therefore, the equilibrium depicted by eq 16 must be established via the associative pathway depicted in eq 17.



2. Kinetics. All kinetic experiments were performed by monitoring either the disappearance of **1** or the appearance of **7**, both of which are singlets in the ^{31}P NMR spectrum. At no time were any intermediates observed.

The reaction of **1p** with an 11-fold excess of norbornadiene did not obey good first- or second-order kinetic behavior. Furthermore, the rate of reaction was found to decrease as the reaction proceeded. On the basis of reactions carried out in the presence of methyl iodide and sulfur, the cause of this behavior is apparently attributable to the rate inhibition associated with the triphenylphosphine byproduct.

Methyl iodide reacts with free triphenylphosphine according to eq 18. In the presence of 5 equiv of this reagent, **1p** reacted with norbornadiene to produce **7p** and $[\text{PPh}_3\text{-CH}_3]\text{I}$, as shown in eq 19. No free phosphine was observed

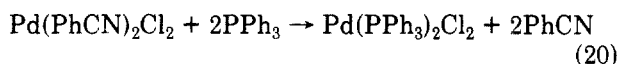


at any time. More important, the reaction was complete after only a few hours, as compared to being only 85% complete after 5 days in the absence of methyl iodide. It is thus reasonable to conclude that methyl iodide accelerated the rate of reaction by removing free triphenylphosphine as the corresponding phosphonium salt.

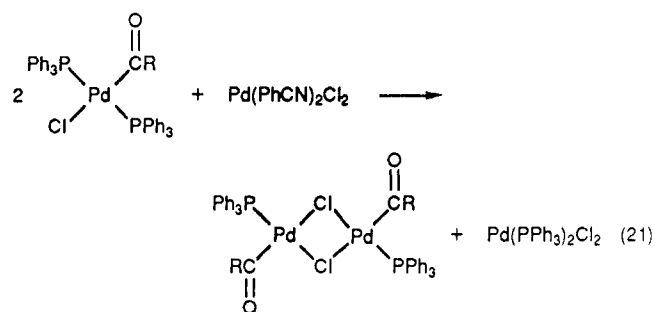
The accuracy of this conclusion is clouded, however, by the observation that halide exchange between **1p** and the phosphonium salt occurred simultaneously with the in-

sertion reaction. Such an exchange would not necessarily constitute a problem, except that the resulting iodo complex, $\text{Pd}(\text{PPh}_3)_2(\text{I})[\text{CO}(p\text{-tolyl})]$, was independently prepared and observed to react at a faster rate than the original chloro complex. Therefore, the rate acceleration by methyl iodide could result from either phosphine removal or the formation of a more highly reactive iodo complex. Both factors are probably involved, since an independent experiment showed that the iodo complex reacted faster in the presence of methyl iodide than in its absence, although the difference in rates was small (approximately a factor of 2).

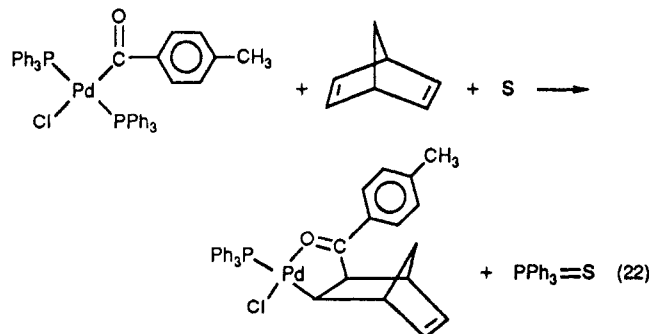
The reaction of **1p** was also accelerated by $\text{Pd}(\text{PhCN})_2\text{Cl}_2$. In this case, the reaction was too fast to monitor spectroscopically, being complete before the initial spectrum was run (ca. 5 min). Since $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ quickly reacts with 2 equiv of triphenylphosphine according to eq 20, the insertion reaction was probably promoted by the



removal of free phosphine from the system. However, it is not clear as to whether this phosphine removal occurred prior to or after insertion, since $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ was also observed to react quantitatively and quickly (also too fast to monitor) with **1a** to form, in addition to $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, a chloro-bridged dimer (eq 21).²⁹ The resulting dimer was observed to react almost instantaneously with norbornadiene to form **7a**.



Finally, the reaction of **1p** with norbornadiene was accelerated by the addition of elemental sulfur. In this case, phosphine was removed as $\text{Ph}_3\text{P}=\text{S}$, as depicted in eq 22.



Free triphenylphosphine was never observed during the reaction, which was complete in approximately 20 min. As with $\text{Pd}(\text{PhCN})_2\text{Cl}_2$, however, **1p** reacted with elemental sulfur in the absence of olefin to form the corresponding chloro-bridged dimer, although, in this case, the rate of dimer formation was slower (by a factor of 2) than the rate of reaction with norbornadiene. Hence, at least some of

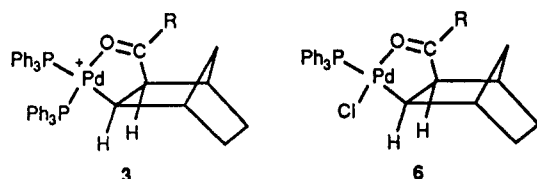
(28) Grim, S. O.; McFarlane, W.; Davidoff, E. F.; Marks, T. J. *J. Phys. Chem.* 1966, 70, 581.

(29) This class of dimers has been described previously; see: (a) Anderson, G. K. *Organometallics* 1983, 2, 665. (b) Hartley, F. R. *Organomet. Chem. Rev., Sect. A* 1970, 6, 119.

the rate enhancement by elemental sulfur must be attributed to removal of the triphenylphosphine product. Therefore, the experimental evidence again suggests that free triphenylphosphine is an inhibitor of the insertion reaction.

Discussion

The reactions of norbornylene and its derivatives with $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})(\text{COR})](\text{BF}_4)$ and $\text{Pd}(\text{PPh}_3)_2(\text{Cl})(\text{COR})$ represent the first direct observation (uncomplicated by subsequent reactions) of intermolecular olefin insertion into a palladium-acyl bond. The products of these reactions (shown for norbornylene)



are stable palladium(II) complexes, containing two of the original ligands and the chelating 2-acetylnorborn-1-yl residue. Because of the high thermodynamic stability associated with the five-membered metallacyclic ring, one of the original ligands is displaced by the carbonyl oxygen.

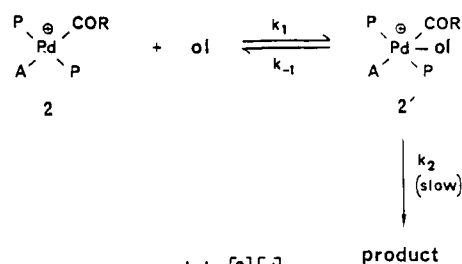
The structures of 3 and 6 were determined by ^1H NMR, ^{31}P NMR, and IR spectroscopy. The stereochemistry about the 1,2-disubstituted norbornane unit was unambiguously established to be exo,exo by an X-ray crystal structure determination of 3a (R = Me). Mechanistically, this stereochemistry is consistent with a concerted process involving acyl migration on the exo face of the olefin, with both the acyl group and the olefin being coordinated to the metal.

The most interesting feature of the crystal structure of 3a is the dramatically different palladium-phosphorus bond distances. To the best of our knowledge, 2.434 Å represents the longest palladium-phosphorus bond known,³⁰ while 2.238 Å is one of the shortest bonds ever observed. Clearly, this phenomenon reflects the very different trans influences of the σ -bonded alkyl and dative-bonded carbonyl groups located trans to the respective phosphine ligands.³¹

Despite the kinetic data, the precise mechanism by which olefins insert into $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})(\text{COR})](\text{BF}_4)$ could not be unambiguously determined from this investigation. This unfortunate conclusion arises because the kinetic data are not perfectly consistent with any reasonable and simple mechanistic possibility. Nonetheless, certain reaction pathways were clearly eliminated and important features of the actual mechanism were deduced.

Insertion from an intermediate having less than four ligands is not consistent with the observed phosphine dependence (or lack thereof). The most rational mechanism involving a five-coordinate intermediate is shown in Scheme I. In this mechanism, the olefin directly coordinates to 2, forming a five-coordinate intermediate, which eventually undergoes olefin insertion. Two rate laws may be derived, one using the steady-state (s-s) approximation and the other a rapid preequilibrium (p-e) assumption. The steady-state approximation is valid when $k_1 \ll k_{-1} + k_2$, while the rapid preequilibrium assumption is used when

Scheme I. Mechanism of the Reaction of 2 with Norbornadiene Involving Olefin Insertion via a Five-Coordinate Intermediate



$$\text{rate (s-s)} = \frac{k_1 k_2 [2] [\text{ol}]}{k_{-1} + k_2}$$

$$\text{rate (p-e)} = \frac{K k_2 \text{Pd}_T [\text{ol}]}{K [\text{ol}] + 1}$$

$$K = k_1/k_{-1} \quad \text{Pd}_T = [2] + [2']$$

$k_2 \ll k_{-1}$ and $k_2 \ll k_1$. The rate laws are shown in Scheme I. From these, expressions for k_{obs} can be derived as shown in eqs 23 and 24.

$$k_{\text{obs}}^{-1}(\text{s-s}) = \frac{k_{-1} + k_2}{k_1 k_2 [\text{ol}]} \quad (23)$$

$$k_{\text{obs}}^{-1}(\text{p-e}) = \frac{1}{k_2} + \frac{1}{K k_2 [\text{ol}]} \quad (24)$$

Only eq 24 is consistent with the experimentally determined olefin dependence (Figure 3). It does not, however, account for the observed acetonitrile dependence (Figure 4). Consequently, olefin insertion does not proceed via the five-coordinate intermediate depicted in Scheme I. The observed dependence on olefin and acetonitrile would also appear to rule out an alternative five-coordinate intermediate involving two triphenylphosphines, two olefins, and an acyl group as ligands. A similar five-coordinate bis(olefin) species has been previously proposed as an intermediate in the insertion of olefins into the Pt-H bond of an analogous cationic platinum complex.³² Finally, we note that theoretical analyses have predicted that insertion from a five-coordinate intermediate is energetically unfavorable.³³

The only other mechanistic alternative is insertion via a four-coordinate intermediate formed by substitution of norbornadiene for acetonitrile. This pathway and the two corresponding rate laws, one each for the steady-state approximation and the rapid preequilibrium assumption, are shown in Scheme II. From these rate laws, expressions for k_{obs} can be derived as shown in eqs 25 and 26. Both

$$k_{\text{obs}}^{-1}(\text{s-s}) = \frac{k_{-1}[\text{A}]}{k_1 k_2 [\text{ol}]} + \frac{1}{k_1 [\text{ol}]} \quad (25)$$

$$k_{\text{obs}}^{-1}(\text{p-e}) = \frac{1}{k_2} + \frac{[\text{A}]}{K k_2 [\text{ol}]} \quad (26)$$

derivations predict that a plot of $1/k_{\text{obs}}$ versus $[\text{CH}_3\text{CN}]$ will yield a straight line having a nonzero intercept. However, when the experimental data are plotted as such (Figure 5), the points clearly do not fall on a straight line. Rather, a distinct curve is formed. Consequently, the

(30) The longest palladium-phosphorus bond reported previously is 2.425 Å; see: Kashiwagi, T.; Yasuoka, N.; Ueki, T.; Kasai, N.; Kakudo, M.; Takahashi, S.; Hagihara, N. *Bull. Chem. Soc. Jpn.* 1968, 41, 296.

(31) Appleton, T. C.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* 1973, 10, 335.

(32) Clark, H. C.; Jablonski, C.; Halpern, J.; Mantovani, A.; Weil, T. A. *Inorg. Chem.* 1974, 13, 1541.

(33) Thorn, D. L.; Hoffmann, R. J. *Am. Chem. Soc.* 1978, 100, 2079.

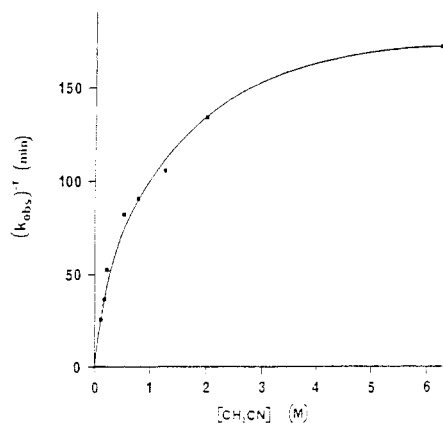
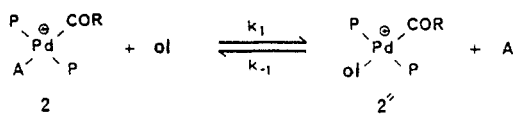


Figure 5. Plot of $1/k_{\text{obs}}$ versus $[\text{CH}_3\text{CN}]$ in the reaction of **2** with norbornadiene.

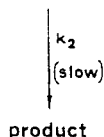
Scheme II. Mechanism of the Reaction of 2 with Norbornadiene Involving Olefin Insertion via a Four-Coordinate Intermediate



$$\text{rate (s-s)} = \frac{k_1 k_2 [2] [\text{ol}]}{k_{-1} [\text{A}] + k_2}$$

$$\text{rate (p-e)} = \frac{K k_2 \text{Pd}_T [\text{ol}]}{K [\text{ol}] + [\text{A}]}$$

$$K = k_1/k_{-1} \quad \text{Pd}_T = [2] + [2']$$

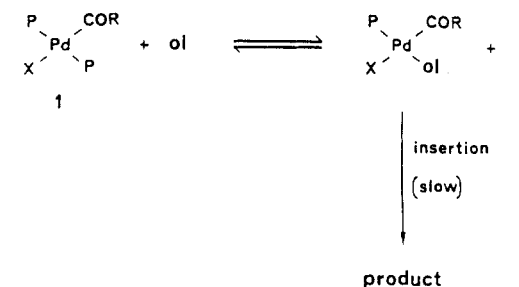


experimental data are also not consistent with this mechanism.

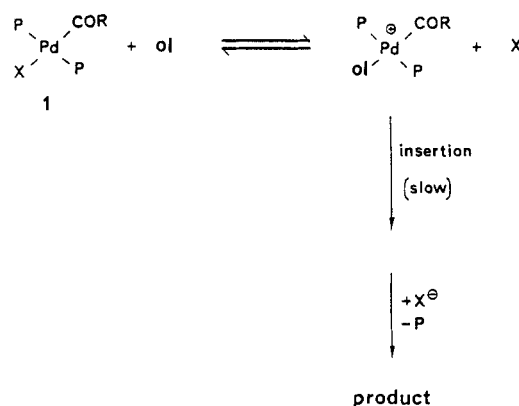
That the experimental data are not consistent with any of the proposed mechanisms is probably a reflection of the complex nature of the overall reaction. The preceding mechanisms are all rather simple and do not address such factors as the associative and dissociative processes of the intermediates or the isomerizations and topological transformations of the intermediates. As an example, consider the pathway depicted in Scheme II. If norbornadiene were to displace acetonitrile, it is possible that the olefin would be initially trans to the acyl group in the intermediate. If this were the case, then an isomerization pathway would have to be invoked to align the olefin and acyl group into the required cis geometry for insertion. Furthermore, it is conceivable that this isomerization is in some way catalyzed by free acetonitrile, thereby making acetonitrile both an inhibitor (preventing olefin coordination) and a catalyst³⁴ (promoting isomerization to the proper geometrical configuration). Such a scenario would certainly result in a very complex rate law. Also possible is a mechanism involving two or more pathways that operate simultaneously. Again, the corresponding rate law would be very complex.

The precise mechanism of olefin insertion into the metal-acyl bond of $\text{Pd}(\text{PPh}_3)_2(\text{Cl})(\text{COR})$ was also not firmly established. However, a pathway encompassing

Scheme III. Mechanism of the Reaction of 1 with Norbornadiene Involving Olefin Insertion from a Four-Coordinate Intermediate Formed by Olefin Displacement of a Triphenylphosphine Ligand



Scheme IV. Mechanism of the Reaction of 1 with Norbornadiene Involving Olefin Insertion from a Four-Coordinate Intermediate Formed by Olefin Displacement of a Halide Ligand

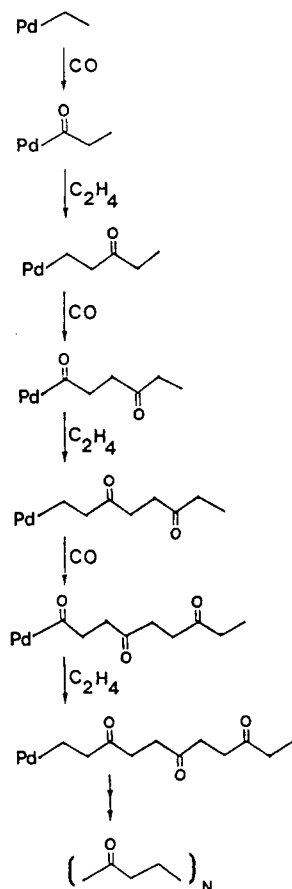


insertion from a four-coordinate intermediate formed by substituting an olefin for a phosphine ligand (Scheme III) is consistent with the mechanistic conclusions derived from a closely related reaction, in which insertion of an internal acetylene into an alkoxy carbonylpalladium(II) complex was observed.^{6b} The following experimental observations are consistent with this mechanism: (1) The reaction of **1** does not obey good first-order kinetics, as would be predicted since free triphenylphosphine is produced as a reaction product. (2) The rate of reaction increases upon increasing the concentration of olefin. (3) Phosphine exchange, presumably involving a dissociative process, was observed between **1o** and **1o***. (4) The rate of reaction increases tremendously upon addition of "phosphine sponge" (methyl iodide, elemental sulfur, and bis(benzonitrile)palladium dichloride).

An additional mechanism, in which insertion takes place via a different four-coordinate intermediate, should also be considered. As shown in Scheme IV, olefin substitution of the halide ion generates a cationic intermediate, which subsequently undergoes olefin insertion. Evidence supporting this pathway is that norbornadiene inserts into $\text{Pd}(\text{PPh}_3)_2(\text{I})[\text{CO}(p\text{-tolyl})]$ at a significantly faster rate than it inserts into $\text{Pd}(\text{PPh}_3)_2(\text{Cl})[\text{CO}(p\text{-tolyl})]$. A faster reaction with the iodo analogue is consistent with a more facile olefin displacement of the more weakly bound iodine ligand. The faster rate observed for the iodo analogue is, however, also consistent with the phosphine dissociative pathway (Scheme III), since the difference in reaction rates may be attributable to the greater trans influence of the iodide ligand.³¹ A rate enhancement would then result because of a greater weakening of the palladium-acyl bond, thus facilitating acyl migration. Therefore, Scheme III most accurately describes the mechanism of olefin insertion into $\text{Pd}(\text{PPh}_3)_2(\text{X})(\text{COR})$, since all of the experimental

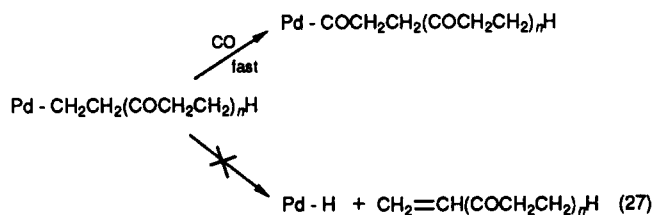
(34) For a discussion of ligand-assisted isomerization in square-planar complexes, see: (a) Wilkins, R. G. *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*; Allyn and Bacon: Boston, 1974; p 352, and references therein. (b) Reference 32.

Scheme V. Chain-Growth Sequence for the Palladium-Catalyzed Alternating Copolymerization of Carbon Monoxide with Ethylene



evidence is consistent with this pathway.

Earlier mechanistic studies on the palladium-catalyzed alternating copolymerization of carbon monoxide with olefins had confirmed a two-step chain-growth sequence involving the alternate insertions of CO and olefin into a palladium-carbon bond (Scheme V).^{3b} The second of these two steps (i.e., the insertion of the olefin into a palladium-acyl bond) is rate-limiting.^{3b} This is because, in the copolymerizations, we did not observe any products arising from a β -hydrogen abstraction process (e.g., eq 27),



which would be expected if the metal-alkyl intermediates were sufficiently long-lived, as is observed for the reaction of $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})(\text{COR})](\text{BF}_4)$ with ethylene and cyclopentene (vide supra). These results indicate that the subsequent insertion of CO is fast.

In view of the critical role of the step involving olefin insertion into palladium-acyl bonds, the present study was undertaken to understand why cationic weakly solvated palladium compounds (e.g., $\text{Pd}(\text{PPh}_3)_2(\text{R})(\text{solvent})^+$) were efficient catalysts for the copolymerization reaction, while their neutral analogues (e.g., $\text{Pd}(\text{PPh}_3)_2(\text{R})(\text{X})$, X = halide) were inactive under the same conditions.³ There are two possible reasons for the difference in reactivity. First, olefin coordination by displacement of a weakly coordinated solvent molecule is expected to be more facile than the corresponding displacement of either a coordinated phosphine or a halide ion (cf. eqs 5 and 6 versus eqs 8 and 9). Second, because of weaker "back-bonding", the olefin is expected to bind less strongly to the cationic, electrophilic palladium center than to the corresponding neutral species. As a result, the activation energy for the insertion step would be lower for the less stable cationic palladium-olefin complex. A similar situation also exists with catalysts for olefin homopolymerizations, where the rate-limiting step is olefin insertion into metal-alkyl bonds. There is now growing evidence that the most active systems involve weakly solvated, cationic metal species.³⁵

Our study allows, for the first time, an assessment of the relative importance of the two factors. At least for the olefin-carbon monoxide copolymerizations, it is clear that the facile coordination of the olefin by ligand displacement is of primary importance. Thus, while the olefin insertion into the palladium-acyl bond of $\text{Pd}(\text{PPh}_3)_2(\text{Cl})(\text{COR})$ is normally slow, in the presence of a "phosphine sponge" the insertion rate becomes at least as fast as that observed with the corresponding cationic compound $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})(\text{COR})]\text{BF}_4$. Hence, the weak ligation of the metal center is more important than its electrophilicity.

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Supplementary Material Available: Tables of bond distances, bond angles, positional parameters, and temperature factors for **3a** (10 pages); a table of calculated and observed structure factors for **3a** (35 pages). Ordering information is given on any current masthead page.

(35) (a) References 6i,k,m. (b) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (c) Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902. (d) Lin, Z.; Le Marechal, J.-F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127.