Journal of Organometallic Chemistry, 316 (1986) 233–241
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PLATINUM(II) TRICHLOROSTANNATE CHEMISTRY. ON THE IMPORTANCE OF THE Pt–Sn LINKAGE IN HYDROFORMYLATION CHEMISTRY AND A NOVEL $PtC(OSnCl_2)R$-CARBENE

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(Received June 10th, 1986)

Summary

The reaction of *trans*-$PtCl(COR)(PPh_3)_2$ (**1**) (R = **a**, C_6H_5; **b**, C_6H_4-*p*-NO_2; **c**, C_6H_4-*p*-CH_3; **d**, C_6H_4-*p*-OCH_3; **e**, CH_3, **f**, Et; **g**, Pr^n; **h**, Hex^n; **i**, CH_2CH_2Ph; **j**, Bu^t) with $SnCl_2$ and $SnCl_2$ plus H_2 are described. The reactions with $SnCl_2$ alone afford a mixture of *trans*-$Pt(SnCl_3)(COR)(PPh_3)_2$ (**2**), and *trans*-$PtCl\{C(OSnCl_2)R\}(PPh_3)_2$ (**3**) with **3** having a tin–oxygen bond. For **1f**, **1h** and **1j**, reactions with $SnCl_2$ plus H_2 give aldehydes and platinum(II) hydride complexes, whereas for **1b** and **1d**, no aldehydes are obtained. The significance of these results in relation to H_2 activation in the hydroformylation reaction is discussed. ^{31}P, ^{119}Sn, ^{195}Pt and, in a few cases, ^{13}C NMR data are presented.

Introduction

There is still considerable uncertainty about the role of the excess tin(II) chloride in the $PtCl_2(PPh_3)_2/SnCl_2$ catalysed hydroformylation reaction [1]. We have found [2] that acyl complexes of the type *trans*-$PtCl(COR)(PPh_3)_2$ (**1**), and *trans*-$Pt(SnCl_3)(COR)(PPh_3)_2$ (**2**), are formed during the catalysis and can be isolated. These acyl complexes in combination with an excess of tin(II) chloride, $SnCl_2$, are also highly active and regioselective hydroformylation catalysts, and may be consid-

0022-328X/86/$03.50

ered late stage intermediates which lead to the production of aldehydes. Indeed the complexes **1** react with $SnCl_2$ to afford new acyl complexes which activate molecular hydrogen. Solvents which prevent this reaction with $SnCl_2$ suppress the hydroformylation [3]. We report here our solution studies on the chemistry related to eq. 1, in which we elucidate the structures of **2** and **3** and throw light on the chemistry related to the significance of **2** and **3** in connection with H_2 activation.

$$\underset{(\mathbf{2})}{\textit{trans}\text{-}PtCl(COR)(PPh_3)_2} + SnCl_2 \rightarrow \textit{trans}\text{-}\underset{(\mathbf{3})}{Pt(SnCl_3)(COR)(PPh_3)_2} + \textit{trans}\text{-}PtCl\{C(OSnCl_2)R\}(PPh_3)_2 \quad (1)$$

Results and discussion

The compounds **1** were prepared by one of two routes as shown in eqs. 2 and 3.

$$Pt(C_2H_4)(PPh_3)_2 + RCOCl \xrightarrow[C_2H_4]{} \underset{(\mathbf{1})}{\textit{trans}\text{-}PtCl(COR)(PPh_3)_2} \quad (2)$$

$$PtCl_2(PPh_3)_2 + CO + \text{olefin} \xrightarrow[EtOH]{} \mathbf{1} \quad (3)$$

The oxidative addition pathway is straightforward [4]. Reaction 3 represents the hydroformylation of the olefin and can be carried out using either (a) ethanol as the hydride source [1,2] or (b) molecular H_2 in the presence of $SnCl_2$ [1,2,5,6]. In view of their relevance to the molecular hydrogen chemistry which follows, we have also prepared the cationic acyl derivatives *trans*-$Pt(RCO)(CO)(PPh_3)_2^+$. These are readily made from **1** by treatment with $AgBF_4$ in the presence of CO (1 atm).

Solution NMR studies

Reaction of *trans*-$PtCl(COR)(PPh_3)_2$ ($R = C_6H_4$-*p*-X, (X = NO_2, CH_3, H, OCH_3), CH_3, Et, Pr^n, Hex^n, CH_2CH_2Ph, Bu^t) with $SnCl_2$ in CH_2Cl_2 affords the $SnCl_3$ complexes *trans*-$Pt(SnCl_3)(COR(PPh_3)_2$ (**2**) whose ^{31}P and ^{119}Sn NMR characteristics are summarized in Table 1. The ^{31}P spectra for the trichlorostannate complexes show that the value of $^1J(Pt, P)$ has been lowered by ca. 300 Hz, relative to those of the analogous chloro compounds. This large *cis* effect of the $SnCl_3$ ligand has been noted previously [7,8], and is in keeping with the view that π acceptor ligands reduce $^1J(Pt, P)$ at the *cis* position.

The most revealing solution data come from ^{119}Sn NMR spectroscopy. The values $^1J(Pt, Sn)$ fall in the range 2003–5265 Hz, with the alkyl R substituents at the lower end. Indeed, the 2003 Hz coupling for R = Bu^t represents the smallest known $^1J(Pt, Sn)$ interaction involving $SnCl_3$. Values for this coupling constant are typically of the order of 10000–30000 Hz for ligands of medium to weak *trans* influence [8,9]. The relatively large 5265 Hz value for the *p*-$C_6H_4NO_2$ analogue suggests that the resonance and inductive effects of the *p*-NO_2 group combine to weaken the donor capability of this acyl ligand significantly, thereby strengthening the Pt–Sn interaction. The values of $\delta(^{119}Sn)$ vary from 44.8–72.3 and cannot be satisfactorily related to the nature of R. This relatively low field position of the tin resonance is normal for a coordinated $SnCl_3$ which is *trans* to a carbon or hydride

TABLE 1

NMR DATA FOR THE TIN-CONTAINING COMPLEXES (δ in ppm; J in Hz)

trans-Pt($SnCl_3$)(COR)L_2 (**1**)	δ(Sn)	^1J(Pt, Sn)	δ(P)	^1J(Pt, P)	J(Sn, P)
R =					
a C_6H_5	60.2	3830	14.3	3071	291
b C_6H_4-*p*-NO_2	44.8	5265	14.7	2976	301
c C_6H_4-*p*-CH_3	62.9	3594	15.2	3093	238
d C_6H_4-*p*-OCH_3	63.4	3540	15.2	3004	308
e CH_3	45.7	2677	14.5	3170	299
f Et [a]	59.6	2557	15.2	3192	301
g Pr^n [a]	58.0	2427	15.2	3214	297
h Hex^n	58.4	2420	15.3	3220	296
i CH_2CH_2Ph	54.2	2846	14.8	3166	299
j Bu^t [a]	72.3	2003	12.6	3288	325
k C_6H_2-3,4,5(OCH_3)$_3$	61.6	3970	15.1	3062	293
trans-PtCl(CO($SnCl_2$)R)L_2	δ(Sn)	^3J	δ(P)	^1J(Pt, P)	J(Sn, P)
R =					
a C_6H_5 [b]	−191.4	800	15.3	2853	78
b C_6H_4-*p*-NO_2					
c C_6H_4-*p*-CH_3 [b]	−218.0	833	16.0	2830	
d C_6H_4-*p*-OCH_3 [c]	−194.0	818	16.0		
e CH_3	−200.7	801	15.8	2903	68
f Et	−191.9	873	16.4	2576	76
g Pr^n	−192.3	915	16.3	2939	81
h Hex^n	−192.3	915	16.4	2960	79
i CH_2CH_2Ph	−216.0 [d]		16.8	3048	78

[a] −60°C, unless otherwise indicated. [b] −90°C. [c] −80°C. [d] −105°C.

ligand [8,10]. The 72.3 ppm value observed in the R = Bu^t compound, combined with its small ^1J(Pt, Sn) value, sets this complex apart. It seems likely that the steric effect of the Bu^t group induces changes in the ligand bond angles and/or lengths to accommodate the crowding due to the presence of four relatively large ligands.

Solutions containing the trichlorostannate complexes **2** reveal additional NMR signals which we assign to **3** (see Fig. 1). Complex **3** is readily distinguished from **2** in that: (a) ^1J(Pt, Sn) decreases to 800–915 Hz; (b) the tin chemical shift moves to much higher field at δ −191.4– −218.0 ppm; (c) ^2J(Sn, P) decreases from its typical value of ca. 300 Hz to between 68 and 81 Hz. It is clear, from point (a) that the $SnCl_3$ (or $SnCl_2$) is no longer directly associated with the platinum as a routine $SnCl_3$ ligand. The reduced spin–spin interaction suggests several intervening bonds between the Pt and Sn spins; however, on the basis solely of these values we cannot exclude a structure such as **4**, in which the chloride is bridging between Pt and Sn [6]. Fortunately there is chemical and spectroscopic evidence in favor of **3**, over **4**. The quantity of **3** present in solution is dependent both on the size and electronic nature of the substituent R. In fact, for R = Bu^t, we find only **2** and no **3** in solution*. Moreover, for our four aryl compounds, the highest percentage of **3** is observed for the *p*-OCH_3 group. We attribute this to the presence of an enhanced

* None detected in the ^{31}P spectrum.

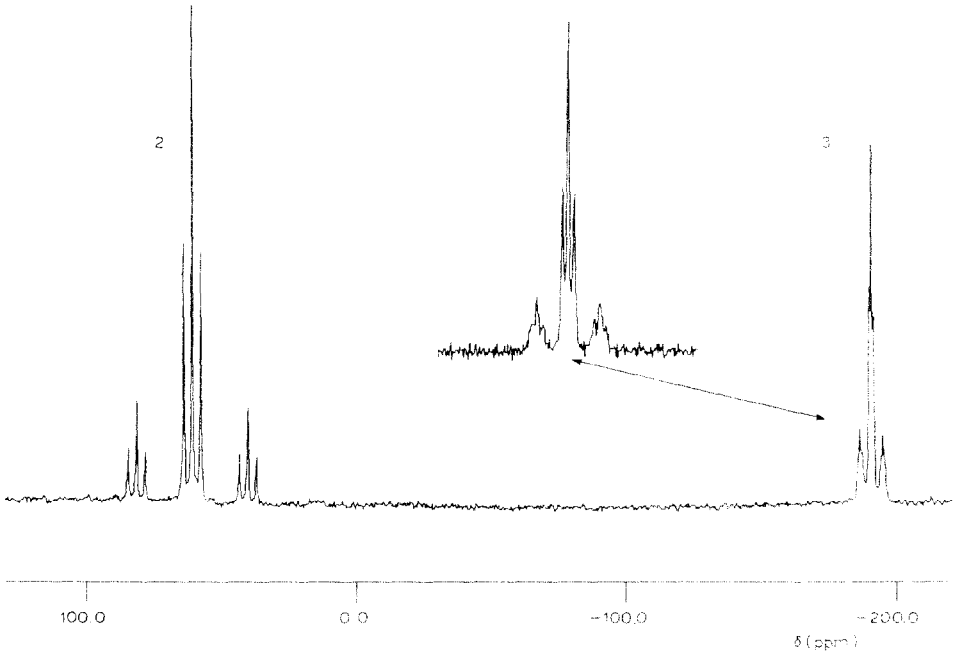
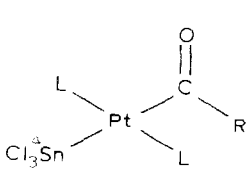
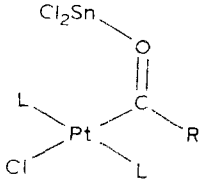


Fig. 1. 93.3 MHz ^{119}Sn NMR spectrum of the reaction solution from *trans*-[PtCl(COC$_6$H$_5$)(PPh$_3$)$_2$]+ $SnCl_2$.

negative charge on the acyl oxygen owing to resonance effects. Both of these points are evidence in favor of **3**, especially as we do not expect structure **4** to be very sensitive to steric effects associated with the acyl ligand.



(2)



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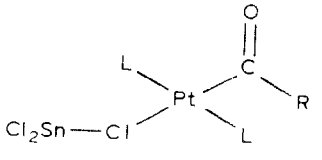


(4)

L = PPh_3

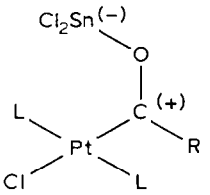
TABLE 2

^{13}C DATA FOR SOME OF THE COMPLEXES **2** AND **3**

R	*trans*-Pt($SnCl_3$)(COR)L_2 (**2**)	*trans*-PtCl(RC($OSnCl_2$))L_2 (**3**)
Ph [a]	217.6	240.2
CH_3 [b]	223.0	252.0
Et	222.2	257.4
Pr^n [c]	222.2	252.2 [d]
CH_2CH_2Ph [e]	222.3	239.5

[a] −60°C, CD_2Cl_2, ^2J(P, C) 8 Hz. [b] −80°C, CD_2Cl_2. [c] −60°C, CD_2Cl_2, ^1J(Pt, C) 776 Hz. [d] ^1J(Pt, C) 920 Hz, ^2J(P, C) 38 Hz. [e] −60°C, CD_2Cl_2.

A structure such as **3** might possess carbene-like properties in that electron density should be drawn from the acyl carbon toward the tin. This would be in keeping with $SnCl_2$ functioning as a Lewis acid. As a consequence, resonance form **5** might contribute to the overall structure. This type of electron redistribution



(**5**)

should be reflected in the ^{13}C characteristics of the acyl carbon of **3**, relative to either **2** or **1**, and to this end we prepared a sample of the benzoyl complex enriched in ^{13}C (> 90 atom%). The method of preparation (see Experimental section) leads to a solution of the complexes **2** and **3** which also contained *trans*-PtClPh(PPh_3)$_2$ and *trans*-PtPh(^{13}CO)(PPh_3)$_2^+$. The conventional trichlorostannate complex **2** shows a carbonyl signal at δ 217.6 ppm with ^1J(Pt, C) 875 Hz and a two-bond coupling ^2J(Sn, C) 843 Hz *. Compound **3** has the analogous resonance at δ 240.2 ppm, with ^1J(Pt, C) 1032 and ^2J(Sn, C) 65 Hz. The 22.6 ppm low-field shift for **3** is fully consistent [11] with a structure containing a contribution from **5**. We have also obtained some ^{13}C data for the CH_3 derivative and find δ 252.0 for the **3** isomer and δ 223.0 ppm for its **2** analogue; a low-field shift of 29 ppm. The signal from the acetyl carbon for *trans*-PtCl($COCH_3$)(PPh_3)$_2$ appears at δ 216.0 ppm. Table 2 contains a summary of these and other ^{13}C data.

Reactivity with molecular hydrogen

The complexes **1b, 1d, 1f, 1h** and **1j** react with $SnCl_2$ and H_2 (1 atm) at room temperature in CH_2Cl_2. The course of the reaction was monitored initially by observing the carbonyl stretching frequencies in the IR spectrum and after 24 h by

* We attribute this large value to the *trans* orientation of these two spins.

TABLE 3

^{31}P NMR DATA[a] FOR THE ACYL COMPLEXES **1**

R	$\delta(^{31}P)$	$^{1}J(Pt,P)$
C_6H_5 [b]	19.9	3398
C_6H_4-*p*-NO_2	19.0 [b]	3276
	19.8 [c]	3275
C_6H_4-*p*-CH_3 [b]	20.0	3415
C_6H_4-*p*-OCH_3 [c]	20.5	3556
CH_3 [d]	20.0	3504
Et [c]	21.0	3516
Pr^n [d]	20.5	3532
Hex^n [d]	20.4	3541
CH_2CH_2Ph [d]	20.4	3495
Bu^t	17.5 [b]	3618
	18.8 [c]	3597
C_6H_2-3,4,5$(OCH_3)_3$	20.2	3368

[a] Chemical shifts in ppm rel. to ext. H_3PO_4, coupling constants in Hz. [b] RT, C_6D_6. [c] −80°C, CD_2Cl_2. [d] RT, CD_2Cl_2.

TABLE 4

THE RELATIVE QUANTITIES OF **2** AND **3** BASED ON ^{31}P NMR INTEGRALS

R	**2**/**3**
C_6H_4-*p*-NO_2	only **2** [a]
Bu^t	only **2** [a]
C_6H_5	1/0.7
CH_3; $-Hex^n$; $-Pr^n$; $-CH_2CH_2C_6H_5$	1/1
C_6H_4-*p*-OCH_3	1/2.3
C_6H_2-3,4,5$(OCH_3)_3$	1/1.2

[a] The presence of small quantities of **3** cannot be excluded.

^{1}H and ^{31}P NMR spectroscopy *. These five compounds were chosen based on our solution observations, e.g., **1j** shows the lowest proportion of complex **3**. Complexes **1f** and **1h** were selected since they arise from the hydroformylation of ethylene and 1-hexene, two commonly used terminal olefins, whereas **1b** and **1d** were expected to provide an insight into reactivity as a function of the aryl substituent.

Complexes **1f**, **1h** and **1j** afford the aldehyde RCHO under these conditions, with **1j** reacting fastest. The approximate times for completion of the reactions are ca. 7 h for **1j**, 24 h for **1h** and 3 d for **1f**. The metal complex which arises, is mainly *trans*-$PtH(SnCl_3)(PPh_3)_2$. The aryl analogues do not react to produce aldehyde but rather (a) *trans*-$PtCl(C_6H_4$-*p*-$NO_2)(PPh_3)_2$ and its $SnCl_3$ derivative, and (b) anisole and *trans*-$PtH(SnCl_3)(PPh_3)_2$.

We consider it significant that **1j**, which gives the largest quantity of **2**, reacts fastest. This is support for our previous suggestions regarding the necessity of forming a Pt–$SnCl_3$ moiety before H_2 activation [2,5,6,12]. It is conceivable that the Pt–$SnCl_3$ unit is necessary only to the extent that it can further react to give a

* For **1j**, the NMR spectroscopy showed the reactions to be complete after ca. 7 h.

platinum cation and an $SnCl_3^-$ anion (i.e. the $SnCl_2$ serves as a halogen extractor) [13]. While we cannot discount this possibility completely, we note that **1**, R = Et or Bu^t with $AgBF_4$ in the presence of CO and H_2, ($H_2/CO = 1$, P_{total} 1 atm), gives the stable cation *trans*-$Pt(COR)(CO)(PPh_3)_2^+BF_4^-$ and no significant amount of aldehyde after 3 d reaction. Consequently the cation $Pt(COR)(solvent)(PPh_3)_2^+$, which would arise from $SnCl_3^-$ dissociation, reacts faster with CO than with H_2, after which no hydrogenolysis occurs at least at room temperature. Accepting the necessity for an intact $Pt-SnCl_3$ bond, it is necessary then to ask what function it performs with respect to hydrogen activation. Reduction of the metal to a lower oxidation state [15] and/or the facilitation of PPh_3 dissociation [12] have already been suggested in our earlier discussions, and we have nothing further to add. It is also noteworthy that H_2 activation with *cis*-$PtCl_2(P(C_6H_4X)_3)_2$ has been shown to be optimum with more than one equivalent of $SnCl_2$ [14] and that hydroformylation is routinely carried out with 5–10 equivalents of $SnCl_2$ per platinum complex [1].

Experimental

NMR spectra were measured using a Bruker WM-250 spectrometer as samples in 10 mm tubes. Chemical shifts are in ppm and coupling constants in Hz. ^{31}P and ^{119}Sn data are reported relative to external H_3PO_4 and Me_4Sn, respectively. The metal chemical shifts are considered to be accurate to ± 0.2 ppm, the ^{31}P shifts to ± 0.1 ppm, and the $^1J(^{195}Pt, ^{119}Sn)$ values to ± 12 Hz.

The solutions containing **2** and **3** were prepared by stirring 1 equivalent each of *trans*-$PtCl(COR)(PPh_3)_2$ and $SnCl_2$ in 3 ml CD_2Cl_2 until the the $SnCl_2$ dissolved (see Table 4 for relative amounts). The complexes **1** were prepared by a published procedure [4] (see Table 3 for ^{31}P data), as was the precursor $Pt(C_2H_4)(PPh_3)_2$ [16]. Some typical preparative procedures are shown below (L = PPh_3 throughout).

trans-PtCl(COEt)L$_2$

$Pt(C_2H_4)L_2$ (1.50 g, 2 mmol) was dissolved in 10 ml of degassed toluene. An excess of C_2H_5COCl (500 mg) was added under N_2 and the solution was stirred for 1 h during which some white product precipitates. Addition of 30 ml of n-hexane caused the precipitation of additional acyl complex. Analytically pure *trans*-$PtCl(COC_2H_5)L_2$ was obtained by recrystallization from benzene/hexane. (Yield 950 mg, 58%) IR (Nujol mull) $\nu(CO)$ at 1642 cm^{-1}. Found: C, 57.5; H, 4.2. $C_{39}H_{35}ClOP_2Pt$ calcd.: C, 57.7; H, 4.3%. ^1H NMR $\delta(CH_3)$ 0.15 ppm (t, J 7.0 Hz); $\delta(CH_2)$ 1.54 ppm (q). With less reactive acyl chlorides (R = aryl or t-butyl) the oxidative addition proceeds too slowly at room temperature, and so these reactions were performed by heating toluene solutions under reflux.

Complexes **1f, 1g, 1h, 1i** were also prepared by treating an ethanol solution of *cis*-$PtCl_2L_2$ (472 mg, 0.6 mmol) with the appropriate α-olefin under CO pressure as previously described [3].

trans-Pt(COR)(CO)L$_2^+$ BF$_4^-$, (R = ethyl, t-butyl)

Complex *trans*-$[PtCl(COEt)L_2]$ (290 mg) was dissolved in 10 ml of dichloromethane at room temperature under a CO atmosphere. Addition of a stoichiometric amount (70 mg, 0.36 mmol) of $AgBF_4$ gave a precipitate of AgCl. The clear solution was then diluted with diethyl ether under a CO atmosphere to give *trans*-

$[Pt(COEt)(CO)L_2]^+ BF_4^-$ as white powder. The product was filtered off and dried in a CO stream. (Yield 260 mg, 82%). IR (CH_2Cl_2) ν(CO) at 2109 and 1665 cm^{-1}. ^1H NMR (CD_2Cl_2) $\delta(CH_3)$ −0.18 ppm (t, J 6.3 Hz); $\delta(CH_2)$ 1.32 ppm (q); phenyl protons 7.3–8.3 ppm. ^{31}P NMR δ(P) 13.2; ^1J(Pt, P) 3070 Hz. Found: C, 53.6; H, 4.0. $C_{40}H_{35}BF_4O_2P_2Pt$ calcd.: C, 53.9; H, 3.9%.

The same procedure was followed for preparation of the t-butyl derivative. IR (CH_2Cl_2) ν(CO) at 2106 and 1646 cm^{-1}. ^1H NMR $\delta(CH_3)$ 0.30 ppm. ^{31}P NMR δ(P) 11.1 ppm; ^1J(Pt, P) 3066 Hz. Found: C, 54.7; H, 4.3. $C_{42}H_{39}BF_4O_2P_2Pt$ calcd.: C, 54.8; H, 4.2%.

Reaction of complexes ***1b, 1d, 1f, 1h, 1j*** *with $SnCl_2$ and molecular hydrogen*

To a thermostatted solution (25°C) of the relevant title complex (0.2 mmol in 8 ml of CH_2Cl_2) was added a stoichiometric amount of $SnCl_2$. The mixture was stirred under N_2 until the tin salt completely dissolved. The N_2 atmosphere was then replaced by hydrogen, and the progress of the reaction was monitored by examining the acyl carbonyl absorption in the IR spectrum at intervals.

Reaction of complexes trans-$Pt(COR)L_2^+$ with synthesis gas

Complex **1f** or **1j** (0.1 mmol) and solid $AgBF_4$ (0.1 mmol) were placed in a small Schlenk tube equipped with a magnetic stirring bar, a gas inlet and a rubber septum. The Schlenk tube was evacuated and purged with syngas ($CO/H_2 = 1/1$) 4 ml of dichloromethane was injected, and stirring begun. After a few minutes AgCl separated out and the clear solution was filtered into another Schlenk tube which was placed in a thermostatted bath (25°C). IR spectroscopy indicated the formation of *trans*-$Pt(COR)(CO)L_2^+ BF_4^-$. The behaviour of the chemistry was periodically checked by IR spectroscopy. No reaction was detected during 3 d and this was confirmed by recording the ^{31}P NMR spectrum of the solution, which showed only the presence of the signals from *trans*-$Pt(COR)(CO)L_2^+ BF_4^-$.

Preparation of ^{13}CO enriched trans-$Pt(SnCl_3)(^{13}COC_6H_5)(PPh_3)_2$

A solution of *trans*-$PtCl(C_6H_5)(PPh_3)_2$ (0.10 g, 0.12 mmol) in 2.5 ml CD_2Cl_2 was then treated with anhydrous $SnCl_2$ (0.030 g, 0.17 mmol) at room temperature for 30 s. The solution was degassed under vacuum then treated with 1 atm ^{13}CO (90% ^{13}C) for 2 h at room temperature.

Acknowledgements

H.J.R. and P.S.P. thank the Swiss National Science Foundation for support and the Johnson Matthey Research Centre (England), for the loan of platinum salts.

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