# Reactions of Acyl(phosphonato)palladium Complexes, $Pd(PMe_3)_2\{C(O)R'\}\{P(O)(OR)_2\}$, with an Alkyl Cation, Yielding Cationic Phosphite Complexes, and with Acid Chlorides, Involving Facile $Pd–P(O)(OR)_2$ Bond Cleavage

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Acyl(phosphonato)palladium complexes, $Pd(PMe_3)_2\{C(O)Ph\}\{P(O)(OR)_2\}$ (R = Et (**1a**), Me (**1b**)), react with $Et_3OBF_4$ below room temperature at the phosphoryl oxygen to give cationic palladium phosphite complexes, $[Pd(PMe_3)_2\{C(O)Ph\}\{P(OEt)(OR)_2\}]BF_4$ (R = Et (**2a**), Me (**2b**)), in good yields, indicating that the phosphoryl oxygen in **1** is more nucleophilic than the benzoyl oxygen. The reaction of **1** with acid chlorides, R′C(O)Cl (R′ = Ph, Me), proceeds rapidly even at 0 °C to give $Pd(PMe_3)_2\{C(O)Ph\}Cl$ and $P(OR)_2\{OC(O)R'\}$ with the Pd–C(O)Ph bond in **1** intact, and with facile $Pd–P(O)(OR)_2$ bond cleavage. The reaction mechanism is discussed. Complex **1** shows no reaction with MeI (below 10 °C) and with ketones (at room temperature). Complexes **1a** and **2a** were characterized by single-crystal X-ray diffraction analyses. Crystal data for **1a**: space group $P2_1$, $a = 11.966(3)$ Å, $b = 9.619(2)$ Å, $c = 10.462(3)$ Å, $\beta = 101.72(2)°$, $Z = 2$, 2699 reflections, $R = 0.038$. Crystal data for **2a**: space group $P\bar{1}$, $a = 10.782(2)$ Å, $b = 10.820(2)$ Å, $c = 13.255(2)$ Å, $\alpha = 84.20(1)°$, $\beta = 79.39(1)°$, $\gamma = 69.94(1)°$, $Z = 2$, 5518 reflections, $R = 0.045$.

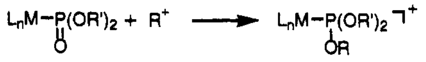
## Introduction

During the course of our studies on the reactions of coordinatively unsaturated group 10 transition-metal complexes with α-keto phosphonates, $R'C(O)P(O)(OR)_2$,[1,2] we found that the C–P bond in $R'C(O)P(O)(OR)_2$ is oxidatively added to 14-electron $Pd(PMe_3)_2$ species to give *trans*-$Pd(PMe_3)_2\{C(O)R'\}\{P(O)(OR)_2\}$. The palladium complex is attracting attention due to the presence of a covalent bond between a transition metal and a pentavalent phosphorus atom. Some $Pd–P(O)Z_2$ (Z = R, OR) type complexes have already been reported,[3] but their reactivity has scarcely been detailed so far.

The reaction of *trans*-$Pd(PMe_3)_2\{C(O)R'\}\{P(O)(OR)_2\}$ with a Lewis acid such as $R^+$ is interesting because the palladium complex has potentially two reactive sites; acyl oxygen and phosphoryl oxygen. An anionic transition-metal acyl complex is well-known to react with $R^+$ at the acyl oxygen to give a Fischer-type carbene complex.[4a] The same type of reaction can be performed even with stable neutral acyl complexes, producing cationic carbene complexes (eq 1).[4b]


(1)

It has been reported that iron phosphonato complexes react with $R^+$ at the phosphoryl oxygen to give cationic phosphite complexes (eq 2).[5]


$$L_nM{-}\underset{\displaystyle \| \atop O}{P}(OR')_2 + R^+ \longrightarrow \left[L_nM{-}\underset{\displaystyle | \atop OR}{P}(OR')_2\right]^+ \qquad (2)$$

In the reaction of *trans*-$Pd(PMe_3)_2\{C(O)R'\}\{P(O)(OR)_2\}$ with $R^+$, if the acyl oxygen is more reactive toward $R^+$ than the phosphoryl oxygen is, a cationic Fischer-type carbene complex with a phosphonato ligand would be formed (Scheme 1(i)). On the other hand, if the phosphoryl oxygen is more reactive, a cationic phosphite complex with an acyl ligand would be prepared (Scheme 1(ii)).

Reactions of $PdL_2R_2$ type complexes (L stands for a two-electron donor such as phosphine or amine, and R stands for a one-electron donor such as alkyl, silyl, or halogen) with alkyl halides or acid chlorides have been well investigated. For example, the reactions of $PdL_2Me_2$ with MeI have been reported to form $PdL_2(Me)I$ and ethane. In these reactions a hexacoordinate Pd(IV) complex is isolated when $L_2$ is a bidentate diamine ligand (eq 3)[6] and is postulated as an intermediate when L is a

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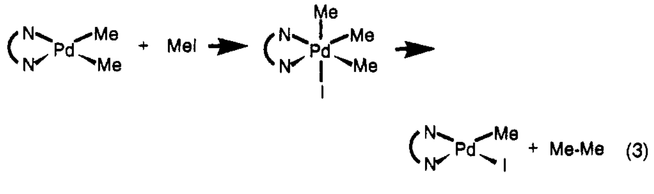
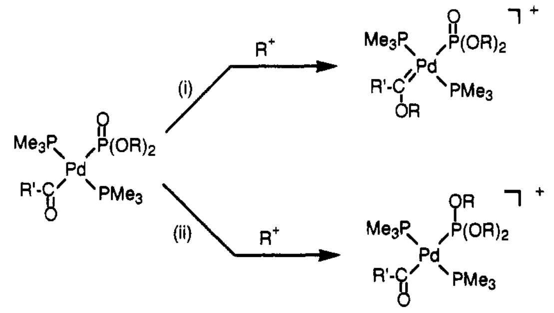


$$PdL_2R_2 + R'X \longrightarrow PdL_2R'X + R\text{-}R \qquad (4)$$

**Scheme 1**

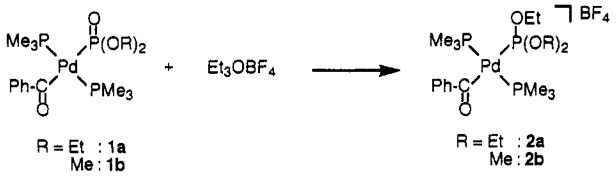


tertiary phosphine (eq 4).[7] *trans*-Pd(PMe$_3$)$_2${C(O)R′}{P(O)(OR)$_2$} is also a complex containing two two-electron-donor ligands (PMe$_3$) and two one-electron-donor ligands (acyl and phosphonato ligands). Therefore, it is interesting to compare PdL$_2$R$_2$ and PdL$_2${C(O)R′}{P(O)(OR)$_2$} in their reactivities with alkyl halides or acid chlorides.

In this paper, we report the reactions of *trans*-Pd(PMe$_3$)$_2${C(O)Ph}{P(O)(OR)$_2$} (R = Et (**1a**), Me (**1b**)) with Et$^+$, MeI, PhC(O)Cl, and MeC(O)Cl. We also report the crystal structures of one of the starting complexes, **1a**, and one of the products, *trans*-[Pd(PMe$_3$)$_2${C(O)Ph}{P(OEt)$_3$}]BF$_4$ (**2a**).

## Results and Discussion

**Reactions with Et$_3$OBF$_4$.** Complex **1** was dissolved in toluene, and the solution was cooled to −60 °C. Addition of a CH$_2$Cl$_2$ solution containing Et$_3$OBF$_4$ resulted in the formation of yellow crystals. The heterogeneous reaction mixture was warmed to room temperature and stirred for 30 min to complete the reaction. The product was the cationic phosphite complex **2** (eq 5). Table 1 summarizes IR ($\nu_{CO}$), $^1$H NMR, and $^{31}$P{$^1$H} NMR data for the palladium complexes formed, together with data for the starting complexes.



(5)

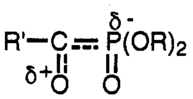
For **2a**, the IR spectrum showed a strong absorption at 1638 cm$^{-1}$, which is assigned to $\nu_{CO}$ of the acyl group coordinating to the palladium. The value is about 34 cm$^{-1}$ higher in frequency than that of the starting complex, which is consistent with the X-ray observation (vide infra) that the C=O bond distance of **2a** is shorter than that of **1a**. The $^{31}$P NMR spectrum showed two resonances mutually coupled with a $J$ value of 77.2 Hz: one is a doublet at −18.68 ppm, and the other is a triplet at 122.22 ppm. The former resonance is due to PMe$_3$, and the latter is attributed to P(OEt)$_3$. The methyl protons in the PMe$_3$ ligands were observed, in the $^1$H NMR spectra, as a virtual triplet with P–H coupling ($J$ = 3.91 Hz). The $^{31}$P and $^1$H NMR data strongly indicate that the product is a square-planar Pd complex with a trans configuration. Complex **2b** showed a similar spectroscopic tendency.

The formation of cationic Pd complexes having mutually trans phosphite and benzoyl ligands was confirmed also by the $^{13}$C NMR spectrum and X-ray diffraction analysis for **2a**. $^{13}$C NMR (in CDCl$_3$): $\delta$ 242.17 (d, $J_{CP}$ = 168.4 Hz, CO), 141.99 (dt, $J_{CP}$ = 53.8, 14.7 Hz, ipso-C$_6$H$_5$), 133.62 (s, *p*-C$_6$H$_5$), 129.59 (s, *o*-C$_6$H$_5$), 129.20 (s, *m*-C$_6$H$_5$), 65.62 (d, $J_{CP}$ = 24.4 Hz, POCH$_2$CH$_3$), 16.35 (d, $J_{CP}$ = 4.9 Hz, POCH$_2$CH$_3$), 15.27 (t, $J_{CP}$ = 15.9 Hz, PCH$_3$). The X-ray structure will be discussed later.

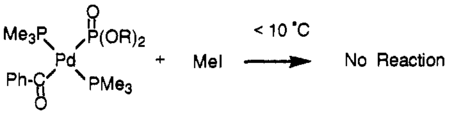
The reaction depicted in eq 5 is very clean and almost quantitative. However, it is difficult to isolate **2** in a pure form in the presence of excess Et$_3$OBF$_4$. The problem could be overcome by using 0.8 equiv of Et$_3$OBF$_4$ based on the starting Pd complex. The isolation yield of **2a** was 80% based on the Pd complex and 96% based on Et$_3$OBF$_4$, and that of **2b** was 73% and 89% based on the Pd complex and Et$_3$OBF$_4$, respectively.

In the reaction of **1** with Et$^+$, a cationic carbene complex expected to form by the nucleophilic attack of the benzoyl oxygen at Et$^+$ (Scheme 1(i)) was not observed at all. Therefore, it is concluded that the phosphoryl oxygen in **1** is more nucleophilic than the benzoyl oxygen.

It has been proposed that there is a p$\pi$–d$\pi$ conjugation in $\alpha$-keto phosphonates which leads to the enhancement and reduction of electron density on the phosphoryl phosphorus and on the carbonyl group, respectively, as depicted below.[8] The similar p$\pi$–d$\pi$ interaction between a p orbital of the carbonyl group and a d orbital of the phosphorus via a palladium d orbital is expected in **1**, which may explain the weaker basicity of the carbonyl oxygen as compared to the phosphoryl oxygen. The observation in the X-ray analyses that the C–O bond distance of the carbonyl group in **1a** (1.24(1) Å) is longer, through marginally, than that in **2a** (1.207(5) Å) (vide infra) is consistent with the existence of the p$\pi$–d$\pi$ interaction.



**Reactions with MeI and Acid Chlorides.** The reaction of **1** with up to 6 equiv of MeI in CH$_2$Cl$_2$ was attempted, but no reaction was observed below 10 °C (eq 6). Above 10 °C, some complicated reactions took place,



(6)

but neither PhC(O)Me nor MeP(O)(OR)$_2$ was observed, both of which were expected to form by an oxidative-addition–reductive-elimination reaction involving Pd(IV) complexes.

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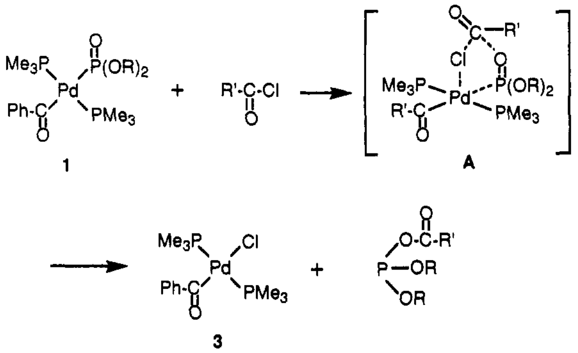
Table 1. Spectroscopic Data

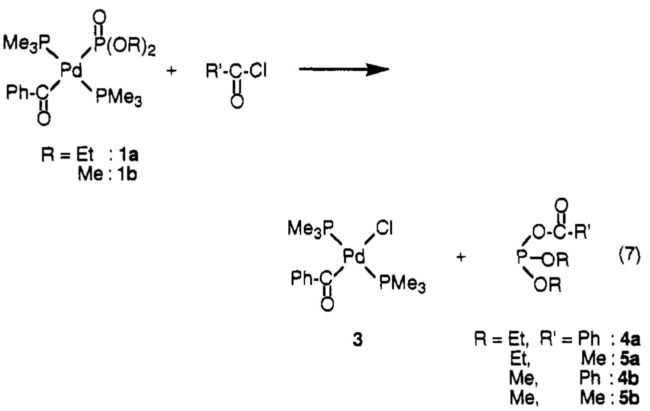
| complex | IR ($\nu_{CO}$), cm$^{-1}$ | $^1$H NMR, ppm | $^{31}$P NMR, ppm |
|---|---|---|---|
| **1a** | 1619$^a$<br>1604 | 8.16 (d, $J$ = 7.32 Hz, 2H, $C_6H_5$)$^d$<br>7.16 (m, 3H, $C_6H_5$)<br>4.33 (dquin, $J$ = 9.77, 7.32 Hz, 2H, $OCH_2$)<br>4.10 (dquin, $J$ = 10.25, 6.83 Hz, 2H, $OCH_2$)<br>1.28 (t, $J$ = 6.84 Hz, 6H, $OCH_2CH_3$)<br>1.13 (t, $J$ = 3.91 Hz, 18H, $PCH_3$) | 88.18 (t, $J_{PP}$ = 74.2 Hz, $P(O)(OEt)_2$)$^c$<br>–18.18 (d, $J$ = 74.2 Hz, $PMe_3$) |
| **1b** | 1604$^a$ | 8.14 (d, $J$ = 7.81 Hz, 2H, $C_6H_5$)$^d$<br>7.16 (m, 3H, $C_6H_5$)<br>3.70 (d, $J$ = 10.26 Hz, 6H, $OCH_3$)<br>1.11 (t, $J$ = 3.66 Hz, 18H, $PCH_3$) | 89.22 (t, $J_{PP}$ = 75.7 Hz, $P(O)(OMe)_2$)$^c$<br>–18.35 (d, $J_{PP}$ = 75.7 Hz, $PMe_3$) |
| **2a** | 1638$^b$ | 7.92 (d, $J$ = 3.90 Hz, 2H, $C_6H_5$)$^e$<br>7.58 (m, 3H, $C_6H_5$)<br>4.21 (quin, $J$ = 6.84 Hz, 6H, $POCH_2CH_3$)<br>1.43 (t, $J$ = 6.84 Hz, 9H, $POCH_2CH_3$)<br>1.34 (t, $J$ = 3.91 Hz, 18H, $PCH_3$) | 122.22 (t, $J_{PP}$ = 77.2 Hz, $P(OEt)_3$)$^b$<br>–18.68 (d, $J_{PP}$ = 77.2 Hz, $PMe_3$) |
| **2b** | 1637$^b$ | 7.93 (m, 2H, $C_6H_5$)$^e$<br>7.59 (m, 3H, $C_6H_5$)<br>4.22 (quin, $J$ = 6.84 Hz, 2H, $POCH_2CH_3$)<br>3.87 (d, $J$ = 11.72 Hz, 6H, $POCH_3$)<br>1.44 (t, $J$ = 6.84 Hz, 3H, $POCH_2CH_3$)<br>1.33 (t, $J$ = 3.91 Hz, 18H, $PCH_3$) | 125.49 (t, $J_{PP}$ = 77.2 Hz, $P(OEt)(OMe)_2$)$^b$<br>–17.85 (d, $J_{PP}$ = 77.2 Hz, $PMe_3$) |
| **3** | 1636$^c$ | 8.14 (d, $J$ = 5.86 Hz, 2H, $C_6H_5$)$^e$<br>7.45 (m, 3H, $C_6H_5$)<br>1.27 (t, $J$ = 3.66 Hz, 18H, $PCH_3$) | –19.21 (s)$^c$ |

$^a$ In $C_6H_6$. $^b$ In $CH_2Cl_2$. $^c$ In $C_6H_5CH_3$. $^d$ In $C_6D_6$. $^e$ In $CDCl_3$.

Scheme 2



In contrast, reactions of 1 with acid chlorides proceeded rapidly even at 0 °C (eq 7). The reaction of **1a** with equimolar PhC(O)Cl at 0 °C gave *trans*-$Pd(PMe_3)_2\{C(O)Ph\}Cl$ (**3**) and $P(OEt)_2\{OC(O)Ph\}$ (**4a**). The reaction of **1a** with MeC(O)Cl yielded **3** and $P(OEt)_2\{OC(O)Me\}$ (**5a**). Complex **1b** reacted with PhC(O)Cl to give **3** and $P(OMe)_2\{OC(O)Ph\}$ (**4b**) and with MeC(O)Cl to give **3** and $P(OMe)_2\{OC(O)Me\}$ (**5b**), similarly.



In every reaction, **3** was isolated as yellow crystals from the reaction mixture. The IR, $^1$H NMR, and $^{31}$P{$^1$H} NMR data are listed in Table 1 and agree well with those for $Pd(PMe_3)_2\{C(O)Ph\}Cl$ reported previously.[9]

The phosphorus-containing products were characterized by $^{31}$P{$^1$H} NMR and GCMS spectroscopy. The $^{31}$P NMR spectra of the reaction mixtures showed two singlets: 135.13 and –19.21 ppm for the reaction of **1a** with PhC(O)Cl, 137.02 and –19.21 ppm for the reaction of **1b** with PhC(O)Cl, 134.49 and –19.21 ppm for the reaction of **1a** with MeC(O)Cl, and 136.36 and –19.21 ppm for the reaction of **1b** with MeC(O)Cl. The common signal observed at –19.21 ppm is ascribed to **3**. The other singlet observed near 135 ppm may be assigned to a phosphite. The formation of $PhC(O)P(O)(OR)_2$ expected by reductive elimination from 1 can be ruled out, because the $^{31}$P NMR chemical shift is –0.58 ppm for R = Et and –0.42 ppm for R = Me.[1] The plausible candidates were $P(OR)_2(OR')$ and $P(OR)_2\{OC(O)R'\}$. Thus, we prepared $P(OEt)_2(OPh)$ from $P(OEt)_2Cl$ and PhOH and $P(OEt)_2\{OC(O)Ph\}$ from $P(OEt)_2Cl$ and PhC(O)ONa. The $^{31}$P NMR chemical shifts were observed at 136.36 ppm for $P(OEt)_2(OPh)$ and at 134.98 ppm for $P(OEt)_2\{OC(O)Ph\}$. The differences is only 1.4 ppm, which might cause incorrect assignment of the phosphorus-containing products in our reactions. Therefore, the GCMS spectra were measured, and it was found that GCMS could offer more definitive evidence. The mass spectrum of $P(OEt)_2(OPh)$ displays the following signals: $m/z$ 214 (parent ion $[M]^+ = [C_{10}H_{15}O_3P]^+$), 186 ($[M - C_2H_4]^+$), 169 ($[M - OC_2H_5]^+$), 158 ($[M - 2C_2H_4]^+$), 141 ($[M - OC_2H_5 - C_2H_4]^+$), 121 ($[M - OC_6H_5]^+$), 93 ($[OC_6H_5]^+$), 77 ($[C_6H_5]^+$), 65 ($[P(OH)_2]^+$). Prominent signals in the mass spectrum of $P(OEt)_2\{OC(O)Ph\}$ include the following: $m/z$ 242 (parent ion $[M]^+ = [C_{11}H_{15}O_4P]^+$), 122 ($[M - CH_3 - C(O)C_6H_5]^+$), 105 ($[C(O)C_6H_5]^+$), 81 ($[P(OH)_2O]^+$), 77 ($[C_6H_5]^+$), 65 ($[P(OH)_2]^+$). The reaction mixture showed the same mass spectrum as that of $P(OR)_2\{C(O)R\}$, and no spectrum due to $P(OR)_2(OR)$ was observed. Therefore, the exclusive formation of $P(OR)_2\{OC(O)R\}$ was proved in the reaction of eq 7.

Since **3** was formed in the reaction of **1** with $CH_3C(O)Cl$ as well as with PhC(O)Cl, a PhC(O)–Pd bond in **1** remains intact during the reaction. The mechanism of eq 7 is

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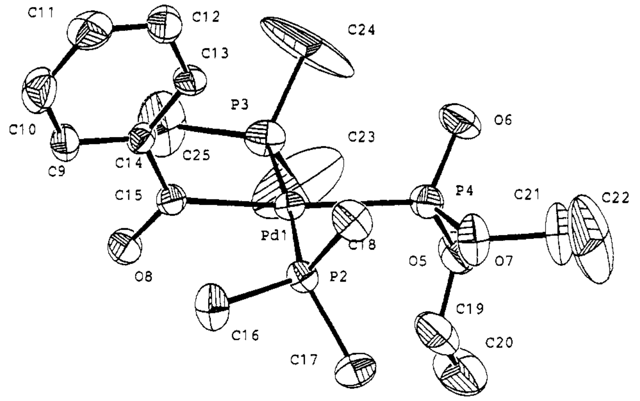


**Figure 1.** ORTEP diagram of **1a** with probability ellipsoids drawn at the 30% level.

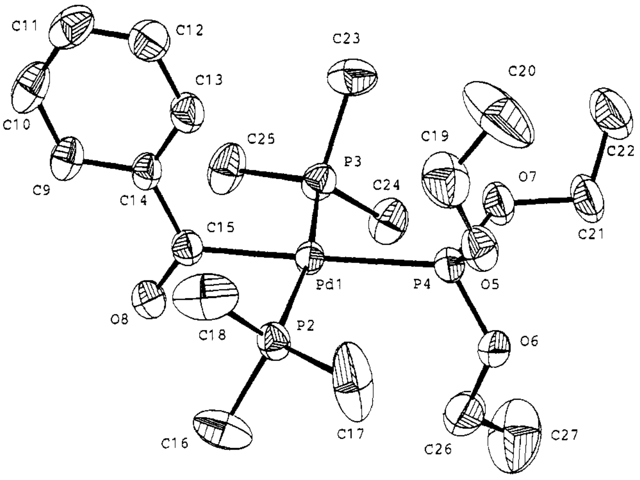
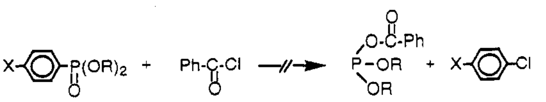


**Figure 2.** ORTEP diagram of **2a** (the $BF_4^-$ counterion is omitted for clarity). Thermal ellipsoids are drawn at the 30% probability level.

considered, as shown in Scheme 2. Since the phosphoryl oxygen in **1** is very nucleophilic, as shown in eq 5, the oxygen nucleophilically attacks the carbonyl carbon in acid chloride to induce the nucleophilic attack of the lone pair on chloride in acid chloride to the palladium leading to the transition state (**A**) involving the O···C and Cl···Pd interactions. Then, the Pd–P and C–Cl bonds are broken with the formation of the O–C and Cl–Pd bonds to give **3** and dialkyl acyl phosphite. We confirmed that the reaction of $RP(O)(OR)_2$ with acid chlorides did not form dialkyl acyl phosphite and RCl (eq 8). Therefore, the reaction forming dialkyl acyl phosphite is characteristic of a transition-metal complex.



(8)

Complex **1** did not react with ketones such as acetone, acetophenone, and benzophenone, which indicates that both of the above two concerted interactions are important for the reaction to proceed.

**Molecular Structures of 1a and 2a.** The single-crystal structures of **1a** and **2a** have been determined by X-ray diffraction. The ORTEP drawings of **1a** and **2a** are displayed in Figures 1 and 2, respectively. The crystal data for **1a** and **2a** are summarized in Table 2. Their selected bond distances and angles are listed in Table 3 for **1a** and in Table 4 for **2a**.

**Table 2. Summary of Crystal Data for 1a and 2a**

| | **1a** | **2a** |
|---|---|---|
| formula | $C_{17}H_{33}O_4P_3Pd$ | $C_{19}H_{38}BF_4O_4P_3Pd$ |
| fw | 500.80 | 616.70 |
| cryst syst | monoclinic | triclinic |
| space group | $P2_1$ | $P\bar{1}$ |
| cell constants | | |
| $a$, Å | 11.966(3) | 10.782(2) |
| $b$, Å | 9.619(2) | 10.820(2) |
| $c$, Å | 10.462(3) | 13.255(2) |
| $\alpha$, deg | | 84.20(1) |
| $\beta$, deg | 101.72(2) | 79.39(1) |
| $\gamma$, deg | | 69.94(1) |
| $V$, Å$^3$ | 1179.0(5) | 1426.5(3) |
| $Z$ | 2 | 2 |
| $D_{calcd}$, g cm$^{-3}$ | 1.41 | 1.43 |
| $\mu$, cm$^{-1}$ | 9.08 | 7.76 |
| cryst size, mm | 0.65 × 0.32 × 0.10 | 0.47 × 0.40 × 0.10 |
| radiation | Mo K$\alpha$ ($\lambda$ = 0.710 73 Å) | Mo K$\alpha$ ($\lambda$ = 0.710 73 Å) |
| scan technique | $\omega$–$2\theta$ | $\omega$–$2\theta$ |
| scan range, deg | $3 < 2\theta < 55$ | $3 < 2\theta < 55$ |
| scan rate, deg min$^{-1}$ | 6.0 | 6.0 |
| no. of unique data | 2877 | 6535 |
| no. of unique data, $F_o > 3\sigma(F_o)$ | 2699 | 5518 |
| $R$ | 0.038 | 0.045 |
| $R_w$ | 0.044 | 0.042 |

**Table 3. Selected Bond Distances (Å) and Angles (deg) for 1a**

| Bond Distances | | | |
|---|---|---|---|
| Pd(1)–P(2) | 2.323(2) | O(5)–C(19) | 1.40(1) |
| Pd(1)–P(3) | 2.315(3) | O(7)–C(21) | 1.46(1) |
| Pd(1)–P(4) | 2.368(2) | O(8)–C(15) | 1.24(1) |
| Pd(1)–C(15) | 2.050(7) | C(9)–C(10) | 1.37(2) |
| P(2)–C(16) | 1.814(9) | C(9)–C(14) | 1.40(1) |
| P(2)–C(17) | 1.82(1) | C(10)–C(11) | 1.40(2) |
| P(2)–C(18) | 1.819(9) | C(11)–C(12) | 1.36(1) |
| P(3)–C(23) | 1.77(2) | C(12)–C(13) | 1.39(1) |
| P(3)–C(24) | 1.70(1) | C(13)–C(14) | 1.38(1) |
| P(3)–C(25) | 1.86(1) | C(14)–C(15) | 1.49(1) |
| P(4)–O(5) | 1.602(9) | C(19)–C(20) | 1.43(2) |
| P(4)–O(6) | 1.504(6) | C(21)–C(22) | 1.21(3) |
| P(4)–O(7) | 1.607(8) | | |
| **Bond Angles** | | | |
| C(15)–Pd(1)–P(2) | 87.8(3) | O(5)–P(4)–O(6) | 103.0(5) |
| C(15)–Pd(1)–P(3) | 87.1(3) | O(6)–P(4)–O(7) | 108.8(5) |
| P(2)–Pd(1)–P(4) | 94.31(9) | O(5)–P(4)–O(7) | 102.7(4) |
| P(4)–Pd(1)–P(3) | 90.9(1) | P(4)–O(5)–C(19) | 118.5(8) |
| Pd(1)–P(2)–C(16) | 117.3(3) | O(5)–C(19)–C(20) | 113(1) |
| Pd(1)–P(2)–C(17) | 116.7(3) | P(4)–O(7)–C(21) | 123.1(8) |
| Pd(1)–P(2)–C(18) | 112.6(3) | O(7)–C(21)–C(22) | 121(1) |
| C(16)–P(2)–C(17) | 101.2(4) | Pd(1)–C(15)–O(8) | 122.7(7) |
| C(17)–P(2)–C(18) | 104.7(4) | Pd(1)–C(15)–C(14) | 119.0(6) |
| C(16)–P(2)–C(18) | 102.4(4) | O(8)–C(15)–C(14) | 118.2(6) |
| Pd(1)–P(3)–C(23) | 116.7(8) | C(15)–C(14)–C(9) | 120.2(7) |
| Pd(1)–P(3)–C(24) | 119.5(8) | C(15)–C(14)–C(13) | 120.2(6) |
| Pd(1)–P(3)–C(25) | 118.3(5) | C(9)–C(14)–C(13) | 119.4(8) |
| C(23)–P(3)–C(24) | 97(1) | C(14)–C(9)–C(10) | 120.0(8) |
| C(24)–P(3)–C(25) | 104.8(9) | C(9)–C(10)–C(11) | 119.2(8) |
| C(23)–P(3)–C(25) | 96.2(8) | C(10)–C(11)–C(12) | 122(1) |
| Pd(1)–P(4)–O(5) | 115.3(3) | C(11)–C(12)–C(13) | 118.6(9) |
| Pd(1)–P(4)–O(6) | 116.0(3) | C(12)–C(13)–C(14) | 121.2(7) |
| Pd(1)–P(4)–O(7) | 109.9(3) | | |

It was found that both **1a** and **2a** have trans square-planar structures, which are consistent with the structures predicted from their spectroscopic data. A palladium and four coordinated atoms make a plane: the sum of bond angles around palladium is 360.11° for **1a** and 360.15° for **2a**. With **1a**, the two $PMe_3$ ligands are situated on the plane away from the phosphonato ligand (P(2)–Pd(1)–P(3) = 174.71°), which indicates that the phosphonato ligand is slightly bulkier than the benzoyl ligand. The bending is greater for **2a** (P(2)–Pd(1)–P(3) = 168.52°) than

**Table 4. Selected Bond Distances (Å) and Angles (deg) for 2a**

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Pd(1)–P(2) | 2.344(1) | O(8)–C(15) | 1.207(5) |
| Pd(1)–P(3) | 2.338(1) | C(9)–C(10) | 1.372(9) |
| Pd(1)–P(4) | 2.346(2) | C(9)–C(14) | 1.393(8) |
| Pd(1)–C(15) | 2.046(5) | C(10)–C(11) | 1.37(1) |
| P(2)–C(16) | 1.777(6) | C(11)–C(12) | 1.37(1) |
| P(2)–C(17) | 1.80(1) | C(12)–C(13) | 1.376(8) |
| P(2)–C(18) | 1.799(7) | C(13)–C(14) | 1.385(6) |
| P(3)–C(23) | 1.810(6) | C(14)–C(15) | 1.504(6) |
| P(3)–C(24) | 1.804(6) | C(19)–C(20) | 1.39(2) |
| P(3)–C(25) | 1.821(7) | C(21)–C(22) | 1.48(1) |
| P(4)–O(5) | 1.588(3) | C(26)–C(27) | 1.40(1) |
| P(4)–O(6) | 1.564(4) | B(28)–F(29) | 1.25(1) |
| P(4)–O(7) | 1.575(3) | B(28)–F(30) | 1.25(1) |
| O(5)–C(19) | 1.44(1) | B(28)–F(31) | 1.34(1) |
| O(6)–C(26) | 1.398(8) | B(28)–F(32) | 1.25(1) |
| O(7)–C(21) | 1.476(8) | | |
| | Bond Angles | | |
| C(15)–Pd(1)–P(2) | 83.9(1) | P(4)–O(5)–C(19) | 118.8(4) |
| C(15)–Pd(1)–P(3) | 85.5(1) | O(5)–C(19)–C(20) | 113.9(8) |
| P(2)–Pd(1)–P(4) | 95.92(4) | P(4)–O(6)–C(26) | 123.5(5) |
| P(4)–Pd(1)–P(3) | 94.83(4) | O(6)–C(26)–C(27) | 114.0(8) |
| Pd(1)–P(2)–C(16) | 110.5(2) | P(4)–O(7)–C(21) | 122.2(3) |
| Pd(1)–P(2)–C(17) | 119.7(4) | O(7)–C(21)–C(22) | 108.3(6) |
| Pd(1)–P(2)–C(18) | 116.0(2) | Pd(1)–C(15)–O(8) | 121.8(4) |
| C(16)–P(2)–C(17) | 103.7(4) | Pd(1)–C(15)–C(14) | 117.8(3) |
| C(17)–P(2)–C(18) | 101.4(5) | C(15)–C(14)–C(9) | 119.2(4) |
| C(16)–P(2)–C(18) | 103.8(4) | C(15)–C(14)–C(13) | 122.0(5) |
| Pd(1)–P(3)–C(23) | 112.3(2) | C(9)–C(14)–C(13) | 118.8(4) |
| Pd(1)–P(3)–C(24) | 115.3(2) | C(14)–C(9)–C(10) | 119.9(5) |
| Pd(1)–P(3)–C(25) | 117.8(2) | C(9)–C(10)–C(11) | 120.8(7) |
| C(23)–P(3)–C(24) | 104.8(3) | C(10)–C(11)–C(12) | 119.8(6) |
| C(24)–P(3)–C(25) | 101.1(3) | C(11)–C(12)–C(13) | 120.3(5) |
| C(23)–P(3)–C(25) | 103.9(3) | C(12)–C(13)–C(14) | 120.3(6) |
| Pd(1)–P(4)–O(5) | 116.2(2) | F(29)–B(28)–F(30) | 109.4(8) |
| Pd(1)–P(4)–O(6) | 119.3(2) | F(29)–B(28)–F(31) | 114(1) |
| Pd(1)–P(4)–O(7) | 113.2(1) | F(29)–B(28)–F(32) | 106.6(7) |
| O(5)–P(4)–O(6) | 96.0(2) | F(30)–B(28)–F(31) | 111.6(7) |
| O(6)–P(4)–O(7) | 105.1(2) | F(30)–B(28)–F(32) | 107(1) |
| O(5)–P(4)–O(7) | 104.6(2) | F(31)–B(28)–F(32) | 107.8(7) |

for **1a**, presumably owing to $P(OEt)_3$ being bulkier than $P(O)(OEt)_2$ and the $Pd–P(OEt)_3$ bond distance being shorter than that of $Pd–P(O)(OEt)_2$ (vide infra).

With **1a**, the carbonyl and phosphoryl groups are located in a near s-trans orientation (torsional angle O(6)–P(4)–C(15)–O(8) = 140.5°). This is distinct from the s-cis feature in a trans square-planar diacyl Pt complex, *trans*-$Pt(PPh_3)_2\{C(O)Ph\}\{C(O)Et\}$ (torsional angle O–C–C–O = 15.5°),[10] though the reason is not clear.

Some palladium complexes containing a $Pd—P(O)Z_2$ (Z = R, OR) fragment have been reported,[3] and three of them have been characterized by X-ray analysis.[3c,d,f] However, all of them have an additional $P(OH)Z_2$ ligand cis to the $P(O)Z_2$ ligand, and an intramolecular hydrogen bond $P{=}O\cdots H—O—P$) is formed between the two ligands. Therefore, **1a** is the first example of a $Pd—P(O)Z_2$—type complex without such a hydrogen bond, characterized by X-ray analysis.

As observed in the previous reports,[5b,11] the geometry of the phosphonato ligand in **1a** is distorted from an ideal tetrahedral angle by an opening of the $Pd—P{=}O$ angle to 116.0° and a concomitant closing of the O—P—O angle to 102.7°.

The observed P=O bond distance (1.504 Å) is a reasonable value compared with those of other $M—P(O)Z_2$ type complexes having no $P{=}O\cdots H—O—P$ hydrogen bond: 1.487 Å for $Cp(CO)_2Cr\{P(OMe)_3\}\{P(O)(OMe)_2\}$,[11c] 1.478 Å for $Cp(CO)_2Fe\{P(O)(CF_3)_2\}$,[12] 1.495 Å for $Cp(CO)_2Fe\{P(O)(OEt)_2\}$,[5b] 1.487 and 1.492 Å for $CpCo\{P(OMe)_3\}\{P(O)(OMe)_2\}_2$,[11b] 1.480 Å for $[CpCo(dppe)\{P(O)(OMe)_2\}]^+$,[13] 1.485 Å for $CpCoI\{PPh_2NHCH(Me)Ph\}\{P(O)(OMe)_2\}$,[11d] 1.499 Å for $CpCoI\{PPh_2NHCH(Me)Ph\}\{P(O)(OMe)Ph\}$,[11d] 1.48 Å for $CpCo(C_3F_7)\{PPh_2NHCH(Me)Ph\}\{P(O)\{OMe)_2\}$,[11e] 1.496 Å for $CpCo(CF_3)\{PPh_2NHCH(Me)Ph\}\{P(O)(OMe)Ph\}$,[14] 1.497 Å for $CpCo(C_3F_7)\{PPh_2NHCH(Me)Ph\}\{P(O)(OMe)Ph\}$,[14] 1.51 Å for $Pt(PPh_3)(NCR)(Ph)\{P(O)Ph_2\}$,[15] 1.46 Å for $Hg\{P(O)(OEt)_2\}_2$,[11a] and 1.44 Å for $HgCl\{P(O)(OEt)_2\}$.[16]

The Pd—P(phosphite) bond in **2a** (2.346 Å) is shorter than the Pd—P(phosphonato) bond in **1a** (2.368 Å), though the phosphite is bulkier than the phosphonato ligand. The reason for this observation may be due to the difference in electric charge between the two Pd complexes. **2a** assumes a plus charge, so that $P(OEt)_3$ is connected more strongly with the palladium.

It has been suggested that the trans influence of a $P(O)(OR)_2$ group is greater than that of a $P(OR)_3$ ligand.[17] Comparison of the structures **1a** and **2a** shows no difference in trans Pd–acyl bond lengths (2.050(7) Å (**1a**) and 2.046(5) Å (**2a**)). It could result from the cancellation of opposing effects: that is, as one goes from **1a** to **2a**, the pπ–dπ interaction between the acyl carbonyl and the phosphonato phosphorus via a palladium d orbital decreases, which should make the Pd–acyl bond lengthen, whereas $P(OR)_3$ having less trans influence than $P(O)(OR)_2$ makes the Pd–acyl bond shorten.

## Conclusion

The recent isolation of *trans*-$Pd(PMe_3)_2\{C(O)Ph\}\{P(O)(OR)_2\}$, which has an acyl ligand (one of the most important ligands in organometallic transition-metal complexes) and a phosphonato ligand (one of the typical phosphorus ligands with a covalent bond to a transition metal), permitted an evaluation of relative reactivities between the two ligands.

The formation of cationic phosphite complexes with an acyl ligand in the reaction with $Et^+$ revealed that the phosphoryl oxygen is more reactive than the acyl oxygen. This is presumably due to the difference in inherent nucleophilicity between the acyl oxygen and the phosphoryl oxygen but, in addition, might be due to the interaction between a filled p orbital of the carbonyl group and a vacant d orbital of the phosphorus atom via a palladium d orbital. The assumption is compatible with the X-ray results of **1a** and **2a**.

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The reaction with an acyl chloride yielded $Pd(PMe_3)_2\{C(O)Ph\}Cl$ and dialkyl acyl phosphite. The formation of the phosphite is characteristic of a transition-metal complex because $RP(O)(OR)_2$ does not react with acid chloride. The role of a transition metal in this reaction may be explained by a concerted participation of the two interactions between the phosphoryl oxygen and the carbonyl carbon in the acid chloride and between the chloride in the acid chloride and the palladium atom, rather than oxidative addition of acyl chloride at the C–Cl bond to give a palladium(IV) intermediate complex.

In the two reactions with $R^+$ and with acid chlorides, the acyl ligand in the starting complex remains unreacted. This is in contrast to the fact that a decarbonylation reaction of 1 takes place at the acyl ligand by a thermal reaction.[2b]

## Experimental Section

**General Remarks.** All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk tube techniques. All solvents used were purified by distillation: toluene and hexane were distilled from sodium metal, and $CH_2Cl_2$ was distilled from $P_2O_5$. All solvents were stored under a nitrogen atmosphere. *trans*-$Pd(PMe_3)_2\{C(O)Ph\}\{P(O)(OEt)_2\}$ (**1a**) and *trans*-$Pd(PMe_3)_2\{C(O)Ph\}\{P(O)(OMe)_2\}$ (**1b**) were prepared according to the literature methods.[2b] $P(OEt)_2\{OC(O)Ph\}$ and $P(OMe)_2\{OC(O)Ph\}$ were prepared by published procedures.[18]

IR spectra were recorded on a Shimadzu FTIR-4000 spectrometer. JEOL PMX-60, GSX-270, GSX-500, and EX-400 instruments were used to obtain $^1H$, $^{13}C$, and $^{31}P$ NMR spectra. $^1H$ and $^{13}C$ NMR data were referenced to $(CH_3)_4Si$, and $^{31}P$ NMR data were referenced to 85% $H_3PO_4$. A Shimadzu GCMS QP-2000 spectrometer was used to obtain mass spectra.

**Reaction of *trans*-$Pd(PMe_3)_2\{C(O)Ph\}\{P(O)(OEt)_2\}$ (1a) with $Et_3OBF_4$.** $Et_3OBF_4$ (50 mg, 0.26 mmol) was dissolved in 1.5 mL of $CH_2Cl_2$, and this solution was added to a solution of **1a** (157 mg, 0.31 mmol) in 3 mL of toluene cooled to −30 °C. The mixture was warmed to room temperature and stirred for about 30 min. Removal of $CH_2Cl_2$ under reduced pressure yielded yellow crystals, which were isolated by filtration, washed with 4 mL of toluene three times, and then dried in vacuo to give **2a** (155 mg, 0.25 mmol, 80% based on the Pd complex). Anal. Calcd for $C_{19}H_{38}BF_4O_4P_3Pd$: C, 37.01; H, 6.21. Found: C, 37.05; H, 6.22.

**Reaction of *trans*-$Pd(PMe_3)_2\{C(O)Ph\}\{P(O)(OMe)_2\}$ (1b) with $Et_3OBF_4$.** $Et_3OBF_4$ (51 mg, 0.27 mmol) was dissolved in 1.5 mL of $CH_2Cl_2$, and this solution was added to a solution of **1b** (155 mg, 0.33 mmol) in 1.5 mL of toluene cooled to −30 °C. The mixture was warmed to room temperature and stirred for about 30 min. Removal of $CH_2Cl_2$ under reduced pressure yielded yellow crystals, which were isolated by filtration, washed with 3 mL of toluene three times, and then dried in vacuo to give **2b** (141 mg, 0.24 mmol, 73% based on the Pd complex). Anal. Calcd for $C_{17}H_{34}BF_4O_4P_3Pd$: C, 34.69; H, 5.82. Found: C, 34.20; H, 5.72.

**Reaction of 1a and 1b with Acid Chlorides.** A solution of **1a** (48 mg, 0.096 mmol) in toluene (1.5 mL) was cooled to 0 °C, and $PhC(O)Cl$ (11.6 $\mu$L, 0.10 mmol) was added. After the solution was stirred for 1 h at room temperature, hexane (10 mL) was added and the solution was cooled in a refrigerator for one night to give **3** as yellow needle crystals (29 mg, 0.073 mmol, 76%). Reactions of **1b** with $PhC(O)Cl$, of **1a** with $MeC(O)Cl$, and of **1b** with $MeC(O)Cl$ generated **3** in yields of 70%, 70%, and 61%, respectively.

**X-ray Structure Determination for 1a and 2a.** Single crystals of **1a** and **2a** were mounted on a Mac Science MXC3 diffractometer and were irradiated with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å). Unit-cell dimensions were obtained by least squares from the angular settings of 24 accurately centered reflections with $31° < 2\theta < 35°$ and 31 reflections with $31° < 2\theta < 35°$ for **1a** and **2a**, respectively. Reflection intensities were collected in the usual manner at 25 °C, and 3 check reflections measured after every 100 reflections showed no decrease in intensity. $P2_1$ and $P\bar{1}$ were selected as space groups for **1a** and **2a**, respectively, which led to successful refinements.

The structures were solved by a direct method with the program Monte Carlo-Multan.[19] The positions of all hydrogen atoms were calculated by assuming idealized geometries. Absorption and extinction corrections were then applied,[20,21] and several cycles of a full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms led to final *R* values of 0.038 and 0.045 for **1a** and **2a**, respectively. All calculations were performed on a Titan 750 computer using the program system Crystan-G.[19]

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**Supplementary Material Available:** Additional structural data for complexes **1a** and **2a**, including tables of positional parameters and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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