Synthesis and Carbonylation of [Pd(Me)(OMe){(*S,S*)-bdpp}] [(*S,S*)-bdpp = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane]

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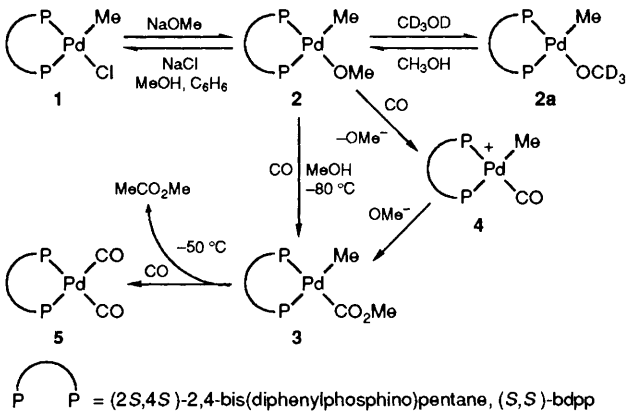
Synthesis of [Pd(Me)(OMe){(*S,S*)-bdpp}] **2** by NaOMe metathesis with [Pd(Me)(Cl){(*S,S*)-bdpp}] **1** is reported along with the low temperature carbonylation of **2**; the elimination of methyl acetate from the new carbonylation product [Pd(Me)(CO_2Me){(*S,S*)-bdpp}] **3** proceeds readily even at −50 °C.

Late-transition-metal alkoxides might play an important role as catalytic intermediates in a variety of homogeneous catalytic processes including hydroalkoxycarbonylation of olefins and alkoxycarbonylation of alkyl or aryl halides[1]. It has been shown that alkylplatinum[2] or alkylpalladium alkoxides[3] of the type of [M(R)(OR′)L_2] [M = Pt, Pd; R, R′ = alkyl, L_2 = bis(mono-*tert*-phosphine), di-*tert*-phosphine) insert CO preferably into the metal–alkoxy bond rather than into the metal–alkyl bond to form alkyl(alkoxycarbonyl)platinum or palladium compounds, [M(R)(CO_2R′)L_2]. *cis*- and *trans*-[Pt(R)(CO_2R′)L_2] compounds[2] and *trans*-[Pd(CH_2Ph)(CO_2Me){(PMe_3)$_2$}][4] are reluctant to undergo reductive elimination, whereas *cis*-[Pd(Me)(CO_2R′)(dppe)] [R′ = $CH(CF_3)_2$, CH_2CF_3, $CH(CF_3)$Ph; dppe = 1,2-bis(diphenyl-

phosphino)ethane] compounds readily eliminate the appropriate ester derivatives,[3] thus providing potential support for a methoxycarbonyl route[5] in the methoxycarbonylation mechanism. In the absence of electronegative substituents on R and R′ groups in [Pd(R)(OR′)L_2] the Pd–OR′ bond is highly polarized.[6] A polarized metal–alkoxide bond M–OR′ with β-hydrogens in the alkoxy group, such as M–OMe, is susceptible to β-hydride elimination,[1–3,6] similarly to the metal–alkyl bond in [M(R)(OR′)L_2] when R contains β-hydrogens.[7] Possibly, these are the reasons for the fact that (*i*) the number of known [Pd(R)(OR′)L_2] compounds (where R, R′ = non-substituted alkyl or aryl) is quite limited and that (*ii*) an alkyl(methoxo)palladium compound, [Pd(R)(OMe)L_2] (where R = non-substituted alkyl including Me, CH_2Ph), has never been characterized.

We report here the synthesis and carbonylation of the new methyl(methoxo)palladium compound [Pd(Me)(OMe){(*S*, *S*)-bdpp}] **2** as part of our investigations concerning the mechanism of asymmetric hydromethoxycarbonylation of styrene derivatives catalysed by chiral Pd–bdpp compounds[8] [bdpp = 2,4-bis(diphenylphosphino)pentane[9]]. The methyl group as alkyl ligand in **2** was chosen for the reason that, although Me is electronically similar to the alkyl ligands formed by the insertion of styrene derivatives into a Pd–H bond,[8] it is not susceptible to β-hydride elimination.

When [Pd(Me)(Cl){(*S*,*S*)-bdpp}]† **1** is treated with 1 equiv. of NaOMe in a mixture of dry solvents, MeOH–benzene (1:1), at room temp., the methyl(methoxo) compound **2** is formed, but owing to the equilibrium in its formation, only in about 60% yield (Scheme 1). The halflife ($t_{1/2}$) of **2** in the reaction mixture is more than 12 h at room temperature. The conversion of **1** to **2** is almost quantitative in the presence of a tenfold excess of NaOMe; however the decomposition of **2** by β-hydride elimination is much faster ($t_{1/2}$ *ca.* 1 h) than in the case above. Nevertheless, the new compound **2** can be isolated from the latter reaction mixture in *ca.* 95% purity by a quick work-up procedure.‡ The methyl(methoxo) compound **2** can also be generated and prepared in *ca.* 95% purity by dissolving [Pd(Me)(OBu^t)[{(*S*,*S*)-bdpp}] in dry MeOH.[8] [Owing to the absence of β-hydrogens in the Pd–*tert*-butoxy moiety, the methyl(*tert*-butoxy) compound is stable for a day in the presence of an excess of *tert*-butoxide].



Scheme 1

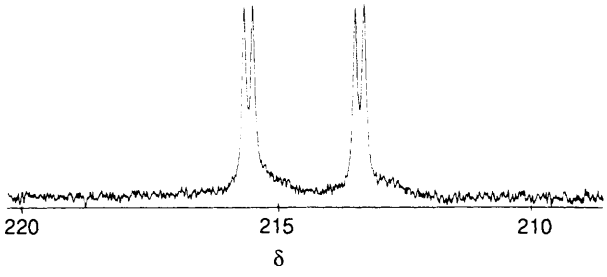


Fig. 1 Part of the ^{13}C NMR (75.5 MHz) spectrum of [Pd(Me)-($^{13}CO_2Me$){(*S*,*S*)-bdpp}] **3** recorded after the carbonylation of **2** under 3 bar of ^{13}CO at −70 °C: δ 214.4, $^2J_{P_tPdC}$ 165 Hz, $^2J_{P_cPdC}$ 12 Hz.

The methyl(methoxo)palladium compound **2** reacts at 3 bar of CO in CD_3OD–$C_6D_5CD_3$ (1:1) at 80 °C to form the methyl(methoxycarbonyl) compound, [Pd(Me)(CO_2Me)-{(*S*, *S*)-bdpp}] **3**, exclusively (Scheme 1). The reaction rate for the conversion of **2** into **3** is first order in the concentration of **2** under the conditions above ($t_{1/2}$ = 50 min at −80 °C, $t_{1/2}$ = 14.5 min at −70 °C, as measured in a spinning 10 mm high-pressure NMR tube). The rate at which methanol exchange (**2** ⇌ **2a**, Scheme 1) takes place is much higher for **2** than for the analogous platinum compound [Pt(Me)(OMe)(dppe)].[7] In fact, the exchange of **2** with deuteriated methanol is immeasurably fast at −70 °C in a mixture of solvents identical to that used in the carbonylation experiment above. The observed relative stability of **2** in methanol compared to that in non-alcoholic media‡ probably is a consequence of this fast exchange, which is much faster than β-hydride elimination from the Pd–OMe moiety. Furthermore, the exchange **2** ⇌ **2a** is much faster than the carbonylation of **2** to give **3**, whereas the opposite has been observed for the platinum analogue, for which an associative mechanism was proposed.[7] In view of the present findings and the fact that Pd–OMe complexes will be partly dissociated in methanol, a dissociative mechanism for the formation of **3** *via* **4** seems plausible.

The reductive elimination of $MeCO_2Me$ from **3** (Scheme 1) is slow below −70 °C; hence **3** could be fully characterized by NMR spectroscopy.§ Fig. 1 shows a partial ^{13}C NMR spectrum of the carbonyl region obtained by the low temperature carbonylation of **2** under 3 bar of ^{13}CO. An intermediate to **3**, such as compound **4** (Scheme 1), could not be detected by NMR spectroscopy. At −50 and −30 °C the reductive elimination (Scheme 1) proceeds at considerable rates; $t_{1/2}$ =

† Compound **1** was prepared by the reaction of [Pd(Me)(Cl)(cod)] (cod = cyclooctadiene) and (*S*,*S*)-bdpp in benzene analogously to the procedure reported in ref. 10. Elemental analyses were satisfactory; ^{31}P NMR ($CDCl_3$, 295 K, rel. 85% H_3PO_4): δ 39.5 (d), 6.6 (d); $^2J_{P,P'}$ = 49 Hz.

‡ The reaction mixture was stirred for about 2–3 min and the orange–yellow solution was concentrated *in vacuo*. The residue was suspended in dry benzene containing 1% MeOH, stirred for several seconds and filtered rapidly. The solvents were quickly evaporated from the mother liquid *in vacuo*, yielding **2** as a beige crystalline solid. The purity of this material was about 95% as judged by NMR. Upon prolonged stirring the reaction mixture turned red gradually, indicating some decomposition of **2**, which can readily be followed by ^{31}P NMR. Compound **2** decomposes in minutes when dissolved in pure solvents such as CH_2Cl_2, tetrahydrofuran (THF) or benzene, resulting in the formation of unstable Pd^0 and Pd^I compounds. Compound **2** also decomposes in solid form when stored at room temperature (*ca.* 5% decomposition in 10 h); thus an elemental analysis has not been attempted. Data for **2**; ^{31}P NMR (CD_3OD, 295 K): δ 42.2 (d), 8.5 (d); $^2J_{P,P'}$ 45 Hz; ^1H NMR (CD_3OD, 295 K): δ 8.0–7.3 (m), (4Ph); 2.87 (m), 2.70 (m), (2CH); 1.80 (m), (CH_2); 1.07 (dd), 0.90 (dd); $^3J_{P,H}$ 14.8 Hz, $^3J_{H,H}$ 7.0 Hz, $^3J_{P',H}$ 10.8 Hz, $^3J_{H,H}$ 7.0 Hz [2Me–(CH)]; 0.48 (dd), $^3J_{P_tPdCH}$ 7.5 Hz, $^3J_{P_cPdCH}$ 3.5 Hz, [Me–(Pd)]; ^{13}C NMR (CD_3OD, 295 K): δ 135.9–128.6 (m), (4Ph); 35.5 (m), (CH_2); 28.1 (dd); 25.3 (d), $^1J_{P,C}$ 30.0 Hz, $^3J_{P,C}$ 7.2 Hz, $^1J_{P',C}$ 18.5 Hz $^3J_{P',C}$ < 3 Hz not res., (2CH); 17.9 (br. s.), 16.5 (br. s.) [2Me–(CH)]; 15.2 (d) $^2J_{P_tPdC}$ 95 Hz, $^2J_{P_cPdCH}$ < 3 Hz not res. [Me–(Pd)]. Owing to the fast and complete exchange with the solvent alcohol, the methoxide signal could not be detected by ^1H and ^{13}C NMR. Thus, when compound **2** was dissolved in CD_3OD, only the formation of one equivalent of CH_3OD could be observed.

§ Compound **3**, ^{31}P NMR (CD_3OD–$C_6D_5CD_3$, 1:1): δ 22.6 (d), 10.5 (d); $^2J_{P,P'}$ 43 Hz. ^{13}C NMR in carbonyl region is given in Fig. 1.

68 and 7 min, respectively. In the presence of CO the dicarbonyl compound **5**¶ is formed stoichiometrically, concomitant with the elimination of $MeCO_2Me$, upon which the colourless solution of **3** turns yellow gradually.

The experiments above clearly demonstrate that it is possible to generate the methyl(methoxo)palladium compound **2** and that once it is formed it will insert CO into the Pd–OMe bond. The methyl(methoxycarbonyl) compound **3** readily eliminates $MeCO_2Me$, thus providing potential support for a methoxycarbonyl route in the hydromethoxycarbonylation mechanism. However, a detailed study[8] on this mechanism shows that the formation of compounds like **2** (thus a methoxycarbonyl route) is unlikely in the absence of added methoxide, such as under the reaction conditions of the catalytic process.

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¶ Compound **5** could not be isolated as it gradually loses CO in the absence of CO atmosphere. Nevertheless, it was well characterized in the reaction mixture (CD_3OD–$C_6D_5CD_3$, 1 : 1); IR (295 K): ν_{CO}/cm^{-1} 2015 s, and 1973 s, ^{31}P NMR (295 K): δ 18.7 s, (183 K): 19.5 (br. s), 14.0 (br. s).

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