further results will be reported in a subsequent publication.

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Registry No. **1**, 80461-63-8; **2**, 80448-48-2; **3**, 80448-50-6; **4**, 80448-52-8; **5**, 80448-54-0; **6**, 80448-56-2; **7**, 80448-58-4; **8**, 80448-60-8; **9**, 80448-62-0; **10**, 80448-64-2; **11**, 80461-65-0; **12**, 80448-66-4; **13**, 80448-68-6; **14**, 80448-70-0; **15**, 80448-72-2; **16**, 80448-74-4; **17**, 80448-76-6; **18**, 80461-67-2; **19**, 80461-69-4; $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]PF_6$, 80448-77-7; $[Rh_2(CO)_2(\mu\text{-}Cl)(DAM)_2]PF_6$, 74965-10-9; $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](B(C_6H_5)_4)_2$, 74977-80-3.

Supplementary Material Available: Tables I and IV giving analytical and conductance data, respectively (2 pages). Ordering information is given on any current masthead page.

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Dicationic Tetrakis(triphenylphosphine)palladium(II) and Tetrakis(triphenyl phosphite)palladium(II) Complexes

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The synthesis and properties of the cationic palladium(II) complexes are described. Dicationic $[Pd(PPh_3)_4](X)_2$ ($X = BF_4^-, PF_6^-$) and $[Pd(P(OPh)_3)_4](PF_6)_2$ have been prepared by the reaction of $Pd(PPh_3)_4$ with CPh_3X ($X = BF_4^-, PF_6^-$). A pentacoordinated Pd(II) complex of the heterocyclic ligand 1,10-phenanthroline, $[Pd(1,10\text{-phen})_2(PPh_3)](X)_2$, was obtained from the reaction of $[Pd(PPh_3)_4](X)_2$ with 1,10-phen. Monocationic $[Pd(CH_3COCHCO\text{–}R)(PPh_3)_2](X)$ (R = Me, OMe) has been isolated from the reaction of $Pd(PPh_3)_4$ with CPh_3X in the presence of acetylacetone or methyl acetoacetate. Likely structures and some features for these new complexes are proposed from ^1H NMR and IR spectrometry.

Although the cationic platinum(II) acetylacetonate complex $[Pt(acac)(PPh_3)](BF_4)$ has been prepared,[1] its palladium analogue has been elusive. Recently, the preparation of cationic hydride complexes of the type $[Pt(PPh_3)_3H](X)$ ($X = ClO_4^-, HSO_4^-$, or BF_4^-) by the oxidative-addition reaction of $Pt(PPh_3)_4$ has been reported.[2] However, a square-planar Pd(II) complex having only unidentate phosphine[3,4] or phosphite ligands has not yet been reported.

I have succeeded in isolating the tetrakis(triphenylphosphine)palladium(II) complex $[Pd(PPh_3)_4](X)_2$ ($X = BF_4^-, PF_6^-$) and its phosphite analogue $[Pd(P(OPh)_3)_4](PF_6)_2$. Also the pentacoordinated complex $[Pd(1,10\text{-phen})_2(PPh_3)](X)_2$ was isolated. In this paper, the preparation and some reactions for these complexes are described.

Experimental Section

All the solvents were purified by the distillation of commercial solvents over Na or $CaCl_2$. All the reactions were carried out in vacuo or under nitrogen, but the products are thermally stable and air stable, and isolations were carried out in air.

Tetrakis(triphenylphosphine)palladium(0) was prepared by a literature procedure[5] or by the reduction of $PdCl_2(PPh_3)_2$ (4.4 g) with sodium borohydride in 130 mL of hot EtOH containing 5 g of PPh_3. The yellow suspended solution slowly turned to canary yellow. The reaction was completed in 10 min, and the solution was cooled in cold water. Then the canary yellow solids were filtered and washed with water, EtOH, and heptane (yield 83%).

Tetrakis(triphenyl phosphite)palladium(0) was prepared by following the procedure of the preparation of tetrakis(triphenyl phosphite)platinum(0).[6] $Pd(PPh_3)_4$, 1.3 g, was dissolved in 15 mL of benzene, and an excess amount of $P(OPh)_3$ (~2 g) was added. The yellow solution slowly lost its color. The transformation to $Pd(P(OPh)_3)_4$ was completed in 6 h, the solvent was removed under reduced pressure to about half of the total volume, and addition of pentane to the solution gave white crystals (yield 100%).

Tetrakis(triphenylphosphine)palladium(II) Complex, $[Pd(PPh_3)_4](BF_4)_2\cdot(CH_3)_2CO$. A 2.0-g quantity of $Pd(PPh_3)_4$ was dissolved in 15 mL of benzene, and an acetone solution of CPh_3BF_4, 1.4 g in 20 mL, was added to the complex solution. Then the mixed solution was left agitating for 6 h. The solvent was removed under reduced pressure to one-fifth of the total volume. Addition of diethyl ether to the residue solution gave pale yellow crystals (2.2 g, 90%). Anal. Calcd for $[Pd(PPh_3)_4](BF_4)_2\cdot(CH_3)_2CO$: C, 64.93; H, 4.80. Found: C, 64.32; H, 4.43. IR (Nujol mull): $\nu(CO)$ of the acetone of solvation 1710 cm^{-1} (strong). The PF_6^- salt was prepared analogously, giving yellow crystals (61%). Anal. Calcd for $[Pd(PPh_3)_4](PF_6)_2\cdot(CH_3)_2CO$: C, 59.91; H, 4.43. Found: C, 60.05; H, 4.58. IR (Nujol mull): $\nu(CO)$ of the acetone of solvation 1710 cm^{-1} (strong).

Tetrakis(triphenyl phosphite)palladium(II) Complex, $[Pd(P(OPh)_3)_4](PF_6)_2\cdot(CH_3)_2CO$. A 1.6-g of quantity of $Pd(P(OPh)_3)_4$ was dissolved in 15 mL of benzene, and an acetone solution of CPh_3PF_6, 0.97 g in 20 mL, was added. The reaction was completed in 24 h, the solvents of the solution were removed under reduced pressure to one-fifth of the total volume, and addition of pentane to the residue solution gave white crystals (0.8 g, 50%). Anal. Calcd for $[Pd(P(OPh)_3)_4](PF_6)_2\cdot(CH_3)_2CO$: C, 57.46; H, 4.24. Found: C, 57.40; H, 4.99. IR (Nujol mull): $\nu(CO)$ of the acetone of solvation 1723 cm^{-1}.

Bis(1,10-phenanthroline)(triphenylphosphine)palladium(II) Complex, $[Pd(1,10\text{-phen})_2(PPh_3)](BF_4)_2\cdot(CH_3)_2CO$. A 0.7-g of quantity of $[Pd(PPh_3)_4](BF_4)_2\cdot(CH_3)_2CO$ was dissolved in 20 mL of acetone, and 0.25 g of 1,10-phenanthroline was added to the solution. The yellow solution slowly turned to red. Transformation to the bis(1,10-phenanthroline)palladium(II) complex was completed after 3 h, and the solvent was removed under reduced pressure to give orange solids,

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Table I. Some Physical Properties of Cationic Pd(II) Complexes

complex	$\nu(C{\cdots}O) + \nu(C{\cdots}C)^a$			$\Lambda_m{}^b$	chemical shifts (diketonate)^c		
					δ_{Me}	δ_{CH}	δ_{OMe}
$[Pd(PPh_3)_4](BF_4)_2$				212			
$[Pd(PPh_3)_4](PF_6)_2$				212			
$[Pd(P(OPh)_3)_4](PF_6)_2$				443			
$[Pd(1,10\text{-phen})_2(PPh_3)](BF_4)_2$				335			
$[Pd(1,10\text{-phen})_2(PPh_3)](PF_6)_2$				260			
$[Pd(acac)(PPh_3)_2](BF_4)$	1563		1523	148	1.57 (6)	5.56 (1)	
$[Pd(acac)(PPh_3)_2](PF_6)$	1561		1523	175	1.50 (6)	5.38 (1)	
$[Pd(maac)(PPh_3)_2](BF_4)$	1591	1572	1517	135	1.47 (3)	4.92 (1)	2.70 (3)
$[Pd(acac)(2,2'\text{-bpy})](BF_4)$	1558		1523				
$[Pd(maac)(2,2'\text{-bpy})](BF_4)$	1587	1570	1522				

[a] In cm^{-1}; measured in Nujol mulls. [b] Conductivity ($\Omega^{-1}\ cm^{-1}\ mol^{-1}$) of ca. 10^{-3} M acetone solutions measured on a DKK AO-6 instrument. [c] Measured in $CDCl_3$; recorded on a JEOL 100 spectrometer. Chemical shifts are relative to Me_4Si at 0.00.

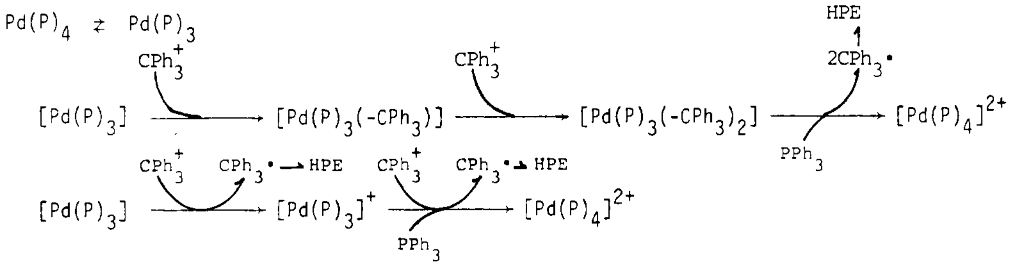

Figure 1. Possible mechanisms for the oxidation of $Pd(P)_4$ (P = PPh_3, $P(OPh)_3$) with $CPh_3{}^+$.

which were recrystallized from acetone–ether to give deep orange prisms (0.45 g, 81%). Anal. Calcd for $[Pd(1,10\text{-phen})_2(PPh_3)](BF_4)_2 \cdot (CH_3)_2CO$: C, 56.25; H, 3.88; N, 5.82. Found: C, 56.26; H, 4.01; N, 5.80. IR (Nujol mull): ν(CO) of the acetone of solvation 1717 cm^{-1}.

The $PF_6{}^-$ salt was prepared analogously (yield 55%). Anal. Calcd for $[Pd(1,10\text{-phen})_2(PPh_3)](PF_6)_2 \cdot (CH_3)_2CO$: C, 50.18; H, 3.46; N, 5.19. Found: C, 51.59; H, 3.09; N, 4.97. IR (Nujol mull): ν(CO) of the acetone of solvation 1711 cm^{-1}.

Bis(triphenylphosphine)(acetylacetonato)palladium(II) Complex, $[Pd(CH_3COCHCOCH_3)(PPh_3)_2](BF_4) \cdot (CH_3)_2CO$. $[Pd(CH_3COCHCOCH_3)(PPh_3)_2](BF_4) \cdot (CH_3)_2CO$ was prepared by CPh_3BF_4 (0.38 g) oxidation of $Pd(PPh_3)_4$ (1.2 g) in the mixed solvents benzene–CH_2Cl_2 (25 mL) containing acetylacetone (0.1 g) at room temperature. The yellow solution turned to green, transformation to acetylacetonate complex being completed after 24 h. The solvents were removed under reduced pressure to about one-third of the total volume, and addition of diethyl ether to the residue solution gave greenish yellow crystals. Recrystallization from acetone–ether gave yellow prisms of $[Pd(CH_3COCHCOCH_3)(PPh_3)_2](BF_4) \cdot (CH_3)_2CO$ (0.63 g, 70%). $[Pd(CH_3COCHCOCH_3)(PPh_3)_2](BF_4) \cdot (CH_3)_2CO$ was also prepared from the reaction of $[Pd(PPh_3)_4](BF_4)_2 \cdot (CH_3)_2CO$ with an equimolar quantity of Na(acac) in warmed CH_3OH–acetone (yield 100%); mp 164.5 °C. Anal. Calcd for $[Pd(CH_3COCHCOCH_3)(PPh_3)_2](BF_4) \cdot (CH_3)_2CO$: C, 60.40; H, 5.18. Found: C, 60.40; H, 4.74. The $PF_6{}^-$ salt was prepared analogously (yield 90%). Anal. Calcd for $[Pd(CH_3COCHCOCH_3)(PPh_3)_2](PF_6) \cdot (CH_3)_2CO$: C, 56.27; H, 4.26. Found: C, 56.53; H, 4.30. IR (Nujol mull): ν(CO) of the acetone of solvation 1709 cm^{-1}.

Bis(triphenylphosphine)(methyl acetoacetato)palladium(II) Complex, $[Pd(CH_3COCHCOOCH_3)(PPh_3)_2](BF_4)$. A 1.1-g quantity of $Pd(PPh_3)_4$ was dissolved in 20 mL of benzene, and a solution of 15 mL of acetone containing 0.33 g of CPh_3BF_4 and 0.5 g of methyl acetoacetate was added to the solution. After the solution was agitated for 48 h, the solvents were removed under reduced pressure to about one-fifth of the total volume. Addition of diethyl ether to the residue solution gave yellow prisms, which were recrystallized from acetone–ether (0.8 g, 100%); mp 124.5 °C. Anal. Calcd for $[Pd(CH_3COCHCOOCH_3)(PPh_3)_2](BF_4)$: C, 59.12; H, 4.48. Found: C, 60.24; H, 4.36.

Hexaphenylethane, $C_2(C_6H_5)_6 \cdot CH_2Cl_2$. In each reaction of $Pd(PPh_3)_4$ with CPh_3X (X = $BF_4{}^-$, $PF_6{}^-$), the residue solution of the second filtrate gave white crystals of hexaphenylethane (HPE), which were recrystallized from CH_2Cl_2; mp 147–149 °C. Anal. Calcd for $C_2(C_6H_5)_6 \cdot CH_2Cl_2$: C, 81.94; H, 5.64. Found: C, 82.33; H, 5.67. ^1H NMR ($CDCl_3$): δ 3.80 (4 H).

Table II. ^1H NMR Data of $[Pd(1,10\text{-phen})_2(PPh_3)](X)_2$

complex	chemical shifts				$J_{H,H}$, Hz
	2,9-H	4,7-H	5,6-H	3,8-H	
1,10-phen^a	9.12 dd	8.48 dd	8.00 s	7.76 dd	$J_{2,3} = J_{8,9} = 4.5$, $J_{2,4} = J_{9,7} = 1.5$, $J_{3,4} = J_{7,8} = 8.0$
$X = BF_4{}^{-\,b}$	9.12 dd	8.72 dd	8.10 s	7.82 dd	$J_{2,3} = J_{8,9} \approx 4.3$, $J_{2,4} = J_{9,7} \approx 2.3$, $J_{3,4} = J_{7,8} \approx 9.0$
$X = PF_6{}^{-\,b}$	8.88 dd	8.75 dd	8.17 s	7.75 dd	$J_{2,3} = J_{8,9} \approx 5.4$, $J_{2,4} = J_{9,7} \approx 1.9$, $J_{3,4} = J_{7,8} \approx 9.8$

[a] Measured in $Me_2SO\text{-}d_6$. [b] Measured in acetone-d_6.

Results and Discussion

A simple oxidation of $Pd(PPh_3)_4$ with the organic acid CPh_3X (X = $BF_4{}^-$, $PF_6{}^-$) gave tetrakis(triphenylphosphine)palladium(II) in good yield. Also tetrakis(triphenyl phosphite)palladium(II) was isolated from the reaction of $Pd(P(OPh)_3)_4$ with CPh_3PF_6. Some physical properties of these cationic complexes are shown in Table I. With 1,5-cyclooctadiene, vinyl ketone, carbon monoxide, and acetic acid, they showed no loss of phosphine and phosphite. But with the hard base of an N-heterocyclic ligand, 1,10-phenanthroline, the novel five-coordinated complex $[Pd(1,10\text{-phen})_2(PPh_3)](X)_2$ was obtained in good yield.

^1H NMR data of $[Pd(1,10\text{-phen})_2(PPh_3)]^{2+}$, as shown in Table II, exhibit that the halves of ligand 1,10-phen are equivalent in solution of the NMR time scale. The chemical shifts were assigned from coupling constants and integral ratio based on those of the free ligand.[7] The aromatic protons of PPh_3 have the proper chemical shifts for Pd^{II}–PPh_3, medial main signal showing at 7.3–7.5 ppm. These data coincide well with those of the analogous cyano complex[8] $[Pt(1,10\text{-phen})_2(CN)]^+$. An X-ray crystal analysis and ^{13}C and ^{31}P

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NMR data of the dication Pd complexes having neutral ligands are now being obtained, with the addition of analogous complexes of phenanthroline derivatives.

In contrast to the phosphine complexes, the analogous dication complex of phosphite reacted with 1,10-phenanthroline stoichiometrically to give $[Pd(1,10\text{-phen})_2](PF_6)_2$.

When an acetone solution of $[Pd(PPh_3)_4](X)_2$ was refluxed in the presence of acetylacetone or its sodium salt, $[Pd(CH_3COCHCOCH_3)(PPh_3)_2](X)$ was obtained in good yield. IR and NMR show acetylacetonate and methyl acetoacetate (prepared by the Experimental Section procedure) coordinated to Pd(II) with Pd(II)–O bonding in the chelate. The methyl acetoacetate complex is less thermally stable in organic halide solvents than the acetylacetonate complex, and it slowly decomposes to palladium black metal in solution. Both complexes exhibited some lability, and with 2,2′-bipyridine, bpy-substituted products, $[Pd(CH_3COCHCO\text{–}R)(2,2'\text{-bpy})](BF_4)$,[9] which are insoluble in organic solvents, were obtained.

Oxidative-addition reactions of $M(PPh_3)_4$ (M = Pd, Pt) proceed via the predominant species $[M(PPh_3)_3]$ (M = Pd,[10] Pt[11,12]). In each reaction of $Pd(PPh_3)_4$ with CPh_3X ($X = BF_4^-, PF_6^-$), the organic product hexaphenylethane (HPE, now well-known as to have a methylenecyclohexadiene structure[13,14]) was isolated in good yield from the second residue solution separated from the complexes.

It is reasonable that the oxidation reaction of $Pd(L)_4$ ($L = PPh_3, P(OPh)_3$) by the attack of the carbocation CPh_3^+ proceeds in two steps, e.g., those shown in Figure 1: first via the paramagnetic species $[Pd(\text{–}CPh_3)(PPh_3)_3]$ and then through the diamagnetic compound $[Pd(\text{–}CPh_3)_2(PPh_3)_3]$, the latter forming $[Pd(PPh_3)_4]^{2+}$ and trityl radical by dissociation, alternatively first by $[Pd(PPh_3)_3]^+$ and then by $[Pd(PPh_3)_4]^{2+}$, both giving trityl radical.

The preparation of the ionic hydride complex $[Pd(PPh_3)_3H]X$ ($X = ClO_4^-, HSO_4^-, Cl^-$, or BF_4^-) prompted me to isolate the analogous complex $[Pd(PPh_3)_3(\text{–}CPh_3)]X$, but I have not succeeded, possibly because of its extreme lability if it is produced.

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Registry No. $[Pd(PPh_3)_4](BF_4)_2$, 80583-63-7; $[Pd(PPh_3)_4](PF_6)_2$, 80583-64-8; $[Pd(P(OPh)_3)_4](PF_6)_2$, 80583-66-0; $[Pd(1,10\text{-phen})_2(PPh_3)](BF_4)_2$, 80583-68-2; $[Pd(1,10\text{-phen})_2(PPh_3)](PF_6)_2$, 80583-69-3; $[Pd(acac)(PPh_3)_2](BF_4)$, 33680-09-0; $[Pd(acac)(PPh_3)_2](PF_6)$, 80583-70-6; $[Pd(maac)(PPh_3)_2](BF_4)$, 80583-72-8; $[Pd(acac)(2,2'\text{-bpy})](BF_4)$, 80583-74-0; $[Pd(maac)(2,2'\text{-bpy})](BF_4)$, 80583-76-2; $Pd(PPh_3)_4$, 14221-01-3; $Pd(P(OPh)_3)_4$, 22372-54-9; $C_2(C_6H_5)_6$, 17854-07-8.

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