Journal of Organometallic Chemistry, 390 (1990) 267–274
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20805

Carbon monoxide insertion into *trans*-Pt(η^1-C_3H_5)-(phosphine$_2$)Cl complexes in benzene. Crystal structure of *trans*-[Pt($COCH_2CH{=}CH_2$](PPh$_3$)$_2$Cl

S. Dirè, R. Campostrini, G. Carturan,
Department of Engineering, University of Trento, 38050 Mesiano, Trento (Italy)

M. Calligaris and G. Nardin
Department of Chemical Sciences, University of Trieste, Piazzale Europa 1, 34127 Trieste (Italy)

(Received January 17th, 1990)

Abstract

η^1-Allylplatinum(II) complexes of the type *trans*-Pt(η^1-C_3H_5)(phosphine$_2$)Cl-((phosphine)$_2$ = (PPh$_3$)$_2$, (P(C_6H_{11})$_3$)$_2$) have been shown to react with carbon monoxide in benzene to give products of insertion of CO into the σ-metal–carbon bond. The acyl group has the allyl double bond unconjugated with the carbonyl moiety, which was indicated by ^{1}H NMR spectroscopy and confirmed by an X-ray structural determination in the case of *trans*-Pt($COCH_2CH{=}CH_2$)(PPh$_3$)$_2$Cl. The reaction mechanism is discussed in respect of allyl group coordination and the role of the solvent.

Introduction

The unusual reactions of η^1-allyl complexes of both square planar d^8 and octahedral d^6 metal ions has been demonstrated in a large number of studies of reactions that permit direct comparison with the corresponding reactions of ordinary alkylmetal compounds [1–3]. In all cases the nature of the coordinated ligands and the coordination number of the metal appear to be of paramount importance in determining the nature of the reactions of the η^1-allyl species: these factors can be chosen to favour or disfavour maintenance of the η^1-allyl coordination during the reaction, and so determine the course of the reaction [4,5].

For square planar d^8 complexes, the η^1-allyl bonding, shown to be present in the solid state [5,6], can in solution readily be transformed by elimination of one ligand into η^3-allyl coordination, particularly when the complexes are involved in reactions with other species. In these cases, knowledge of allyl group coordination mode in the starting species is a minor factor in predicting the nature of the product, since this is essentially determined by ligand organization during the reaction course. Examples are provided by the reaction of TCNE with (η^3-allyl)$_2$M (M = Pd, Pt), SO_2 insertion into η^1-allyl complexes of platinum(II) and the reactions of CO with allylpalladium complexes [7]. As a further example involving allylplatinum(II) complexes, we report here a study of the reactions of CO with η^1-allyl platinum(II) complexes. The reaction was studied in non-polar aprotic solvents for complexes containing coordinated phosphino ligands with different basicity and steric hindrance. In such solvents the η^1-allyl form is dominant and should favour normal CO insertion; indeed, in the absence of η^1-allyl ligands, CO does not insert into palladium(II) complexes [7c]. The experimental conditions we used were different from those used by Volger and Vrieze [8], who reported more than 20 years ago the formation of a $CH_3CH{=}CHCO$ moiety by reaction of carbon monoxide with allylplatinum(II) compounds in $CHCl_3$.

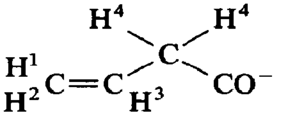
Experimental

General procedures and measurements

Air-sensitive compounds were manipulated under nitrogen. Commercial reagent-grade chemicals, included phosphines, were used without further purification. The complexes Pt(η^1-C_3H_5)(L_2)Cl were prepared as previously described [5]. IR spectra were recorded on a Perkin Elmer model 683 spectrophotometer in the range 4000–200 cm^{-1} at Nujol mulls between CsI windows. The spectra were calibrated with polystyrene and the frequency is estimated to be accurate to ±2 cm^{-1}. ^1H NMR spectra were recorded in CD_2Cl_2 on a Varian FT 80 spectrometer with TMS as internal standard. $^{31}P\{^1H\}$ NMR spectra were recorded on the same instrument at 32.203 MHz in CD_2Cl_2 with aqueous H_3PO_4 as external standard.

Reaction of trans-Pt(η^1-C_3H_5)(L_2)Cl with CO

Complex 1a (L_2 = 2PPh_3). **1a** (1.050 g, 1.32 mmol) was partially dissolved under nitrogen in 30 ml of dry benzene and the slurry was stirred at room temperature in a glass lined stainless steel autoclave under 10 atm of CO pressure for 48 h. The solution formed was concentrated to 10 ml under reduced pressure and 10 ml of ether were added, to give a white precipitate which was filtered off, washed with pentane, and dried in vacuo (0.780 g, yield 71.7%). IR: ν(Pt–Cl) 260 cm^{-1}, ν(C=O) 1650 cm^{-1}. Analysis: Found: C, 58.4; H, 4.3; Cl, 4.6. $C_{40}H_{35}ClOP_2Pt$ calcd.: C, 58.29; H, 4.28; Cl, 4.30%. ^1H NMR: phosphine protons in the interval 7.1–8.1 ppm. Allylic protons of:



H^1 3.8 ppm, $^2J_{1\text{-}2}$ 2.2 Hz; H^2 4.3 ppm, $^3J_{2\text{-}3}$ 9.0 Hz; H^3 4.6 ppm, $^3J_{3\text{-}4}$ 6.0 Hz, $^3J_{1\text{-}3}$ 15.0 Hz; H^4 2.1 ppm, $^4J_{2\text{-}4}$ 0.7 Hz, $^4J_{1\text{-}4}$ −1.2 Hz.

Complex 1b (L_2 = 2P(C_6H_{11})$_3$). Reaction of 0.4 g (0.481 mmol) of **1b** with CO under the conditions described above gave 0.220 g (yield 53.2%) of a white solid. IR: ν(Pt–Cl) 260 cm^{-1}, ν(C=O) 1630 cm^{-1}. Analysis: Found: C, 55.9; H, 8.5; Cl, 4.6. $C_{40}H_{71}ClOP_2Pt$ calcd.: C, 55.83; H, 8.32; Cl, 4.21%. ^1H NMR: phosphine protons

Table 1
Crystallographic data collection for $Pt(COC_3H_5)(PPh_3)_2Cl$

Formula	$C_{40}H_{35}ClOP_2Pt/0.5\ CH_2Cl_2$
Mol. wt.	882.74
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	17.867(6)
b (Å)	15.595(5)
c (Å)	15.159(4)
β (°)	114.66(2)
Z	4
V (Å^3)	3838
ρ (calc., g cm^{-3})	1.53
μ (cm^{-1})	41.0
Radiation	Mo-K_α (λ 0.71069 Å)
2θ range (°)	4.0:54.0
Scan type	$\omega/2\theta$
No. of independent data	3377
R (obs. reflection)	0.071
R_w	0.078

in the interval 1.5–2.9 ppm. Allylic protons: H^1 5.1 ppm, $^2J_{1\text{-}2}$ 2.2 Hz; H^2 6.3 ppm, $^3J_{2\text{-}3}$ 9.0 Hz; H^3 6.6 ppm, $^3J_{3\text{-}4}$ 6.0 Hz, $^3J_{1\text{-}3}$, 14.0 Hz; H^4 3.5 ppm tentative assignments: the assignments of δ and J values give the best agreement between simulated and experimental spectra.

Crystallographic data

Suitable crystals for X-ray diffraction were obtained by slow diffusion of n-pentane into a solution of $Pt(COC_3H_5)(PPh_3)_2Cl$ in CH_2Cl_2. Weissenberg photographs indicated low crystallinity. However, a plate of 0.1 × 0.4 × 0.8 mm was good enough for intensity collection on an Enraf–Nonius CAD-4 four-circle diffractometer. Cell constants were obtained by least squares fit of the 2θ values of 25 reflections ($11° \leq \theta \leq 18°$) by use of the centering routines of the Enraf–Nonius CAD-4/SDP diffractometer [9]. Crystallographic data and details of the data collection are given in Table 1.

Three standard reflections, measured every 400 min, were used to check the stability of the crystal and no significant variations were detected. The orientation of the crystal was checked every 100 reflections. Intensity data were corrected for Lorentz and polarization effects and for adsorption using the azimuthal ψ scans of four close-to-axial reflections.

The intensities of 3377 independent reflections with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. All calculations were carried out by use of the Enraf–Nonius SDP library [9]. Neutral atom scattering factors and anomalous disperion corrections applied to all non-hydrogen atoms were those given by Cromer and Waber [10].

The structure was solved and refined by conventional three-dimensional Patterson, Fourier, and full-matrix least-squares methods. Broad peaks were attributed to CH_2Cl_2 molecules, but their low electron densities were indicative of a statistical occupation and were consistent with an occupancy factor of 0.5. Probably the low

Table 2

Positional parameters and their estimated standard deviations

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2) ^{a}
Pt	0.22502(4)	0.09551(5)	0.47802(6)	4.26(1)	C^{20}	0.122(1)	0.028(2)	0.713(2)	7.9(8)
Cl^{1}	0.3004(3)	−0.0394(4)	0.5249(4)	6.0(1)	C^{21}	0.074(1)	−0.037(2)	0.726(2)	9.3(8)
P^{1}	0.2177(3)	0.0834(3)	0.3234(3)	4.1(1)	C^{22}	0.059(1)	−0.108(2)	0.670(2)	8.9(8)
P^{2}	0.2188(2)	0.1015(3)	0.6266(3)	4.0(1)	C^{23}	0.090(1)	−0.119(2)	0.604(2)	7.8(8)
O	0.1110(9)	0.233(1)	0.410(1)	7.2(5)	C^{24}	0.137(1)	−0.056(1)	0.592(2)	5.9(6)
C^{1}	0.157(1)	−0.009(1)	0.256(1)	5.1(5)	C^{25}	0.3188(9)	0.097(1)	0.728(1)	4.1(4)
C^{2}	0.131(1)	−0.068(2)	0.304(2)	7.7(8)	C^{26}	0.387(1)	0.126(2)	0.718(1)	6.3(6)
C^{3}	0.085(1)	−0.139(2)	0.256(2)	9.9(9)	C^{27}	0.464(1)	0.130(2)	0.795(2)	7.1(7)
C^{4}	0.068(2)	−0.149(2)	0.162(2)	10(1)	C^{28}	0.474(1)	0.105(2)	0.883(2)	6.9(6)
C^{5}	0.091(2)	−0.092(2)	0.113(2)	13(1)	C^{29}	0.410(1)	0.072(1)	0.897(2)	6.9(7)
C^{6}	0.135(2)	−0.022(2)	0.157(2)	9.6(8)	C^{30}	0.330(1)	0.069(2)	0.819(2)	6.8(7)
C^{7}	0.317(1)	0.075(1)	0.318(1)	5.7(6)	C^{31}	0.173(1)	0.201(1)	0.652(1)	4.8(5)
C^{8}	0.325(1)	0.064(3)	0.236(2)	11(1)	C^{32}	0.091(1)	0.208(2)	0.604(2)	6.4(6)
C^{9}	0.403(1)	0.058(3)	0.234(2)	12(1)	C^{33}	0.055(1)	0.285(2)	0.621(2)	7.5(7)
C^{10}	0.471(1)	0.065(2)	0.314(2)	7.9(8)	C^{34}	0.099(1)	0.345(2)	0.683(2)	7.6(7)
C^{11}	0.464(1)	0.073(2)	0.396(2)	8.2(8)	C^{35}	0.181(1)	0.333(2)	0.731(2)	8.3(8)
C^{12}	0.387(1)	0.083(2)	0.397(2)	8.8(8)	C^{36}	0.221(1)	0.261(1)	0.717(2)	6.1(6)
C^{13}	0.167(1)	0.172(1)	0.240(1)	5.6(6)	C^{37}	0.180(1)	0.213(1)	0.446(1)	5.7(5)
C^{14}	0.212(2)	0.243(1)	0.234(2)	7.9(7)	C^{38}	0.249(1)	0.277(1)	0.486(2)	6.0(6)
C^{15}	0.171(2)	0.314(2)	0.182(2)	11(1)	C^{39}	0.215(2)	0.372(2)	0.461(3)	12(1)
C^{16}	0.085(2)	0.314(2)	0.134(2)	11(1)	C^{40}	0.247(4)	0.429(2)	0.515(3)	26(3)
C^{17}	0.042(2)	0.242(2)	0.140(2)	8.5(8)	C^{41}	0.711(2)	0.265(3)	0.470(3)	6(1) ^{b}
C^{18}	0.082(1)	0.173(2)	0.193(2)	7.4(7)	C^{12}	0.6521(8)	0.3485(9)	0.4529(9)	7.8(3) ^{b}
C^{19}	0.155(1)	0.019(1)	0.646(1)	4.9(5)	C^{13}	0.8095(9)	0.280(1)	0.514(1)	9.1(4) ^{b}

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}\Sigma(a^2B_{1,1}+b^2B_{2,2}+c^2B_{3,3}+ab(\cos\gamma)B_{1,2}+ac(\cos\beta)B_{1,3}+bc(\cos\alpha)B_{2,3})$. ^{b} Atoms were refined isotropically.

degree of crystallinity of the available crystals is due to partial loss of the solvent of crystallization. The positions of the hydrogen atoms were calculated by the "Hydro" program of SDP and checked with the difference Fourier map. All atoms were refined with anisotropic thermal parameters. The carbon and chlorine atoms of the methylene chloride molecule were refined isotropically. During the last stage of the refinement the hydrogen atoms were introduced at their calculated positions, with B 7.0 Å^2, but not refined. The final R value was 0.071 using unit weights. The final atomic coordinates for non hydrogen atoms are listed in Table 2. A table of bond lengths and angles, and lists of thermal parameters and structure factors are available from the authors.

Results and discussion

The complexes *trans*-Pt(η^1-C_3H_5)(L_2)Cl (**1**: L = PPh_3, $P(C_6H_{11})_3$) react slowly in benzene or toluene solution with carbon monoxide (10 atm) to afford the corresponding *trans*-Pt(COC_3H_5)(L_2)Cl products (eq. 1).

$$\underset{(\mathbf{1})}{\textit{trans}\text{-Pt}(\eta^1\text{-}C_3H_5)(L_2)Cl} + CO \rightarrow \underset{(\mathbf{2})}{\textit{trans}\text{-Pt}(COC_3H_5)(L_2)Cl} \qquad (1)$$

(**a**, L = PPh_3; **b**, L = $P(C_6H_{11})_3$)

The products are present in good yield after two days. The presence of a strong IR band between 1650–1620 cm^{-1} shows the presence of an acyl group. The original ligand coordination is maintained for both phosphines and chloride. $^{31}P\{^1H\}$ NMR spectrum shows a single peak for **2a** (δ 20.6 ppm, ^1J(Pt–P) 3475 Hz) and **2b** (δ 18.2 ppm, ^1J(Pt–P) 3120 Hz) indicating that the two phosphines are in a *trans* disposition. The ν(Pt–Cl) bond is at 260 cm^{-1} consistent with a Pt–Cl bond weakened by a strong *trans*-activating ligand.

The complex *cis*-Pt(η^1-C_3H_5)($Ph_2PC_2H_2PPh_2$)Cl did not react under the same conditions, and was recovered unchanged even after seveal days under 10 atm of CO.

The structure of the COC_3H_5 moiety in products **2a** and **2b** was revealed by ^{1}H NMR spectroscopy. The five protons of the allyl group of **2a** appear as a doublet centered at 2.12 ppm (2 protons) and a very complex multiplet in the range 3.5–5.2 ppm. Simulation based on the ABX_3 pattern for the $CH_3CH{=}CH$ moiety leads to a spectrum totally in disagreement with experimental spectrum, but a substantial agreement is obtained for an A_2BCD pattern ($CH_2{=}CHCH_2$ structure). The ^{1}H NMR parameters were derived from spectra simulations and decoupling experiments. The ^{1}H NMR data for product **2b** are also consistent with such a structure for the C_3H_5CO ligand. These assignments agree with those reported for analogous CO insertion products for η^1-allylpalladium(II) complexes [7c]; moreover, in our case, the absence of any coupling of allylic protons with ^{195}Pt excludes any possible bonding interaction in solution between free double bond and the platinum(II) ion. To give more information about the structure and solid state disposition of the C_3H_5CO ligand an X-ray analysis of the compound **2a** was undertaken. Although several methods were used to seek good single crystals, only a low quality X-ray crystal was available for the structural determination, but the overall geometry of Pt(COC_3H_5)(PPh_3)$_2$Cl was unequivocally established (Fig. 1). The crystal consists

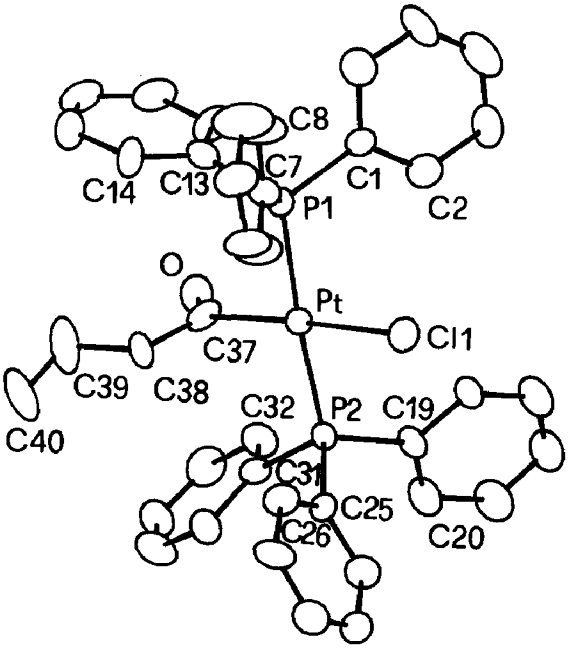
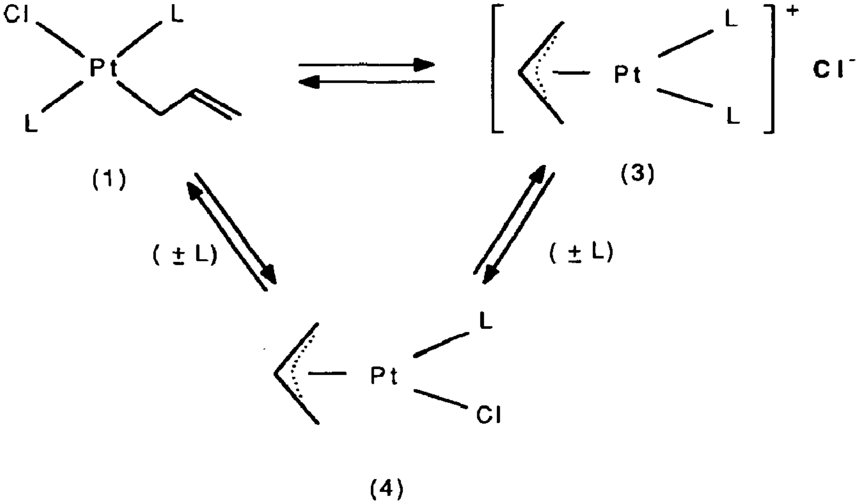


Fig. 1. ORTEP plot of $Pt(COC_3H_5)(PPh_3)_2Cl$, showing the atom numbering scheme. Atoms are drawn at 20% probability level. Hydrogen atoms are omitted for clarity.

of discrete monomeric molecules having a distorted square-planar geometry about the platinum centre. Pt, Cl^1, P^1, P^2 and C^{37} are coplanar within 0.30 Å.

As expected the PPh_3 ligands are in a *trans* disposition (Pt–P^1 2.301(5), Pt–P^2 2.303(5) Å, P^1–Pt–P^2 174.0(2)°). The other two positons are occupied by Cl^1 and C^{37} atoms. (Pt–Cl^1 2.439(5) Å, Pt–C^{37} 1.98(3) Å, Cl^1–Pt–C^{37} 171.4(6)°). The Pt–Cl^1 bond distance of 2.439(5) Å reflects the large *trans* influence of a carbon-bonded ligand [6,11]. The crystallographic results clearly show that there has been insertion of the CO molecule into the metal–σ-allyl bond. Bond distances in the organic residue are consistent with the localization of the double bond between the two terminal C atoms (C^{39}–C^{40} 1.19(5) Å, C^{37}–C^{38} 1.50(3) Å, C^{38}–C^{39} 1.59(3) Å). The short C^{39}–C^{40} distance and its high standard deviation could possibly be attributed to high thermal motion or to statistical occupation of the two carbon atom positions (see Table 2) but these effects would also increase the C^{38}–C^{39} bond length, whereas it is in fact very close to that expected for a $C(sp^2)$–$C(sp^3)$ bond. The bond angles around C^{38} and C^{39} support the suggested bonding scheme since the C^{37}–C^{38}–C^{39} 111(2)° and C^{38}–C^{39}–C^{40} 120(4)° bond angles are indicative of a tetrahedral and a trigonal geometry around C^{38} and C^{39} atoms, respectively.

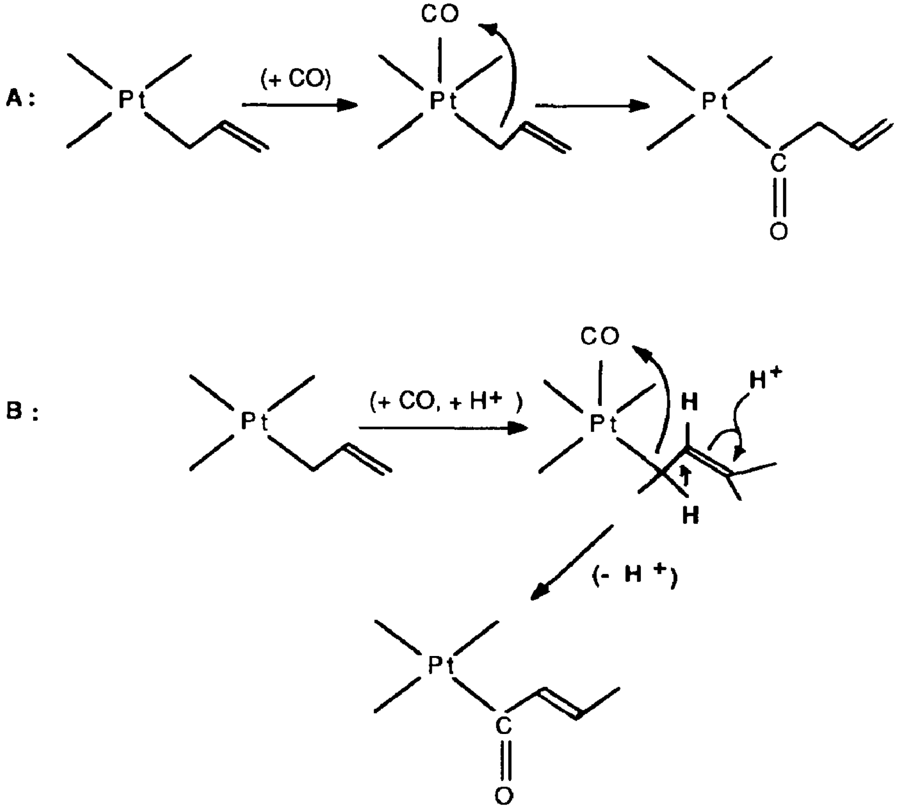
It has been clearly established that in polar chlorinated solvents Pt(allyl)(phosphine)$_2$Cl complexes are involved in the equilibria shown in Scheme 1 [12], with species **3** being greatly dominant. In contrast, in the present case the initial η^1-allyl complex can be taken to be the only species present in benzene or toluene solutions, in which the formation of the η^3-allyl species is suppressed. It is likely that the carbon monoxide attack yields a five-coordinated intermediate in which the allyl fragment is held σ-bonded to the metal ion; thus allyl migration to coordinated CO



Scheme 1

appears to be the most likely mechanism, as in classic CO insertion into ordinary metal–carbon σ-bonds.

The reaction mechanism here proposed is shown in path A of Scheme 2. The initial attack of carbon monoxide on the central metal is attributable to its



Scheme 2

nucleophilic character, and the formation of an η^2-coordinated zwitterionic intermediate, often proposed in case of electrophilic attack [7b], appears unlikely. Reaction 1 does not occur under our mild conditions in the case of Pt(η^1-C_3H_5)(Ph_2PCH=$CHPPh_2$)Cl in which steric and thermodynamic effects arising from the presence of the chelating ligand reduce the reactivity of the complex: a reduction in the reactivity of η^1-allylplatinum(II) complexes arising from steric hindrance was previously observed in the case of SO_2 insertion [7b].

It is noteworthy that Volger and Vrieze showed that when reaction 1 is carried out in $CHCl_3$ the CH_3CH=CHCO moiety is formed. Since the insertion must involve the η^1-allyl species, although in equilibrium with cationic η^3-allyl counterpart, the formation of the CH_3CH=CHCO ligand could be related to the possible presence of H^+ donors due to $CHCl_3$ decomposition. Acids yielding H^+ can in fact protonate the double bond of an η^1-allyl group [7b,13], and so the presence of such an acid during η^1-allyl migration to the carbonyl ligand could promote allyl group isomerization, as in path B of Scheme 2. Indeed, the formation of CH_3CH=CHCO ligands appear to restrict to carbonylations carried out in chloroform. Our CH_2=$CHCH_2COPt$ products are indefinitely stable even in CH_2Cl_2, in which no isomerization is observed.

Acknowledgments

The Ministry of Education (Rome) and CNR (Rome) are thanked for financial support.

References

1 A. Wojcicki, in M. Tsutsui, Y. Ishi, Y. Huang (Eds.), Fundamental Research in Organometallic Chemistry, Van Nostrand-Reinhold, New York, 1982, p. 569–597.
2 M. Rosenblum, Acc. Chem. Res., 7 (1974) 122.
3 (a) P.B. Bell and A. Wojcicki, Inorg. Chem., 20 (1981) 1585; (b) L.S. Chen, S.R. Su and A. Wojcicki, Inorg. Chim. Acta, 27 (1978) 79; (c) A. Cutler, D. Ehntholt, P. Lennon, K. Nicholas, D.F. Marten, M. Madhavarso, S. Raghu, A. Rosan and M. Rosenblum, J. Am. Chem. Soc., 97 (1975) 3199.
4 R. Bertani, A.M. Maccioni, P. Traldi and G. Carturan, Inorg. Chim. Acta, 121 (1986) 147 and 155.
5 M. Calligaris, G. Carturan, G. Nardin, A. Scrivanti and A. Wojcicki, Organometallics, 2 (1983) 865.
6 J.A. Kaduk, J.A. Ibers, J. Organomet. Chem., 139 (1977) 199.
7 (a) R. Bertani, G. Carturan, A. Scrivatni, A. Wojcicki, Organometallics, 4 (1985) 2139; (b) Yeh-Rom Hu, A. Wojcicki, M. Calligaris, G. Nardin, Organometallics, 6 (1987) 1561; (c) F. Ozawa, T. Son, K. Osakada, A. Yamamoto, J. Chem. Soc. Chem. Commun., (1989) 1067.
8 H.C. Volger, K. Vrieze, J. Organomet. Chem., 13 (1968) 495.
9 Enraf-Nonius Structure Determination Package (SDP); Enraf–Nonius, Delft, Holland, 1983.
10 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England, 1962.
11 B. Jvanovich, L. Manojlovic-Muir, K.W. Muir, J. Chem. Soc. Dalton Trans., (1974) 195.
12 (a) G. Carturan, A. Scrivanti, U. Belluco, F. Morandini, Inorg. Chim. Acta, 27 (1978) 37 and 26 (1978) 1; (b) S. Numata, R. Okawara, H. Kurosawa, Inorg. Chem., 16 (1977) 1737; (c) H. Kurosawa, G. Yoshida, J. Organomet. Chem., 120 (1976) 297; (d) N.M. Boag, M. Green, J.L. Spencer, F.G.A. Stone, J. Chem. Soc. Dalton Trans., (1980) 1208.
13 (a) M.L.H. Green, P.L.I. Nagy, J. Organomet. Chem., 1, (1963) 58; (b) M.L.H. Green, A.N. Stear, J. Organomet. Chem., 1, (1963) 230; (c) M. Cousins, M.L.H. Green, J. Chem. Soc., (1963) 889; (d) M.L.H. Green, P.L.I. Nagy, J. Chem. Soc., (1963) 189.