

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

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The reactions of the square-planar methylplatinum–*cis*-diphosphine complexes, Pt(Me)(Cl){(*S,S*)-BDPP}, **1**, and Pt(Me)(SnCl₃){(*S,S*)-BDPP}, **2**, (BDPP = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane) with CO, and a mixture of CO/H₂ = 1/1 have been studied in CD₂Cl₂ solutions by variable temperature high-pressure NMR spectroscopy to establish the role of Pt–SnCl₃ 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 = SnCl₃, **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}]⁺SnCl₃[–], **5**, respectively. At room temperature, **5** but not **4** reacts further in the presence of hydrogen, resulting in the formation of acetaldehyde and an unidentified 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 SnCl₂ 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 PPh₃.^{1g,j,2} The presence of NMR active nuclei such as ¹⁹⁵Pt, ³¹P, ¹¹⁷Sn and ¹¹⁹Sn 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)(L₂) complexes (where R = alkyl, aryl; X = halide; L = monoter-
tiary phosphine), five-coordinate Pt(R)(CO)(X)L₂ 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 PPh₃, 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)(L₂) compounds¹ⁱ 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 enantioselective⁷ and other⁸ olefin hydroformylations utilize bidentate instead of monodentate

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Table 1. NMR and IR Data^a

compd	temp (K)	$\delta(\text{P}^{\text{A}})$ (ppm)	$\delta(\text{P}^{\text{B}})$ (ppm)	$J_{\text{Pt-P}^{\text{A}}}$ (Hz)	$J_{\text{Pt-P}^{\text{B}}}$ (Hz)	$J_{\text{P}^{\text{A}}-\text{P}^{\text{B}}}$ (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	$J_{\text{Pt}-^{13}\text{C}(\text{O})}$: 1371 Hz, satellites $J_{\text{P}^{\text{A}}-^{13}\text{C}(\text{O})}$: 129 Hz $J_{\text{P}^{\text{B}}-^{13}\text{C}(\text{O})}$: 8.3 Hz IR ($\nu(\text{CO})$): 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 ($\nu(\text{CO})$): 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 ($\nu(\text{CO})$): 2108; 1706 cm ⁻¹
6	193	9.6	5.8	3741	1570	31.5	

^a All NMR and IR spectra are recorded in CD₂Cl₂ and CH₂Cl₂, respectively.

phosphines as ligands. However, the carbonylation of Pt(R)-(X)(L-L), where X = halide or SnCl₃, 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 SnCl₃⁻ anion thus has scarcely been studied in Pt-diphosphine complexes.⁹

Here we show the ready availability 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)-BDPP}]⁺A⁻, where A⁻ = SnCl₃⁻ 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 role of Pt-SnCl₃ 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 CD₂Cl₂ (stored under N₂) and ¹³CO at ~11 bar pressure were purchased from Campro Scientific. Solvents for syntheses were dried and freshly distilled under N₂ before use. The synthesis of compounds 1 and 2 as well as their dissolution for carbonylation experiments were carried out under N₂ atmosphere. Anhydrous SnCl₂ (Aldrich) was also kept under N₂. The NMR spectra were recorded on a Bruker AMX-300 and a Bruker AC-100 instruments (³¹P frequency 121.5 and 40.5 MHz, respectively) in quadrupolar 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 measurements were performed in a 7 mL conductometric cell by using a Pt-ring electrode at 7.7 mmol/L concentrations in CH₂Cl₂ 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 C₃₀H₃₃ClP₂Pt: C, 52.51; H, 4.81; P, 9.04. Found: C, 51.92; H, 4.85; P, 8.87. ¹H NMR (300.1 MHz, CD₂Cl₂, 293 K): 7.96–7.26 m, 20H; 2.94 m, 1H; 2.70 sept., (³J_{HH} = ²J_{PBH} = 7.1 Hz) 1H; 1.94 triplet of multiplets, (³J_{PAH} = ³J_{PBH} = 21 Hz) 2H; 1.11 dd, (³J_{PAH} = 14.6 Hz, ³J_{HH} = 7.1 Hz) 3H; 0.99 dd, (³J_{PBH} = 12.3 Hz, ³J_{HH} = 7.1 Hz) 3H; 0.45 dd, (³J_{PAH} = 4.2 Hz, ³J_{PBH} = 7.3 Hz, ²J_{PH} = 54.6 Hz satellites) 3H; P_A is *cis* to Me-(Pt). ³¹P NMR data are given in Table 1.

Pt(Me)(SnCl₃){(S,S)-BDPP} (2). To the colorless solution of 686 mg (1 mmol) of 1 in 30 mL of CH₂Cl₂, 199 mg (1.05 mmol) of anhydrous SnCl₂ 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 CH₂Cl₂/ether, yielding ~550 mg (63%) of a beige-yellow crystalline. Anal. Calcd for C₃₀H₃₃Cl₃P₂SnPt: C, 41.14; H, 3.77; P, 7.08. Found: C, 42.02; H, 3.83; P, 6.92. ¹H NMR (300.1 MHz, CD₂Cl₂, 293 K): 7.75–7.42 m, 20H; 2.93 m, 1H; 2.75 sept., (³J_{HH} = ²J_{PBH} = 7.1 Hz) 1H; 1.99 triplet of multiplets, (³J_{PAH} = ³J_{PBH} = 20 Hz) 2H; 1.11 dd, (³J_{PAH} = 14.3 Hz, ³J_{HH} = 7.1 Hz) 3H; 1.04 dd, (³J_{PBH} = 13.5 Hz, ³J_{HH} = 7.1 Hz) 3H; 0.55 t, (³J_{PAH} = ³J_{PBH} = 5.8 Hz, ²J_{PH} = 55.7 Hz satellites) 3H; P_A is *cis* to Me-(Pt). ³¹P 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 CD₂Cl₂ 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, ¹³CO-enriched CO or pure ¹³CO, CO/H₂ and ¹³CO/H₂ = 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, carrying, 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 CH₂Cl₂ and the solution was transferred into

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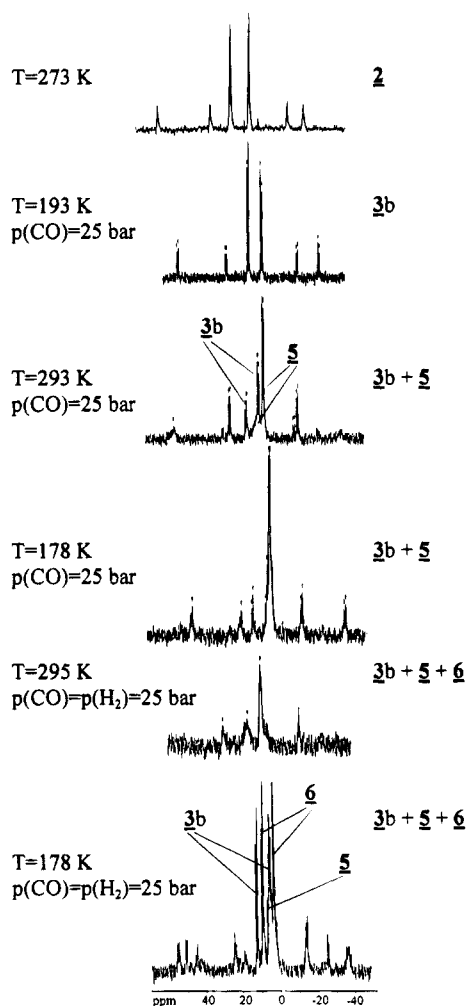


Figure 1. High-pressure ^{31}P NMR spectra at different stages of the reaction of $\text{Pt}(\text{Me})(\text{SnCl}_3)\{(\text{S},\text{S})\text{-BDPP}\}$, **2**, with CO and $\text{CO}/\text{H}_2 = 1/1$ in CD_2Cl_2 .

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 transferred 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 $(\text{S},\text{S})\text{-BDPP}$ was chosen as it is presently one of the most effective chiral ligands in Pt-catalyzed enantioselective hydroformylation.^{7b,12} When $\text{Pt}(\text{Me})(\text{SnCl}_3)\{(\text{S},\text{S})\text{-BDPP}\}$, **2**, was carbonylated in CD_2Cl_2 solution in a high-pressure NMR tube¹¹ 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

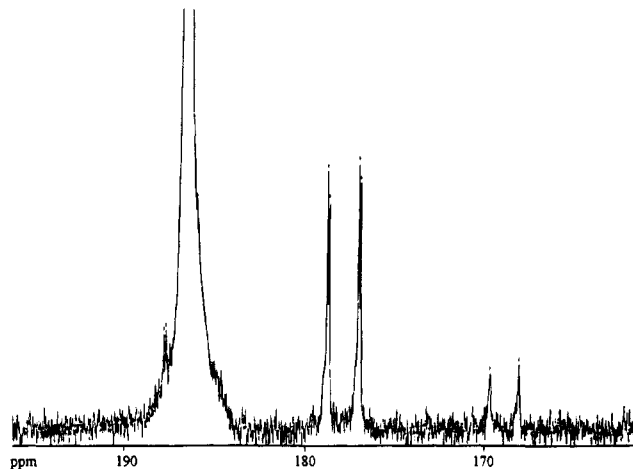


Figure 2. ^{13}C NMR spectrum of $[\text{Pt}(\text{Me})(^{13}\text{CO})\{(\text{S},\text{S})\text{-BDPP}\}]^+\text{SnCl}_3^-$, **3b**, formed by the reaction of compound **2** with ^{13}CO (6 bar) at 203 K in CD_2Cl_2 at the carbonyl region. Downfield $^1J_{\text{Pt}-^{13}\text{C}}$ satellites are partly 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 $^1J_{^{195}\text{Pt},^{13}\text{C}}$ satellites, as shown in Figure 2, which is in the range of terminal Pt-carbonyls.¹⁸ 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, $[\text{Pt}(\text{Me})(\text{CO})\{(\text{S},\text{S})\text{-BDPP}\}]^+\text{SnCl}_3^-$, **3b** (Scheme 1). Compounds analogous to **3b** are known only with *trans* alkyl and carbonyl groups in Pt complexes of monodentate phosphines.^{18j,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 $\text{Pt}(\text{Cl})(\text{SnCl}_3)(\text{L-L})$ compounds (L-L = diphosphine) with monodentate phosphines (L), resulting in the formation of $[\text{Pt}(\text{Cl})(\text{L})(\text{L-L})]^+\text{SnCl}_3^-$ ionic square-planar complexes.¹³ The ionic structure of compound **3b** is also indicated by the lack of $^2J_{\text{Sn,P}}$ and $^2J_{\text{Sn,C}}$ 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, $[\text{Pd}(\text{Me})(\text{CO})\{(\text{S},\text{S})\text{-BDPP}\}]^+\text{BF}_4^-$.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, $[\text{Pt}(\text{COMe})(\text{CO})\{(\text{S},\text{S})\text{-BDPP}\}]^+\text{SnCl}_3^-$, **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

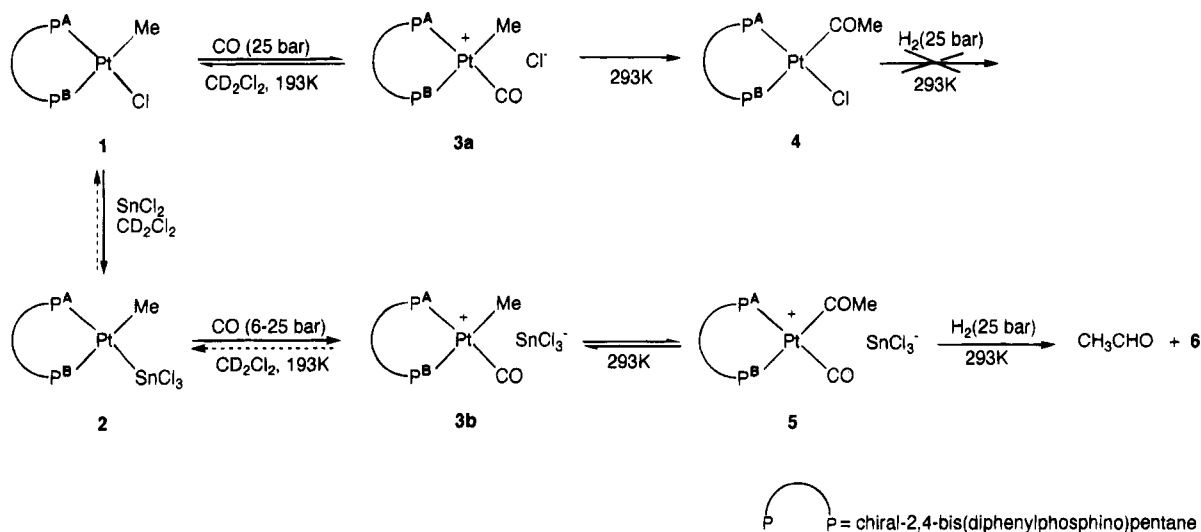


Table 2. Conductivity Data

compd	temp (K)	λ (cm ² Ω^{-1} mol ⁻¹)	compd	temp (K)	λ (cm ² Ω^{-1} mol ⁻¹)
CH ₂ Cl 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 CH₂Cl₂ 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 Pt⁵ and Pd¹⁴ 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 CD₂Cl₂ solution under 25 bar of CO (¹²CO and ¹³CO) at 193 K, the slow

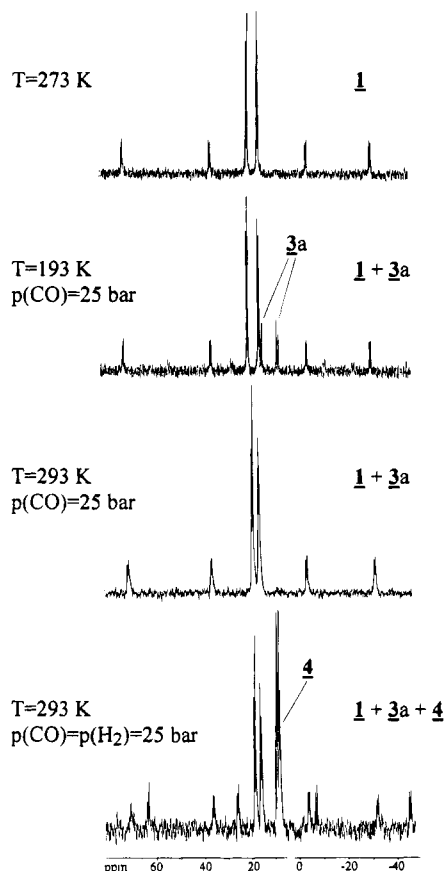


Figure 3. High-pressure ³¹P NMR spectra of the reaction of Pt(Me)-(Cl){(*S,S*)-BDPP}, 1, with CO and CO/H₂ = 1/1 in CD₂Cl₂.

formation of a species was observed which showed identical ³¹P and ¹³C 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,

(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 structure of analogous *trans*-[Pt(R)(CO)L₂]⁺A⁻ compounds has been inferred from the indifference of their ³¹P and ¹³C 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/H₂ = 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/H₂ = 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/H₂ = 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 H₂, 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/H₂ = 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)-BDPP}]⁺SnCl₃⁻, although a hydride resonance in its ¹H NMR spectrum could 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 hydrogenolysis²¹ 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 N₂. 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 SnCl₃ 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)-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)-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 catalysts²⁴ and/or by increasing the solvent polarity. The role of SnCl₂ cocatalyst is obvious in increasing the cationic character of Pt as demonstrated above; SnCl₃⁻ 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.

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- (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/H₂ 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/H₂ = 1/1, the slow formation (5%) of PtCl₂{(S,S)-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 CD₂Cl₂ or to the reaction of divalent PtH(Cl){(S,S)-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.