CO Insertion in Four-Coordinate *cis*-Methyl(carbonyl)platinum-Diphosphine Compounds. An Ionic Mechanism for Platinum-Diphosphine-Catalyzed Hydroformylation

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Received May 4, 1994[⊗]

The reactions of the square-planar methylplatinum-*cis*-diphosphine complexes, Pt(Me)(Cl){(*S,S*)-BDPP}, **1**, and Pt(Me)($SnCl_3$){(*S,S*)-BDPP}, **2**, (BDPP = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane) with CO, and a mixture of CO/H_2 = 1/1 have been studied in CD_2Cl_2 solutions by variable temperature high-pressure NMR spectroscopy to establish the role of Pt-$SnCl_3$ bond in the CO insertion and hydrogenolysis steps of the Pt-diphosphine-catalyzed olefin hydroformylation reaction. At low temperatures (193-213 K), the formation of the unprecedented four-coordinate ionic *cis*-methyl(carbonyl)platinum-diphosphine compound, [Pt(Me)(CO){(*S,S*)-BDPP}]$^+X^-$, where X = Cl, **3a**, and X = $SnCl_3$, **3b**, has been observed whether CO is applied neat or in a mixture with hydrogen. The formation of compounds **3a** and **3b** involve equilibrium reactions which are facilitated by increasing the CO pressure; however, while the formation of **3b** is a fast (magnitudes faster than that of **3a** at identical conditions) and quantitative reaction, the formation of compound **3a** remains a slow reaction that does not reach completion in the range of 1-50 bar of CO pressure. CO insertion in compounds **3a** and **3b** takes place only at temperatures close to ambient, yielding covalent acetyl compound Pt(COMe)(Cl){(*S,S*)-BDPP}, **4**, and ionic acetyl compound [Pt(COMe)(CO){(*S,S*)-BDPP}]$^+SnCl_3^-$, **5**, respectively. At room temperature, **5** but not **4** reacts further in the presence of hydrogen, resulting in the formation of acetaldehyde and an unidendified Pt-diphosphine compound. Thus, it appears that the hydroformylation by Pt-BDPP complexes proceeds via an ionic reaction mechanism.

Introduction

Insertion of CO into Pt-carbon bonds has been extensively studied in carbonylations of alkyl or aryl Pt complexes containing monodentate phosphine ligands.[1] The role of $SnCl_2$ cocatalyst in promoting the ultimate steps of Pt-Sn-catalyzed hydroformylation, such as the olefin insertion, the CO insertion and the hydrogenolysis of acyl complexes, has also been thoroughly investigated in Pt complexes containing PPh_3.[1g,j,2] The presence of NMR active nuclei such as ^{195}Pt, ^{31}P, ^{117}Sn and ^{119}Sn in these compounds facilitates the elucidation of catalytic intermediates.[3]

It has been generally postulated that CO insertion proceeds by 1,2-migration of the organic group to the coordinated CO ligand, i.e. via the intermediacy of transition metal complexes in which coordinated organic and carbonyl groups are placed in *cis* positions.[1h,4] In the carbonylation of Pt(R)(X)(L_2) complexes (where R = alkyl, aryl; X = halide; L = monotertiary phosphine), five-coordinate Pt(R)(CO)(X)L_2 intermediates (associative mechanism) have been proposed for basic phosphines which are reluctant to dissociate from Pt.[1c,d,e] For less basic phosphines such as PPh_3, the CO insertion has been found to proceed by a dissociative (nonionic) mechanism, through four-coordinate Pt(R)(CO)(X)L intermediates.[1c,e] Several *cis*-alkyl or -aryl carbonyl Pt compounds of the latter type have been described in the literature.[1e,5] However, such compounds[1e] as well as the precursor *cis*-Pt(R)(X)(L_2) compounds[1i] are typically difficult to capture due to their ready conversion to the *trans* analogues. In order to avoid the *cis-trans* isomerization in the formation of *cis*-Pt(R)(CO) compounds it is advantageous to use bidentate instead of monodentate phosphines as ligands.[6] Furthermore, the use of chelating phosphine ligands for mechanistic studies on the CO insertion in Pt complexes is desirable as the potentially most important Pt-catalyzed carbonylation processes, such as enantioselective[7] and other[8] olefin hydroformylations utilize bidentate instead of monodentate

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⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1994.

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Table 1. NMR and IR Data[a]

compd	temp (K)	$\delta(P^A)$ (ppm)	$\delta(P^B)$ (ppm)	J_{Pt-P^A} (Hz)	J_{Pt-P^B} (Hz)	$J_{P^A-P^B}$ (Hz)	other data
Pt(Me)(Cl)(BDPP) (**1**)	293	18.4	15.6	4181	1624	22	
	193	19.1	14.3	4184	1628	22	
Pt(Me)($SnCl_3$)(BDPP) (**2**)	293	23.2	12.2	3488	1836	25.5	
$[Pt(Me)(CO)(BDPP)]^+$ (**3a,b**)	293	14.8	8.1	3142	1580	34	^{13}C NMR: δ 177.9 ppm, dd
	193	13.3	6.3	3134	1570	34	$J_{Pt-^{13}C(O)}$: 1371 Hz, satellites
							$J_{P^A-^{13}C(O)}$: 129 Hz
							$J_{P^B-^{13}C(O)}$: 8.3 Hz
							IR (ν(CO)): 2075 cm^{-1}
Pt(COMe)(Cl)(BDPP) (**4**)	293	7.7	9.2	4450	1340	26.8	^{13}C NMR: δ 236.3 ppm, dd
							IR (ν(CO)): 1710 cm^{-1}
$[Pt(COMe)(CO)(BDPP)]^+$ (**5**)	293	8.5 (broad)	5.4	3677	1481	34	^{13}C NMR: δ 230 ppm, dd; 175 ppm, dd
	178	4.0	2.6	3404	1353	37	IR (ν(CO)): 2108; 1706 cm^{-1}
6	193	9.6	5.8	3741	1570	31.5	

[a] All NMR and IR spectra are recorded in CD_2Cl_2 and CH_2Cl_2, respectively.

phosphines as ligands. However, the carbonylation of Pt(R)(X)(L-L), where X = halide or $SnCl_3$, L-L = chelating diphosphine, requires more drastic reaction conditions than those of analogous compounds with monodentate ligands.[5,6] This is probably the reason why a five- or four-coordinate *cis*-alkyl− or *cis*-aryl−Pt−carbonyl compound containing a bidentate phosphine as an intermediate in the CO insertion, Pt(R)(CO)(L-L)X or $[Pt(R)(CO)(L-L)]^+X^-$ has never been synthesized nor spectroscopically characterized. The mechanism of hydroformylation and the role of $SnCl_3^-$ anion thus has scarcely been studied in Pt−diphosphine complexes.[9]

Here we show the ready availabity of an ionic mechanism for CO insertion by the use of Pt complexes of a chelating phosphine exemplified by the in situ synthesis of the unprecedented ionic four-coordinate *cis*-alkyl−carbonyl species, $[Pt(Me)(CO)\{(S,S)\text{-BDPP}\}]^+A^-$, where $A^- = SnCl_3^-$ or Cl^-, as intermediates in CO insertion. A comparison is also been made in the formation and further reactions (methyl-migration, hydrogenolysis of the formed acyl compounds) of the latter two ionic compound in order to obtain additional information about the the role of Pt−$SnCl_3$ bond in promoting the CO insertion and hydrogenolysis steps of the catalytic process.

Experimental Section

Pt(Me)(Cl)(COD) was prepared as described in ref 5. *S,S*-(−)-BDPP was synthesized from (2*R*,4*R*)-2,4-pentanediol (Aldrich) according to the literature procedure.[10] CD_2Cl_2 (stored under N_2) and ^{13}CO at ~11 bar pressure were purchased from Campro Scientific. Solvents for syntheses were dried and freshly distilled under N_2 before use. The synthesis of compounds **1** and **2** as well as their dissolution for carbonylation experiments were carried out under N_2 atmosphere. Anhydrous $SnCl_2$ (Aldrich) was also kept under N_2. The NMR spectra were recorded on a Bruker AMX-300 and a Bruker AC-100 instruments (^{31}P frequency 121.5 and 40.5 MHz, respectively) in quadrunuclear and multinuclear probes, respectively. High pressure NMR measurements were carried out at a spinning rate of 15 s^{-1} in a home-built assembly consisting of an 10 mm o.d. sapphire high pressure tube and a titanium pressure-head, which is similar to that described by Roe.[11] IR spectra were recorded on a Specord-IR 75 (Carl Zeiss) instrument by using a 0.2 mm IR-cell. The conductivity measuments were performed in a 7 mL conductometric cell by using a Pt-ring electrode at 7.7 mmol/L concentrations in CH_2Cl_2 on a Radelkis OK-104 instrument. Microanalyses were done by the Central Laboratory of University of Veszprém (Veszprém, Hungary).

Pt(Me)(Cl)\{(*S,S*)-BDPP\} (1). A 20 mL volume of benzene was added to a mixture of 880 mg (2 mmol) of *S,S*-BDPP and 707.4 mg (2 mmol) of Pt(Me)(Cl)(COD) with stirring. The initially formed white suspension turned to a colorless solution several minutes after the addition of solvent and then a white precipitate began to separate. The mixture was stirred for two hrs at room temperature. The white precipitate was filtered off after adding 20 mL of pentane to the suspension. The filtrate was washed with 3 × 10 mL of pentane and dried under vacuo, yielding ~1.3 g (95%) of a white microcrystalline solid. Anal. Calcd for $C_{30}H_{33}ClP_2Pt$: C, 52.51; H, 4.81; P, 9.04. Found: C, 51.92; H, 4.85; P, 8.87. ^1H NMR (300.1 MHz, CD_2Cl_2, 293 K): 7.96−7.26 m, *20H*; 2.94 m, *1H*; 2.70 sept., ($^3J_{HH} = {}^2J_{PBH}$ = 7.1Hz) *1H*; 1.94 triplet of multiplets, ($^3J_{PAH} = {}^3J_{PBH}$ = 21 Hz) *2H*; 1.11 dd, ($^3J_{PAH}$ = 14.6 Hz, $^3J_{HH}$ = 7.1Hz) *3H*; 0.99 dd, ($^3J_{PBH}$ = 12.3 Hz, $^3J_{HH}$ = 7.1Hz) *3H*; 0.45 dd, ($^3J_{PAH}$ = 4.2 Hz, $^3J_{PBH}$ = 7.3 Hz, $^2J_{PtH}$ = 54.6 Hz satellites) *3H*; P_A is *cis* to Me−(Pt). ^{31}P NMR data are given in Table 1.

Pt(Me)($SnCl_3$)\{(*S,S*)-BDPP\} (2). To the colorless solution of 686 mg (1 mmol) of **1** in 30 mL of CH_2Cl_2, 199 mg (1.05 mmol) of anhydrous $SnCl_2$ was added with stirring at room temperature. The solution was stirred for 4 h upon which it turned light-yellow gradually. Then 60 mL of pentane was added resulting in the formation of a beige precipitate, which was filtered off and washed with pentane (10 mL). The product was recrystallized from a mixture of CH_2Cl_2/ether, yielding ~550 mg (63%) of a beige-yellow crystalline. Anal. Calcd for $C_{30}H_{33}Cl_3P_2SnPt$: C, 41.14; H, 3.77; P, 7.08. Found: C, 42.02; H, 3.83; P, 6.92. ^1H NMR (300.1 MHz, CD_2Cl_2, 293 K): 7.75−7.42 m, *20H*; 2.93 m, *1H*; 2.75 sept., ($^3J_{HH} = {}^2J_{PBH}$ = 7.1Hz) *1H*; 1.99 triplet of multiplets, ($^3J_{PAH} = {}^3J_{PBH}$ = 20 Hz) *2H*; 1.11 dd, ($^3J_{PAH}$ = 14.3 Hz, $^3J_{HH}$ = 7.1Hz) *3H*; 1.04 dd, ($^3J_{PBH}$ = 13.5 Hz, $^3J_{HH}$ = 7.1Hz) *3H*; 0.55 t, ($^3J_{PAH} = {}^3J_{PBH}$ = 5.8 Hz, $^2J_{PtH}$ = 55.7 Hz satellites) *3H*; P_A is *cis* to Me−(Pt). ^{31}P NMR data are given in Table 1.

High-Pressure NMR Experiments. A 22.6 mg amount (0.033 mmol) of **1** or 28.9 mg (0.033 mmol) of **2** was dissolved in 1.5 mL of CD_2Cl_2 and transferred into the high-pressure NMR tube. In low-temperature NMR measurements for monitoring the formation of compound **3a** and **3b**, the tube was cooled to dry ice temperature and pressurized with the desired gas or gas mixture (CO, ^{13}CO-enriched CO or pure ^{13}CO, CO/H_2 and $^{13}CO/H_2$ = 1/1 mixtures). Then the NMR tube was immersed into the NMR probe which was precooled (preset) at the desired temperature. After allowing 5 min equilibration in the probe (after probe-tuning, locking and shimming), kinetic NMR programs could be started. For monitoring the formation and hydrogenolysis of acetyl compounds (**4** and **5**) the tube was allowed to warm up to room temperature in the probe or was charged at room temperature.

Note: *Although the above described high pressure tubes have been used safely at the University of Amsterdam for years in the pressure range of 1*−50 bar, it is absolutely recommended to avoid direct exposure to a charged high-pressure tube while preparing, carrrying, or immersing into the NMR probe. For more details, see the following: Elsevier, C. J. *J. Mol. Catal.* **1994**, *92*, 285.

IR Measurements. For detection of **3b**, an amount of 30 mg of **2** was dissolved in 5 mL of CH_2Cl_2 and the solution was transferred into

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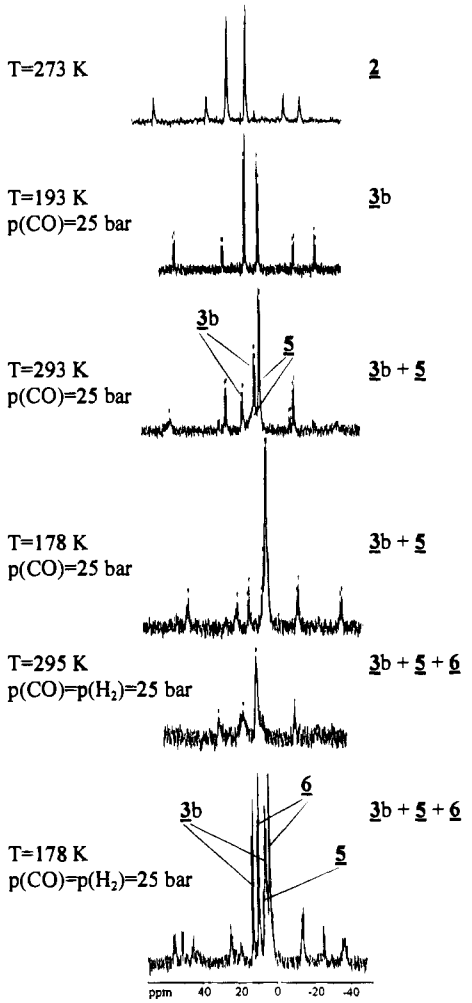

Figure 1. High-pressure ^{31}P NMR spectra at different stages of the reaction of Pt(Me)($SnCl_3$){(*S,S*)-BDPP}, **2**, with CO and CO/H_2 = 1/1 in CD_2Cl_2.

a 20 mL stainless-steel autoclave. The autoclave was cooled to dry ice temperature and then was pressurized to 25 bar with CO. After 30 min of standing at dry ice temperature, the pressure was released and a portion (~1 mL) of the solution was quickly tranferred into the IR cell which was precooled at dry ice temperature and the spectrum was immediately recorded. For detection of **5**, the autoclave containing the rest of the solution was pressurized again to 25 bar with CO and was allowed to warm up to room temperature. After 6 h standing at room temperature, the pressure was released and the spectrum from the solution was immediately recorded at room temperature.

Results and Discussion

Methyl compounds **1** and **2** were used for the study in order to avoid β-hydride elimination from the alkyl group prior or subsequent to the (reversible) CO insertion, resulting in the formation of unstable Pt–hydrides.[9] (*S,S*)-BDPP was chosen as it is presently one of the most effective chiral ligands in Pt-catalyzed enantioselective hydroformylation.[7b,12] When Pt(Me)-($SnCl_3$){(*S,S*)-BDPP}, **2**, was carbonylated in CD_2Cl_2 solution in a high-pressure NMR tube[11] at 25 bar of CO and 193 K, ^{31}P NMR revealed the formation of a single species, as shown in Figure 1. Under these conditions the formation of the new species was completed by the time an NMR spectrum could be recorded, i.e. in about 10 min, and no further reaction could be observed. By using ^{13}CO for similar carbonylation of compound

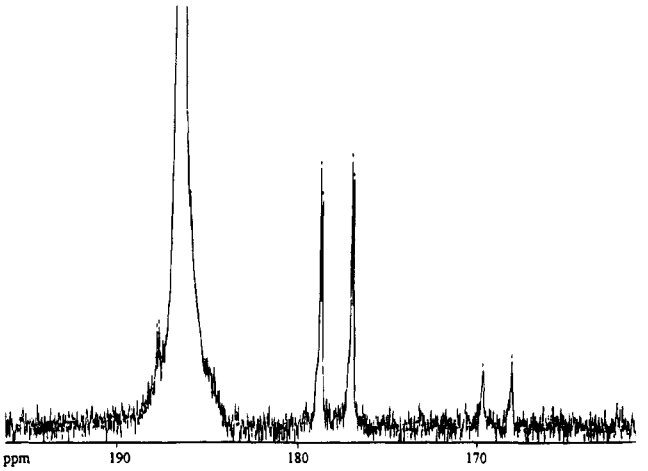

Figure 2. ^{13}C NMR spectrum of [Pt(Me)(^{13}CO){(*S,S*)-BDPP}]$^+SnCl_3^-$, **3b**, formed by the reaction of compound **2** with ^{13}CO (6 bar) at 203 K in CD_2Cl_2 at the carbonyl region. Downfield $^1J_{Pt-^{13}C}$ satellites are partly covered by the strong signal of dissolved (free) CO.

2, the ^{31}P NMR signals of the new species were duplicated. The ^{13}C NMR spectrum showed a doublet of doublet resonance at 177.9 ppm with $^1J_{^{195}Pt,^{13}C}$ satellites, as shown in Figure 2, which is in the range of terminal Pt–carbonyls.[1g] By the observed NMR and IR data, which are summarized in Table 1, the species has been identified as the cationic square-planar *cis*-methyl–carbonyl compound, [Pt(Me)(CO){(*S,S*)-BDPP}]$^+SnCl_3^-$, **3b** (Scheme 1). Compounds analogous to **3b** are known only with *trans* alkyl and carbonyl groups in Pt complexes of monodentate phosphines.[1g,j,2e] The ionic structure of compound **3b**, i.e. the ready substitution of $SnCl_3$ by CO is supported by the increasing conductivity of the solution of compound **2** in a CO atmosphere, as shown in Table 2. A similar observation has been made recently in the reaction of Pt(Cl)($SnCl_3$)(L-L) compounds (L-L = diphosphine) with monodentate phosphines (L), resulting in the formation of [Pt(Cl)(L)(L-L)]$^+SnCl_3^-$ ionic square-planar complexes.[13] The ionic structure of compound **3b** is also indicated by the lack of $^2J_{Sn,P}$ and $^2J_{Sn,C}$ satellites in its ^{31}P and ^{13}C NMR spectra.

Decreasing the CO pressure in the carbonylation of compound **2** slows down the formation of cationic carbonyl compound **3b**. At 6 bar CO pressure and 193 K, for example, it takes about 1 h to carbonylate compound **2** quantitatively. At atmospheric CO pressure, the similar reaction requires several days as shown in Table 2. Thus, the rate of formation of cationic carbonyl compound **3b** is a function of CO concentration as it has also been observed with the recently characterized and closely analogous Pd compound, [Pd(Me)(CO){(*S,S*)-BDPP}]$^+BF_4^-$.[14] Unlike the latter compound, **3b** is reluctant to undergo CO insertion at 193 K. The exchange between the carbonyl group of **3b** and free CO is slow on the NMR time scale at this temperature. By increasing the temperature, the CO exchange becomes fast (coalescence temperature 253 K) but no CO insertion takes place until temperatures are close to ambient. At room temperature under 25 bar of CO pressure, slow CO insertion occurs in compound **3b**, resulting in the exclusive formation of the cationic acetyl–carbonyl compound, [Pt-(COMe)(CO){(*S,S*)-BDPP}]$^+SnCl_3^-$, **5**, in 7 h (Figure 1). Apparently, the slow CO insertion step, which leads to formation of an assumed three-coordinate acetyl compound,[14,15] is followed by a fast and favorable coordination of CO instead of $SnCl_3$ to give the four-coordinate ionic compound **5** (Scheme 1).[16] The

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Scheme 1

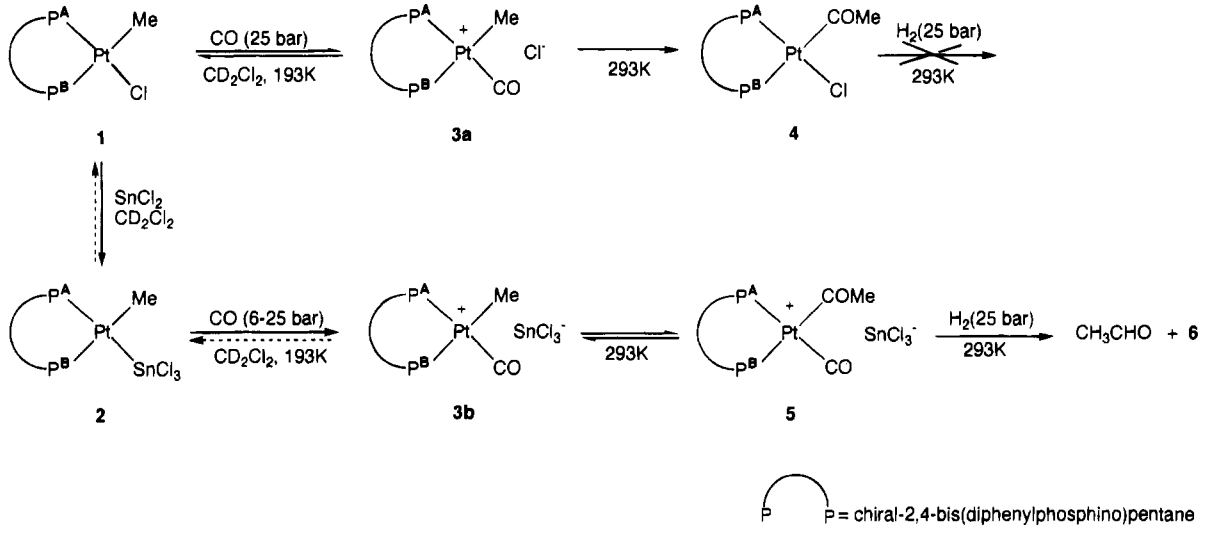

Table 2. Conductivity Data

compd	temp (K)	λ ($cm^2\ \Omega^{-1}\ mol^{-1}$)	compd	temp (K)	λ ($cm^2\ \Omega^{-1}\ mol^{-1}$)
CH_2Cl_2	293	0.18	**2** + **3b** + **5**[a]	293	19.1
2	293	7.20	**3b**[b]	195	28.3

[a,b] Measured by keeping a solution of compound **2** (7.7 mmol/L) in CH_2Cl_2 under atmospheric CO until an equilibrium value was reached *a*, after 18 h, and *b*, after 67 h.

CO insertion in compound **3b** proceeds only at 293 K with a rate comparable to the above analogous Pd compound at 183 K.[14] Plausibly, the metal–alkyl bond is significantly stronger and thus the alkyl group is more reluctant to migration in the Pt compound. Ultimately, it is probably the relative stability of the *cis*-methyl(carbonyl)–Pt–diphosphine compounds, which is responsible for the requirement of significantly higher reaction temperatures than those of the analogous process with similar Pd compounds for the formation of acyl–Pt–diphosphine compounds.[5,6]

The formation of acetyl–carbonyl compound **5** is similar to what has been observed with analogous Pt[5] and Pd[14] compounds. Thus, the CO insertion is completely reversible at room temperature, judged by the fact that by venting CO out of the solution compound **5** decarbonylates in minutes at room temperature to give compound **2** (Scheme 1). The formation of some **2** and **3b** was also observed when the CO pressure on the solution of compound **5** was reduced to atmospheric. As noted previously for the analogous Pd compound,[14] the terminal carbonyl group also shows significantly faster exchange with free CO than the acetyl carbonyl group in compound **5**. This is indicated by the fact that while the CO exchange in the acetyl carbonyl group of compound **5** is still slow on the NMR time scale at room temperature, the terminal carbonyl group shows fast exchange even at 213 K. Thus, a readily available coordination site *cis* to the acetyl group is provided in compound **5** for a facile CO deinsertion and also for dihydrogen addition in the next catalytic step (Scheme 1).

When compound **1** was carbonylated in CD_2Cl_2 solution under 25 bar of CO (^{12}CO and ^{13}CO) at 193 K, the slow formation of a species was observed which showed identical ^{31}P and ^{13}C spectra to those of **3b** (Figure 3). The new species has been identified as the ionic four-coordinate compound [Pt(Me)(CO){(*S,S*)-BDPP}]$^+Cl^-$, **3a** (Scheme 1).[17] In contrast to compound **3b**, compound **3a** forms only with a yield of 31% in an equilibrium reached after 6 h under these conditions (25 bar, 193 K) (Figure 3). The equilibrium in the carbonylation of compound **1** shifts more in favor of the formation of carbonyl compound **3a** by increasing the CO pressure or interestingly,

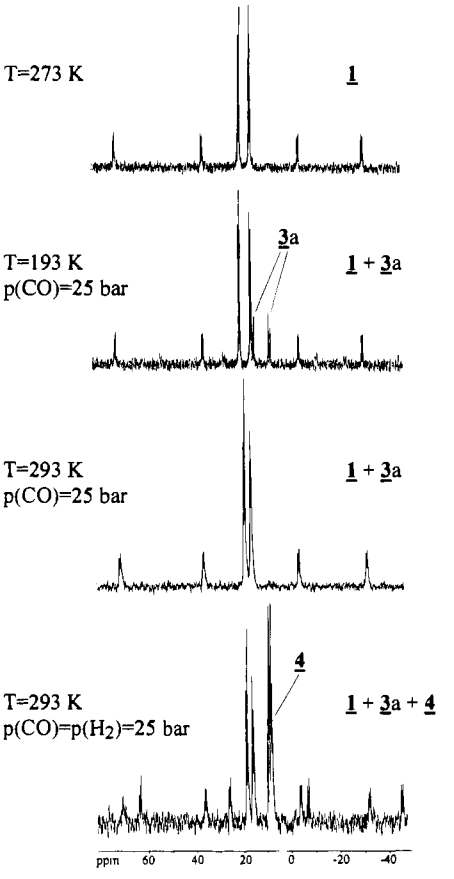

Figure 3. High-pressure ^{31}P NMR spectra of the reaction of Pt(Me)(Cl){(*S,S*)-BDPP}, **1**, with CO and CO/H_2 = 1/1 in CD_2Cl_2.

(16) The presence of cationic five-coordinate species in which an additional CO molecule occupies the fifth, apical coordination site in compounds **3a, 3b**, and **5** cannot be excluded. However, this is only likely if the apically bonded CO shows fast exchange with free CO (thus the apical carbonyl signal is indistinguishable from that of free CO) on the time scale of NMR and IR even at 178 K.

(17) The ionic stucture of analogous *trans*-$[Pt(R)(CO)L_2]^+A^-$ compounds has been inferred from the indifference of their ^{31}P and ^{13}C NMR spectra on the nature of A^- anion in refs 1g and 2e.

by increasing the total pressure by adding high-pressure hydrogen. Thus, for instance, a conversion of 55% to compound **3a** was observed by using 50 bar of $CO/H_2 = 1/1$ mixture in 6 h at 193 K. The substitution of the Cl by CO in compound **1** resulting in the formation of **3a** is particularly a new observation. In analogous reactions either the formation of a covalent five-coordinate Pt(R)(CO)(Cl)(L-L) species (associative mechanism) or the substitution of one of the phosphorus atoms of L-L by CO (dissociative mechanism) was assumed.[6,9] The presence of the former type of covalent five-coordinate species as short-lived intermediates in low concentration in the formation of compounds **3a** and **3b** cannot be excluded.

CO insertion in compound **3a** occurs at reaction rates and temperatures similar to those with **3b**, to give an acetyl compound identified as Pt(COMe)(Cl){(*S,S*)-BDPP}, **4**. Thus, the carbonylation of compound **1** at 293 K under 25 bar CO, results in the slow formation of compound **4** (Table 1, Figure 3). Presumably due to the lower concentration of **3a** than that of **3b**, the formation of acetyl compound **4**, unlike that of compound **5**, was not complete even after 16 h under these conditions.

The formation of carbonyl compound **3a** and thus the formation of acetyl compound **4** is facilitated by using 50 bar of $CO/H_2 = 1/1$ mixture instead of 25 bar CO in the carbonylation of compound **1**. Carbonyl compound **3b** and acetyl compound **5** also readily form in the presence of hydrogen, by using 50 bar $CO/H_2 = 1/1$ in the carbonylation of compound **2**.[18] In sharp contrast to the covalent acetyl compound **4**, only the ionic acetyl compound **5** reacts further at room temperature (Scheme 1) in the presence of H_2, giving off acetaldehyde and an unidentified Pt compound, **6**, as shown in Figure 1. The hydrogenolysis of compound **5** proceeds at a rate similar to that of its formation from **3b** under these conditions (50 bar $CO/H_2 = 1/1$, 293 K). By its J_{Pt-P} couplings compound **6** (Table 1) might be the expected hydrido–carbonyl compound,[9] $[PtH(CO)\{(S,S)\text{-BDPP}\}]^+SnCl_3^-$, although a hydride resonance in its ^1H NMR spectrum could not not be detected.[19]

Other *cis*- and *trans*-acyl–chloro–Pt compounds analogous to compound **4** have also been found to be inert for hydrogenolysis in similar solvents.[9,20] NMR spectra and the reluctance of acetyl compound **4** to undergo hydrogenolysis[21] indicate that the Pt–Cl bond is more covalent in character in acetyl compound **4** than in methyl compound **1**. The covalent character of the Pt–Cl bond of compound **4** in dichloromethane is also supported by the fact, that in contrast to compound **5**, the decarbonylation of compound **4** is a very slow process at room temperature (Scheme 1). In an experiment, the in situ made compound **4** remained essentially unchanged after 1 week standing under N_2. The fact that the CO is not readily eliminated in compound **4**, gives further evidence for the intermediacy of the four-coordinate ionic compound **3a** in the migration of Me from Pt to CO, instead of the covalent five-coordinate Pt(Me)(CO)(Cl){(*S,S*)-BDPP} species. The decarbonylation of *trans*-triphenylphosphine–acyl–Pt complexes has also been found to occur rather through four-coordinate cationic species than through a five-coordinated 18-electron intermediate.[22]

Conclusion

It has been shown that Cl and $SnCl_3$ ligands bonded to Pt are readily substituted by CO, resulting in the formation of unprecedented cationic *cis*-alkyl–carbonyl–Pt–diphosphine compounds, which undergo CO insertion in a medium polar solvent such as dichloromethane. It has also been demonstrated that the alkyl migration (CO insertion) occurs preferably in the four-coordinate cationic $[Pt(Me)(CO)\{(S,S)\text{-BDPP}\}]^+$ rather than in the analogous covalent five-coordinate species. Furthermore, the presence of a cationic acyl compound with a labile ligand *cis* to the acyl group such as $[Pt(COMe)(CO)\{(S,S)\text{-BDPP}\}]^+$ is essential for the success of dihydrogen addition and subsequent hydrogenolysis of the acyl group. Thus, the catalytic hydroformylation activity by Pt–diphosphine complexes such as Pt–BDPP is expected to be facilitated by enhancing the ionic character of the catalyst precursors.[23] This can be achieved by the use of in situ made or isolated cationic hydrido– or alkyl–Pt compounds directly as catalysts[24] and/or by increasing the solvent polarity. The role of $SnCl_2$ cocatalyst is obvious in increasing the cationic character of Pt as demonstrated above; $SnCl_3^-$ is a much better leaving group than Cl^-. The above shown ionic hydroformylation mechanism might be general for analogous Pt–diphosphine compounds which are reluctant to dissociate the chelating phosphine ligand.

Acknowledgment. We thank DSM Research, Geleen, The Netherlands, and the Hungarian National Science Foundation (Grant OTKA T4292) for financial support. The stimulating interest of Dr. Johannes G. de Vries (DSM Research) and the technical assistance of Jan-Meine Ernsting (Universiteit van Amsterdam) in NMR measurements are gratefully acknowledged.

(18) Since the formation of carbonyl compound **3b** is already fast and complete at 193 K under 25 bar CO and the CO insertion step does not seem to be a function of CO concentration (see also in ref 14), a beneficial effect by the use 50 bar CO/H_2 could not be detected.

(19) As shown in ref 9, the detection of a Pt–H resonance in compound **6** by ^1H NMR might be difficult even at 193 K due to ongoing exchange processes.

(20) Cavinato, G.; De Munno, G.; Lami, M.; Marchionna, M.; Toniolo, L.; Viterbo, D. *J. Organomet. Chem.* **1994**, *466*, 277.

(21) Compound **4** is not absolutely inert to hydrogenolysis at room temperature. After 1 day standing under 50 bar of $CO/H_2 = 1/1$, the slow formation (5%) of $PtCl_2\{(S,S)\text{-BDPP}\}$ could be observed. The formation of the latter compound can be attributed to reaction of zerovalent Pt compound, which is formed by the elimination of aldehyde product, with the solvent CD_2Cl_2 or to the reaction of divalent $PtH(Cl)\{(S,S)\text{-BDPP}\}$ with HCl. (HCl might be available through its elimination from the hydrido compound.)

(22) Kubota, M.; Rothrock, R. K.; Geibel, J. *J. Chem. Soc., Dalton Trans.* **1973**, 1267.

(23) The rate-determining step in the mechanism of Pt-catalyzed hydroformylation is generally not a step before CO insertion. See, for example refs 6, 8a, and 9.

(24) (a) Botteghi, C.; Paganelli, S.; Matteoli, U.; Scrivanti, A.; Ciorciaro, R.; Venanzi, L. M. *Helv. Chim. Acta* **1990**, *73*, 284. (b) Botteghi, C.; Paganelli, S. *J. Organomet. Chem.* **1991**, *417*, C41.