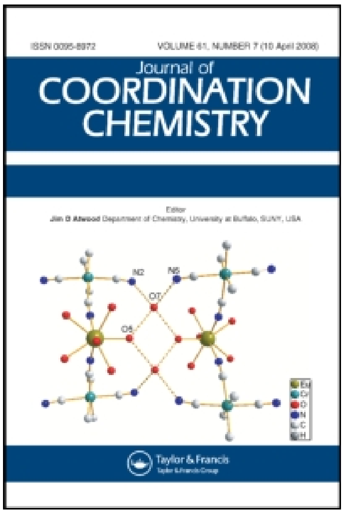


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

DECARBONYLATION OF ACYLCHLOROBIS-(TRIPHENYLPHOSPHINE) PLATINUM(II) COMPLEXES PROMOTED BY TIN(II) CHLORIDE

Mitsuru Kubota[a]; David A. Phillips[a]; Jon E. Jacobsen[a]
[a] Department of Chemistry, Harvey Mudd College, Claremont, California

To cite this Article Kubota, Mitsuru , Phillips, David A. and Jacobsen, Jon E.(1980) 'DECARBONYLATION OF ACYLCHLOROBIS-(TRIPHENYLPHOSPHINE) PLATINUM(II) COMPLEXES PROMOTED BY TIN(II) CHLORIDE', Journal of Coordination Chemistry, 10: 1, 125 — 129

To link to this Article: DOI: 10.1080/00958978008079859

URL: http://dx.doi.org/10.1080/00958978008079859

J. Coord. Chem., 1980, Vol. 10, pp. 125–129
0095-8972/80/1001-0125 $04.50/0

DECARBONYLATION OF ACYLCHLOROBIS-(TRIPHENYLPHOSPHINE) PLATINUM(II) COMPLEXES PROMOTED BY TIN(II) CHLORIDE

MITSURU KUBOTA, DAVID A. PHILLIPS, and JON E. JACOBSEN

Department of Chemistry, Harvey Mudd College, Claremont, California 91711

(Received July 23, 1979; in final form Sept. 26, 1979)

While it might be expected that the availability of vacant coordination sites in the four coordinate acyl complexes trans[Pt(PPh$_3$)$_2$(RCO)Cl] provides low energy pathways for alkyl and aryl migration and subsequent decarbonylation, the decarbonylation has been previously achieved only at elevated temperatures. The addition of $SnCl_2$ greatly facilitates decarbonylation of [Pt(PPh$_3$)$_2$(RCO)Cl] where R is CH_3, C_2H_5, Y–C_6H_4. Compounds of the type [Pt(PPh$_3$)$_2$(RCO)SnCl$_3$] and [Pt(PPh$_3$)$_2$R(SnCl$_3$)] have been isolated. The removal of $SnCl_2$ from these compounds has been achieved with ethanol. A kinetic study of the decarbonylation of [Pt(PPh$_3$)$_2$(RCO)SnCl$_3$] (where R is CH_3, C_2H_5, Y–C_6H_4 for Y=H, CH_3, CH_3O, NO_2, Cl) is reported. The role of 3 and 5 coordinate intermediates in alkyl-aryl migrations in Pt(II) systems is discussed.

INTRODUCTION

The extrusion of carbon monoxide from acyl platinum complexes trans-[Pt(PPh$_3$)$_2$(RCO)Cl] requires high temperatures, for example 188° for R = C_6F_5,[1] 210° for R = C_6H_5,[2] and 210–220° for R = CH_3.[3] Several other acyl complexes yield intractable decomposition products upon efforts extended to thermally decarbonylate them.[4] Decarbonylation proceeds by migration of alkyl or aryl from CO to metal[5] followed by loss of CO. We have previously shown that migration of alkyl or aryl from CO to Ir is greatly facilitated by the presence of a vacant coordination site on the metal.[6] If the availability of vacant coordination sites is a significant requirement for migration, it was of interest to study why decarbonylation is not a facile process for four-coordinate *trans*-[Pt(PPh$_3$)$_2$(RCO)Cl] which has vacant coordination sites. In the course of these studies we have found that tin(II) chloride promotes the decarbonylation reaction.

EXPERIMENTAL

Anhydrous tin(II) chloride was obtained by stirring 10 g $SnCl_2 \cdot 2H_2O$ in 100 ml acetic acid and 50 ml acetic anhydride at 80° for 4 h. After cooling and filtering, the $SnCl_2$ was washed with Et_2O, dried in vacuo at 100°C for 2 h, and stored under dry nitrogen. Acyl chlorides were reagent grade samples which were distilled before use or prepared by reaction of thionyl chloride and the carboxylic acid. [Pt(PPh$_3$)$_4$C$_2$H$_4$] was prepared by the method of Cook and Jauhal.[7] Since the previously described synthesis[8] of [Pt(PPh$_3$)$_2$(RCO)Cl] from [Pt(PPh$_3$)$_4$] and RCOCl did not consistently give the desired product, solutions of [Pt(PPh$_3$)$_2$C$_2$H$_4$] with excess RCOCl in benzene were stirred for 2–3 h to give [Pt(PPh$_3$)$_2$(RCO)Cl]. The benzene was removed under reduced pressure and the products washed with ethanol. The compounds were then recrystallized from CH_2Cl_2–EtOH or C_6H_6–EtOH. A similar method has been described.[9]

General method for [Pt(PPh$_3$)$_2$(RCO)SnCl$_3$. A sample of [Pt(PPh$_3$)$_2$(PhCO)Cl]. (117 mg, 0.14 mmol) was dissolved in 15 ml of dichloromethane. Anhydrous $SnCl_2$ (28 mg, 0.15 mmol) was added and the mixture stirred. After a few minutes, the solution turned yellow. After 20 min the solution was filtered and the filtrate taken to dryness. The orange solid was washed with ligroin (30–60°) and dried in vacuo. Yield: 133 mg (93%). Anal. Calcd for $C_{43}H_{35}Cl_3OP_2PtSn$: C, 49.16; H, 3.35; Cl, 10.11. Found: C, 48.87; H, 3.63; Cl, 10.49. The other acyl–$SnCl_3$ complexes were prepared in a similar manner in approximately 90% yield. Spectral data for these compounds are shown in Table I. Washing the $SnCl_3$ complexes with ethanol or diethyl ether resulted in removal of $SnCl_2$.

Decarbonylation of $[Pt(PPh_3)_2(RCO)SnCl_3]$. A sample of $[Pt(PPh_3)_2(PhCO)SnCl_3]$ (120 mg) was suspended in 25 ml of benzene and the solvent was refluxed with stirring for one hour. After cooling to room temperature, the solvent was removed under reduced pressure and the pale yellow solid was triturated with ligroin (30–60°) and filtered. Yield: 106 mg (91%). Anal. Calcd for $C_{42}H_{35}Cl_3P_2PtSn$: C, 49.36; H, 3.45; Cl, 10.41. Found: C, 49.17; H, 3.53; Cl, 10.41. A sample of $[Pt(PPh_3)_2(SnCl_3)(C_6H_5)]$ (43 mg) was stirred with 12 ml EtOH for 15 min. The white product was collected by filtration and washed with 5 ml EtOH. The product was found to be identical by its IR with $[Pt(PPh_3)_2Cl(C_6H_5)]$. Complete decarbonylation of $[Pt(PPh_3)_2(RCO)SnCl_3]$ where R is CH_3 and $p\text{-}CH_3C_6H_4$ in refluxing benzene for one hour was also demonstrated in a similar manner.

$[Pt(PPh_3)_2(PhCO)Cl]$ (125 mg) in 20 ml toluene was heated at reflux for 2.5 h. The solvent was removed under reduced pressure and the product was washed with Et_2O. Colorless crystals of the decarbonylated compound were obtained from 10 ml benzene and 10 ml EtOH containing 50 mg Ph_3P. Mp 265–270 (dec.) Anal. Calcd for $C_{42}H_{35}ClP_2Pt$: C, 60.0; H, 4.30. Found C, 60.7; H, 4.49. The product was carbonylated by dissolving it in 10 ml CH_2Cl_2 with 1 mg $SnCl_2$ and stirring it with 30 psi for 16 h. Ethanol (10 ml) was added and the volume of solvent reduced to give the original starting $[Pt(PPh_3)_2(PhCO)Cl]$.

Catalytic decarbonylation. Samples of 100 mg $[Pt(PPh_3)_2(PhCO)Cl]$ in 20 ml benzene and 52 mg $[Pt(PPh_3)_2(C_2H_5CO)Cl]$ in 10 ml ethanol were heated at reflux temperature for 90 min. The solvents were distilled and products were washed with Et_2O. The infrared spectra indicated that the original reactants were unchanged, hence that there was no decarbonylation. A sample of $[Pt(PPh_3)_2(PhCO)Cl]$ (100 mg, 0.116 mmol) and 5 mg (0.017 mmol) $SnCl_2$ were stirred in CH_2Cl_2 for 5 min to give a yellow solution. The dichloromethane was evaporated under reduced pressure and the product was heated in refluxing benzene (20 ml) for 1 hr. The benzene was stripped and the product was washed with Et_2O. The infrared spectrum of the sample indicated complete decarbonylation.

RESULTS AND DISCUSSION

Solutions of *trans*-$[Pt(PPh_3)_2(RCO)Cl]$ (R = Ph, Et) in benzene heated at reflux temperature for 1.5 h did not give decarbonylation. The addition of catalytic amounts of anhydrous $SnCl_2$ to such solutions promoted decarbonylation.

$$\text{trans-}[Pt(PPh_3)_2(C_6H_5CO)Cl] \xrightarrow[SnCl_2]{80^\circ,\ C_6H_6} \text{trans-}[Pt(PPh_3)_2(C_6H_5)Cl] \quad (1)$$

To elucidate the role of $SnCl_2$, the reactions of the acyl platinum complexes with $SnCl_2$ were investigated. This reaction was carried out in CH_2Cl_2 for 30 min. Longer reaction times gave loss of CO at 25°C. The excess $SnCl_2$ was filtered and the orange products were recovered with petroleum ether.

$$\text{trans-}[Pt(PPh_3)_2(RCO)Cl] + SnCl_2 \longrightarrow \text{trans-}[Pt(PPh_3)_2(RCO)SnCl_3] \quad (2)$$

Pertinent infrared spectral data for these compounds are given in Table I.

The absence of intense IR absorption in the 540–550 cm^{-1} region indicates that all the acyl complexes are *trans*.[10] Each of the acyl (Pt–C(O)R) compounds has a strong band in the 1620–1652 cm^{-1} region due to CO stretching. The frequency of this band is relatively insensitive to whether the acyl moiety is *trans* to Cl or $SnCl_3$. As previously noted, the band in the 254–270 cm^{-1} region which is due to Pt–Cl stretching indicates that the acyl group is a strongly *trans* labilizing group.[11] Addition of $SnCl_2$ to the chloro-platinum complexes gives the Pt–$SnCl_3$ compounds which have ν(Sn–Cl)

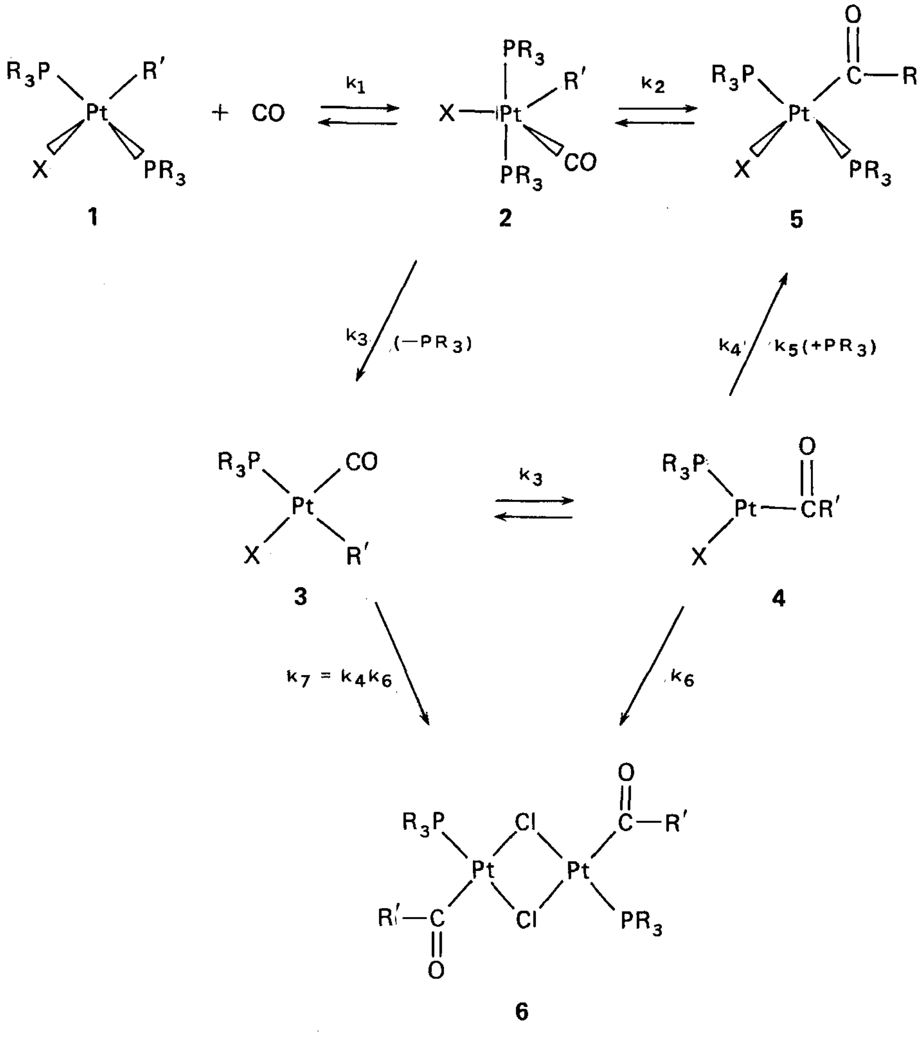
TABLE I
Infrared Spectral Data

	ν(CO) cm^{-1}	OTHER cm^{-1}
$PtL_2(CH_3CO)Cl^a$	1650	257
$PtL_2(CH_3CO)SnCl_3$	1652	342, 320
$PtL_2(C_2H_5CO)Cl$	1661	254
$PtL_2(C_2H_5CO)SnCl_3$	1660	344, 321
$PtL_2(PhCO)Cl$	1616	260, 885
$PtL_2(PhCO)SnCl_3$	1625	870
$PtL_2(p\text{-}CH_3C_6H_4CO)Cl$	1632	263, 890
$PtL_2(p\text{-}CH_3C_6H_4CO)SnCl_3$	1625	875
$PtL_2(p\text{-}CH_3OC_6H_4CO)Cl$	1613	260
$PtL_2(p\text{-}O_2NC_6H_4CO)Cl$	1630	270
$PtL_2(p\text{-}O_2NC_6H_4CO)SnCl_3$	1629	879

^{a}L is PPh_3.

in the 340 and 320 cm^{-1} region.[12] The chloro-aroyl complexes have an intense band in the 885–890cm^{-1} region which shifts slightly to lower energy in the $SnCl_3$ complexes. The alkyl acyl compounds do not have this intense absorption band.

A kinetic study of the decarbonylation of the $[Pt(PPh_3)_2(RCO)SnCl_3]$ complexes was conducted. The rates were followed by measuring the CO evolved using gas chromatography (molecular sieves 5A), manometrically, and by changes in the ultraviolet spectra (310 nm). The rate of decarbonylation was found to be first order with respect to acyl compound. The radical scavenger galvinoxyl and the radical initiator benzoyl peroxide did not greatly affect the rates of decarbonylation, but the rate of decarbonylation was found to be photo sensitive to UV radiation. The rate constants determined spectrophotometrically by following the disappearance of an absorption band at 305 nm due to the reactant acyl complex appeared to be much larger than the rate constants determined by measuring the appearance of product CO. See Table II. This difference is indicative of a multi-step process with two or more slow steps in which relatively stable intermediates are formed. At least one such species with ν(CO) at 2100 cm^{-1} has been isolated in this study. This



Scheme 1.

TABLE II
Rate Constants for Decarbonylation of
$[Pt(PPh_3)_2(RCO)SnCl_3]$

R	$k_1 \times 10^4 (sec^{-1})^a$	$k_1 \times 10^5 (sec^{-1})^b$
CH_3	2.5	1.2
C_2H_5	2.9	–
p-$CH_3OC_6H_4$	1.9	2.5
p-$CH_3C_6H_4$	2.1	2.5
C_6H_5	2.2	5.6
p-ClC_6H_4	2.0	–
p-$O_2NC_6H_4$	2.2	6.9

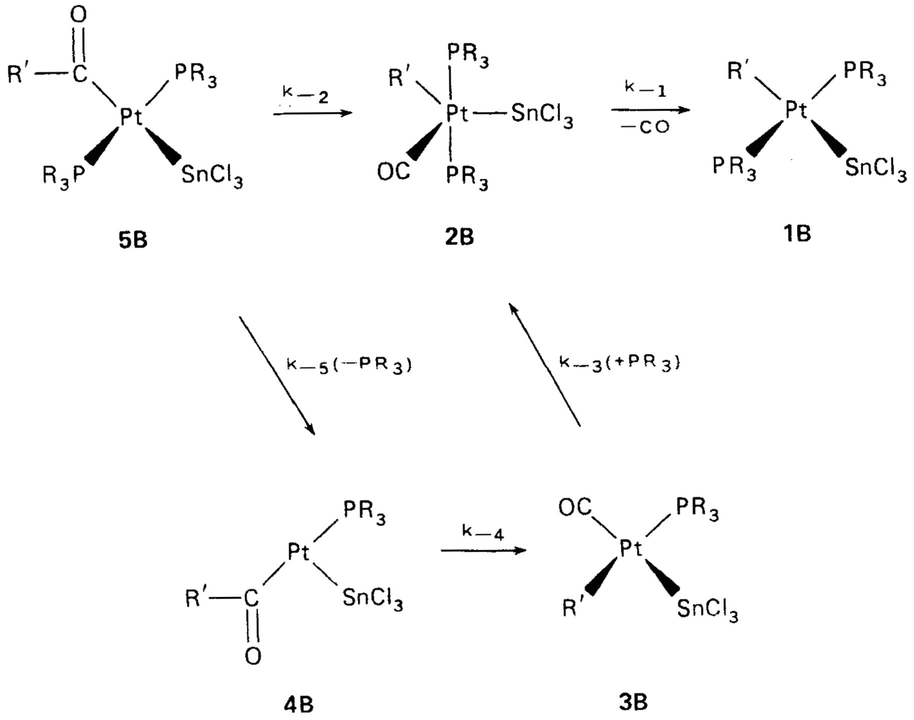
[a] Rate constants determined for reaction in 1,1,2,2-tetrachloroethane at 25°C by spectrophotometrical measurement of absorption at 304 nm;

[b] Rate constants determined for reaction in CH_2Cl_2 at 40° by gas chromatographic assay of CO.

species releases CO upon treatment with PPh_3. The spectrophotometric rates thus give the rates for formation of **3B** $[PtR(PPh_3)(CO)SnCl_3]$, vide infra. While such species have not been isolated in the present study, their chloro analogs have been isolated by others.[13] The rates of formation of the complexes **3B** are not greatly affected by the nature of R. The rates of CO evolution, on the other hand appear to be only slightly more rapid for aryl R groups compared with alkyl groups and also slightly more rapid for electron withdrawing substituents. The differences of rates, however, are too small to support any definitive role of the R group in the rate-determining step in the decarbonylation reaction.

The promotion of decarbonylation of the acyl platinum complexes may be accounted for in terms of the microscopic reverse of the mechanisms for carbonylation[14] shown in Scheme I. Examples of the five coordinate complex **2** have been isolated.[14] The direct migration step (k_2) is minor and the major pathway (83–98%) is the dissociative rate (k_3, k_4, k_5). The migration of R to CO proceeds for **3**, but not for its other geometric isomers.[15] Kinetic studies indicate that the reaction of **3** with PR_3 to give **5** goes via the three-coordinate intermediate **4** instead of the five-coordinate species 2.[13] The compound **3** forms the dimer **6** (the extent varying with $PhCH_2 > Me > Ph > Et$) presumably via **4**.[15]

The proposed mechanism for the $SnCl_2$ facilitated decarbonylation shown in Scheme 2 depends on the unique properties of the $SnCl_3$ ligand. These include: (1) the increased tendency of labilization of PR_3 by the strongly labilizing $SnCl_3$ ligand;[16] (2) the



Scheme 2.

stabilization of the five-coordinate species **2B** by the pi-bonding $SnCl_3$ ligand; and (3) the decreased tendency for formation of the chloride bridged dimer **6** in Scheme 1 when the non-bridging $SnCl_3$ ligand is used. As mentioned previously IR evidence indicative of species containing Pt–CO bonded species **3B** characterized by ν(CO) at 2100 cm^{-1} has been obtained. This species releases CO upon treatment with PPh_3. When PPh_3 is initially added to a freshly prepared tetrachloroethane solution of $[Pt(PPh_3)_2(RCO)SnCl_3]$, the rate of decarbonylation was found to be retarded. The equilibrium leading to formation of **4B** from **5B** is not favored in the presence of excess PPh_3. On the other hand, if PPh_3 is added 500 sec after the rearrangement reaction has been initiated, there is a large enhancement of rate of CO evolution. It is likely that there is a build-up of species **3B** which reacts with PPh_3 to give CO. The direct migration pathway k_{-2} is not expected to be as important as the pathway involving **3B** and the three-coordinate species **4B**. Such three-coordinate species are being increasingly recognized as important intermediates for rearrangements in platinum(II) complexes.[13,14]

ACKNOWLEDGEMENT

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this research. J. E. J. was a National Science Foundation Undergraduate Research Participant.

REFERENCES

1. A. J. Mukhedar, M. Green and F. G. A. Stone, *J. Chem. Soc. A*, 947 (1970).
2. M. C. Baird and G. Wilkinson, *J. Chem. Soc. A*, 865 (1967).
3. C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, 45, 30 (1967).
4. G. Booth and J. Chatt, *J. Chem. Soc. A.*, 634 (1966).
5. (a) A. Wojcicki, *Adv. Organometal Chem.*, 11, 87 (1973); (b) F. Calderazzo, *Angew. Chem. Int. Ed. Engl.*, 16, 299 (1977).
6. (a) M. Kubota and D. M. Blake, *J. Am. Chem. Soc.*, 93, 1368 (1971). (b) M. Kubota, D. M. Blake, and S. A. Smith, *Inorg. Chem.*, 10, 1430 (1971).
7. C. D. Cook and G. S. Jauhal, *Inorg. Nucl. Chem. Lett.*, 3, 31 (1967).
8. C. D. Cook and G. S. Jauhal, *Canad. J. Chem.*, 45, 301 (1967).
9. S. P. Dent, C. Eaborn, A. Pidcock, and B. Ratcliff, *J. Organomet. Chem.*, 46, C68 (1972); 97, 307 (1975).
10. S. H. Mastin, *Inorg. Chem.*, 13, 1003 (1974).
11. M. Kubota, R. K. Rothrock, and J. Geibel, *J. Chem. Soc. Dalton Trans.*, 1267 (1973).
12. J. F. Young in "Advances in Inorganic Chemistry and Radiochemistry," H. J. Emeleus and A. G. Sharp, Ed., Academic Press, New York, Vol. XI, pp 91–145.
13. C. J. Wilson, M. Green, and R. J. Mawby, *J. Chem. Soc. Dalton Trans.*, 1293 (1974).
14. (a) P. E. Garrou and R. F. Heck, *J. Am. Chem. Soc.*, 98, 4115 (1976); (b) N. Sugita, J. V. Minkiewicz, and R. F. Heck, *Inorg. Chem.*, 17, 2809 (1978).
15. G. K. Anderson and R. J. Cross, *J. Chem. Soc. Chem. Commun.*, 819 (1978).
16. (a) G. W. Parshall, *J. Am. Chem. Soc.*, 88, 704 (1976); (b) R. V. Lindsey, Jr., G. W. Parshall and U. G. Stolberg, *J. Am. Chem. Soc.*, 87, 658 (1965).
17. (a) J. H. Price, J. P. Birk, and B. B. Wayland, *Inorg. Chem.*, 17, 2245 (1978); (b) R. Romeo, D. Minniti, and M. Trozzi, *Inorg. Chem.*, 15, 1134 (1976).