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Synthesis and Identification by High-Pressure NMR Spectroscopy of the Cationic Square-Planar *cis*-Methyl(carbonyl)palladium Diphosphine Compound $[Pd(CH_3)(CO)\{(S,S)\text{-BDPP}\}]BF_4$, an Intermediate in CO Insertion into the Pd–Me Bond[†]

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As part of our study on the mechanism of asymmetric hydroesterification catalyzed by Pd complexes of chiral diphosphines, here we report on the synthesis and identification of the cationic square-planar *cis*-methyl(carbonyl)palladium diphosphine complex, $[Pd(Me)(CO)\{(S,S)\text{-BDPP}\}]BF_4$ (**3**)((S,S)-BDPP = (2S,4S)-2,4-bis(diphenylphosphino)pentane), which represents the first square-planar *cis*-alkyl(carbonyl)–transition-metal complex containing a chelating diphosphine and is the single observable intermediate in the formation of the appropriate CO inserted acyl complex.

Insertion of CO into a transition-metal–carbon σ-bond is an elementary step in the most important homogeneous catalytic processes utilizing CO, such as the oxo synthesis, acetic acid synthesis, olefin hydrocarboxylation, and olefin copolymerization.[1] It has been shown by extensive mechanistic studies that the CO insertion should proceed through intermediates in which the coordinated carbonyl and organic groups are situated in *cis* positions, in order that the organic groups can subsequently migrate to the coordinated carbonyl groups.[2] The 1,2-migration of an alkyl (or aryl group), and hence the CO insertion, can be facilitated by easing the dissociation of the alkyl group by the introduction of a phosphine ligand in a position *trans* to the alkyl group.[2c,d] *Cis*-alkyl or -aryl transition-metal carbonyls as direct intermediates in CO insertion are known in various six-,[2b,3] five-,[4] and four-coordinate[2e,l,5] complexes containing monodentate phosphines. A stable octahedral d^6 *cis*-methylFe(II)–carbonyl phosphine complex has also been described.[6] However, some of the catalytic processes with CO, such as asymmetric hydroformylation[7] and olefin copolymerization,[8] prefer the use of d^8 transition-metal compounds containing chelating bidentate ligands as catalysts. To our knowledge, a transition metal compound in which a *cis*-chelating diphosphine is planar with a coordinated alkyl or aryl and a carbonyl group where the alkyl or aryl group is not part of the ligand has never been synthesized nor spectroscopically characterized. Probably in most cases the elusiveness of such complexes is due to the facile migratory CO insertion taking place, as has been proposed in many instances,[1,2c,7-9] to give acyl complexes. Recently, several cationic *cis*-methyl(carbonyl)platinum and -palladium complexes with P–N bidentate ligands have been detected by low-temperature IR and NMR spectroscopy in this laboratory.[10] However, the latter compounds possess coordinated nitrogen instead of phosphorus atoms in position *trans* to the methyl groups. Thus, as argued, these compounds may not necessarily be direct intermediates for CO insertion, which might also be reflected in their relative stability.[10] On the other hand, reactive yet unusually stable acyl- and alkylpalladium(II) compounds have been obtained by employing rigid bidentate nitrogen ligands.[11]

As shown in Scheme I, solvated cationic methyl complexes **2**, containing the chiral chelating diphosphine (2S,4S)-2,4-bis(diphenylphosphino)pentane ((S,S)-BDPP),[12] can be readily formed by the reaction of $Pd(Me)(Cl)\{(S,S)\text{-BDPP}\}$,[13] (**1**) with $AgBF_4$ in solvent compositions containing water or MeOH. The coordination of water or MeOH in compounds **2** is inferred from the a significant high-frequency shift in the phosphorus signals of **2** as compared to those of **1**,[14] which is due to the weaker *trans*-influence of the coordinated solvent than that of Pd–Cl.[15] Compound **2** is not formed by using dry CH_2Cl_2 and $AgBF_4$; thus for its stability, the presence of a solvent such as water or MeOH is essential.

When the in situ formed $Pd(Me)(S)\{(S,S)\text{-BDPP}\}$ (**2**) was carbonylated with ^{13}CO in a high-pressure NMR tube[16] at 3 bar and 183 K,[17] ^{31}P NMR revealed the formation of one unique species which is not an acetyl complex. Since the lifetime of the species was about 8 h at 183 K and 100 min at 193 K, respectively, ^{13}C NMR could also be utilized for identification. By its chemical shift values and $^2J_{P,C}$ coupling constants in ^{31}P and ^{13}C NMR spectra the species has been unambiguously identified as the square-planar carbonyl compound **3**.[18] Concomitant with the decomposition of compound **3**, another compound was formed that again by its chemical shift and $^2J_{P,C}$ values in ^{31}P and ^{13}C NMR spectra and by its IR spectrum has been identified as

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(14) An amount of 30 mg of compound **1** and 9 mg of $AgBF_4$ were stirred in 2 mL of wet CD_2Cl_2 or in 2 mL of CD_2Cl_2–MeOH (1:1) for 30 min, the separated AgCl was subsequently filtered off, and the solution was transfered to a sapphire high-pressure NMR tube (see ref 16) under nitrogen atmosphere. ^{31}P NMR (CD_2Cl_2, 293 K): $[Pd(Me)(H_2O)(BDPP)]BF_4$, δ 45.5 (d), 8.7 (d, $^2J_{P,P} = 48$ Hz); $[Pd(Me)(MeOH)(BDPP)]BF_4$, δ 48.2 (d), 8.5 (d, $^2J_{P,P} = 48$ Hz).

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(17) After compound **2** was detected, the sapphire tube was pressurized with CO at dry ice temperature and immersed into the precooled NMR probe.

(18) $[Pd(Me)(^{13}CO)(BDPP)]$ BF_4 (**3**) ^{31}P NMR (CD_2Cl_2, 183 K): δ 29.8 (dd, $^2J_{C,P_A} = 115$ Hz, $^2J_{P_B,P_A} = 58$ Hz, P_A *trans* to ^{13}CO), 4.4 (dd, $^2J_{C,P_B} = 13.4$ Hz, $^2J_{P_A,P_B} = 58$ Hz). ^{13}C NMR (at the carbonyl region, 183 K): δ 181.9 (dd, $^2J_{P_A,C} = 115$ Hz, $^2J_{P_B,C} = 13.4$ Hz).

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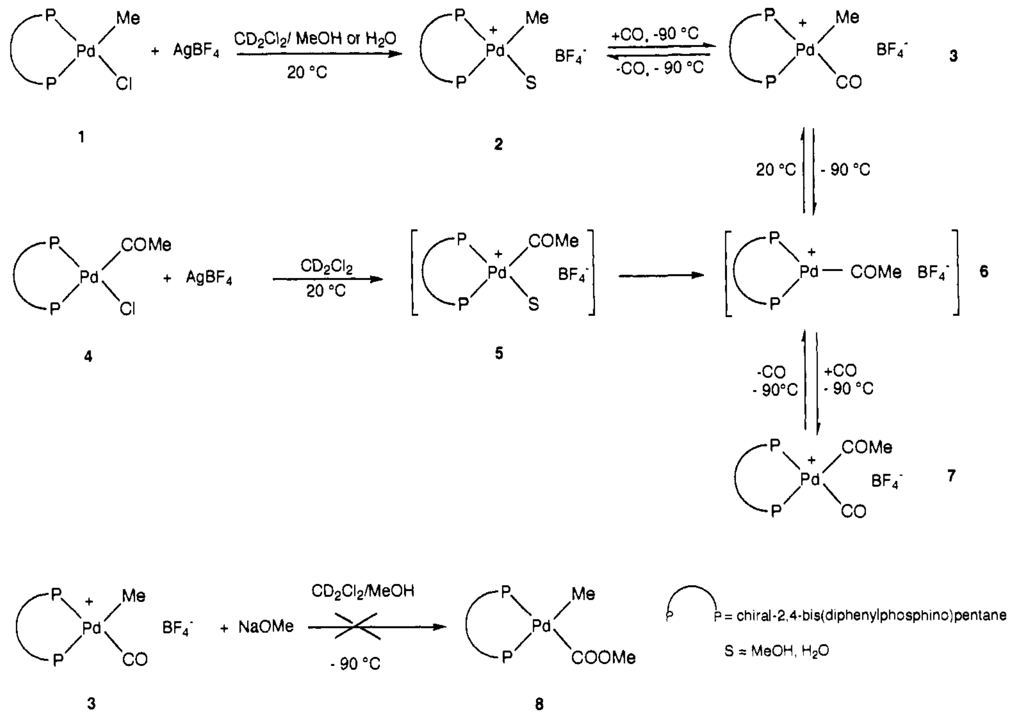
Scheme I



[Pd(COMe)(CO){(*S*,*S*)-BDPP}]BF$_4$, (7).[19] A solvated acetyl compound (**5**) as a product of CO insertion in compound **3** could not be detected; thus apparently the coordination of CO to the assumed three-coordinate intermediate of CO insertion, **6**, is more facile than that of the solvent (Scheme I). The formation of the methyl(carbonyl) complex **3** is remarkably accelerated, while the rate of its transformation to the acetylcarbonyl complex **7** (CO insertion followed by the coordination of another CO ligand) is not influenced by increasing the CO pressure from atmospheric to 10 bar, as judged by high-pressure NMR studies at 183 K. This is more consistent with the mechanism shown in Scheme I than with one involving a five-coordinate intermediate. Analogous mechanisms with monodentate ligands, both through three- and five-coordinate intermediates, are well known in the literature.[4]

The formation of both compounds **3** and **7** is completely reversible at room temperature, as judged by the fact that the reaction of Pd(COMe)(Cl){(*S*,*S*)-BDPP,[20] (**4**) with AgBF$_4$ in the absence of added CO yields compound **2** and **7** in about 1:1 ratio. Analogous decarbonylation upon the reaction of covalent acyl complexes with silver salts has been previously noted.[9] In the presence of CO, a similar reaction of covalent acyl compound **4** yields the cationic acyl(carbonyl) compound **7** nearly quantitatively,which decarbonylates to compound **2** by venting CO out from the solution.The carbonyl group of compound **7** and probably that of compound **3** exchange with free CO immeasurably fast at 183 K, as determined by the incorporation rates of ^{12}CO into the carbonyl groups when ^{13}CO pressure was replaced by that of ^{12}CO. In contrast to this, the acetyl ^{13}CO-carbonyl group of **7** does not incorporate free ^{12}CO up to -50 °C, where the terminal carbonyl group of **7** shows fast exchange with free CO on the NMR time scale as well.

Several experiments were carried out to investigate whether the methyl(carbonyl) complex **3** is also an intermediate in the formation of the methyl(methoxycarbonyl) compound, Pd(Me)(COOMe){(*S*,*S*)-BDPP},[13] (**8**). However, the latter compound could not be formed by the addition of NaOMe solutions to those of **3** at 183 K.[21] Instead, the immediate formation of compound **7** and MeCOOMe was observed. The ester cannot be the product of a reductive elimination from compound **8**, as the latter has been found to be stable at this temperature.[13] Thus, it seems that, contrary to what has been previously suggested,[13] compound **3** is not an intermediate in the insertion of CO into a Pd–OMe bond. In contrast to that shown above for a Pd–Me bond of an ionic compound, CO insertion into a Pd–OMe bond probably follows the associative pathway as observed for analogous Pt complexes.[22]

Concluding, this work has revealed the existence and intermediacy of *cis*-Pd(Me)(CO)(P–P) complexes, which were thus far elusive compounds on the route toward Pd–acyl complexes containing chelating diphosphines.

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Supplementary Material Available: Sequence of ^{31}P and ^{13}C NMR spectra showing the formation of compounds **2**, **3**, and **7** (2 pages).

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(19) [Pd(^{13}COMe)(^{13}CO)(BDPP)] BF$_4$ (**7**) ^{31}P NMR (183 K): δ 18.3 (dt, $^2J_{C_2,P_A} \sim {}^2J_{P_B,P_A}$ = 79 Hz, $^2J_{C_1,P_A}$ = 9.2 Hz, P$_A$ *trans* to ^{13}C(O)Pd = C$_2$); 5.0 (dt, $^2J_{C_1,P_B} \sim {}^2J_{P_A,P_B}$ = 79 Hz, $^2J_{C_2,P_B}$ = 19.8 Hz). ^{13}C NMR (at the carbonyl region, 183 K): δ 232.9 (dd, $^2J_{P_B,C_1}$ = 82.8 Hz, $^2J_{P_A,C_1}$ = 9.2 Hz, $^2J_{C_1,C_2}$ not observed (probably very small), ^{13}C(Pd)(O)Me = C$_1$); 177.3 (dd, $^2J_{P_A,C_2}$ = 76.1 Hz, $^2J_{P_B,C_2}$ = 19.8 Hz, C$_2$). IR (CD$_2$Cl$_2$, 293 K): $\nu_{^{13}CO}$/cm^{-1} 2077 s, 1711 s.

(20) In contrast to the experience with analogous acetyl compounds in ref 9, Pd(COMe)(Cl)(BDPP) (**4**) could be readily isolated by the following procedure: A solution of 200 mg of compound **1** in 5 mL of CH$_2$Cl$_2$ was pressurized to 10 bar of CO in a stainless steel autoclave. After the solution was stirred for several minutes at room temperature, the CO pressure was released and the solution was poured into 15 mL of pentane. The separated white precipitate was collected by filtration, washed with some additional pentane, and dried (~170 mg). Compound **4** can also be prepared by bubbling atmospheric CO for 10 min into a similar solution of **1**. Anal. Calcd for C$_{31}$H$_{33}$ClOP$_2$P: C, 59.53; H, 5.28; P, 9.92. Found: C, 59.42; H, 5.36; P, 10.00. ^{31}P NMR(CD$_2$Cl$_2$, 295K): δ 25.4 (d), 3.7 (d, $^2J_{P,P}$ = 69.5 Hz). ^{13}C NMR (at the carbonyl region): δ 243 (dd, $^2J_{P_1,C}$ = 118 Hz, $^2J_{P_2,C}$ = 14 Hz).

(21) After the formation of compound **3** was observed in a high-pressure NMR tube at 183 K, the tube was placed into liquid nitrogen bath and the CO pressure was released. Precooled (195 K) solution of NaOMe in methanol was then added to the frozen solution of **3** in CD$_2$Cl$_2$, and the tube was warmed up again to 183 K in the NMR probe.

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