Journal of Organometallic Chemistry, 81 (1974) 261–270
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ELECTROPHILICITY OF COORDINATED CARBON MONOXIDE IN ALKOXYDIENYLPLATINUM(II) CARBONYL COMPLEXES

SYNTHESIS OF (DIENE)PLATINUM(II) ALKOXYCARBONYL COMPLEXES

ALDO VITAGLIANO

Istituto Chimico, University of Naples, via Mezzocannone 4, 80134 Naples (Italy)

(Received May 20th, 1974)

Summary

If alkoxydienyl complexes of the type $[Pt(dieneOR)Cl]_2$ are allowed to react with carbon monoxide under mild conditions, unstable carbonyl complexes are formed. The carbonyl complexes may react with an alcohol to give alkoxycarbonyl complexes of the type (diene)PtClCOOR. This reaction involves nucleophilic attack of alcohol on the coordinated carbonyl group, and expulsion of the alkoxyl group from the dienyl moiety with formation of a coordinated carbon—carbon double bond. This reaction, however, is not of general occurrence. A comparison is made between the electrophilicities of coordinated carbon monoxide and coordinated carbon—carbon double bond.

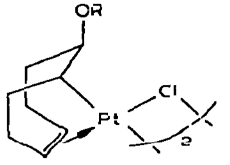
Introduction

Many examples of additions of weak nucleophiles to coordinated carbon monoxide in transition metal complexes are reported in literature. Alcohols, amines, hydrazine, react with carbonyl complexes to give alkoxycarbonyl, carbamoyl and isocyanato complexes respectively. Such additions are said to give stable products only for cationic carbonyl complexes, probably because of the poor stability of alkoxycarbonyl or carbamoyl complexes carrying a negative charge [1]. Further, electrophilic ligands compete for the nucleophiles with CO. For instance, it has been found in the cases reported in the literature that the coordinated carbonyl group has a greater electrophilic tendency than coordinated nitrosyl [2] but smaller than thiocarbonyl [3], whereas for the isocyanide group both directions of the nucleophile attack (at CO and CN—R) have been observed [4].

In the present paper the preparation of some new alkoxycarbonyl complexes of Pt$^{(II)}$ from neutral carbonyl complexes is described, this permits comparison of the electrophilicities of coordinated carbon monoxide and coordinated carbon—carbon double bonds*.

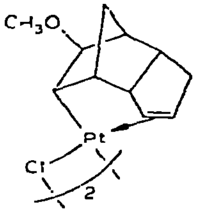
Results and discussion

We have synthesized the alkoxydienyl complexes Ia-Va from the corresponding diene complexes using known procedures [6], sometimes slightly modified as described in the experimental section. Some of these compounds (Ia$_2$, Ia$_3$, IIIa, IVa and Va) have not been described in the literature previously. For IIIa, methoxide ion addition occurs at the 2-position of the diene moiety, as is proved by reduction of IIIa with sodium borohydride, giving rise to 2-methoxyhexane**. For IV and Va we have not made a structural characterization, consequently the relative positions of methyl and methoxyl groups are not known. However, since IVa and Va are well-crystallized products, and since in their NMR spectra the resonance peaks of the methoxyl and methyl protons are sharp singlets, we believe we can exclude the possibility that IVa and Va consist of isomeric mixtures. Moreover, the integrated NMR spectra of IVa and Va (see Table 4) are consistent with the presence of a single olefinic proton in both compounds, indicating that methoxide addition occurs at the non-methylated double bond.

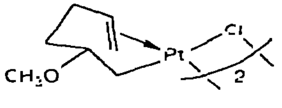


1 R = CH_3
2 R = n-C_3H_7
3 R = i-C_3H_7

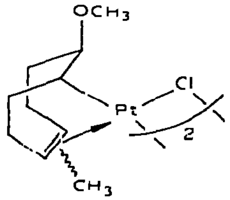
(Ia$_1$) (Ia$_2$) (Ia$_3$)



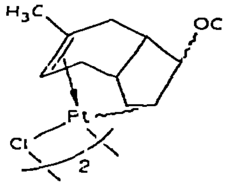
(IIa)



(IIIa)



(IVa)



(Va)

Carbonyl complexes

Suspensions of compounds Ia-Va in various solvents (chloroform, dichloromethane or toluene) absorb CO readily (molar ratio CO/Pt = 1) at atmospheric

---

* Part of this work has appeared in a preliminary communication [5].

** Purified by GLPC and identified by comparison with an authentic sample.

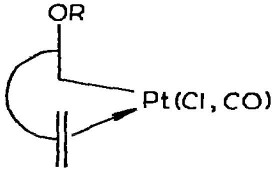
TABLE 1

SELECTED DATA FROM THE IR AND NMR[a] SPECTRA OF CARBONYL COMPLEXES Pt(dieneOR)(CO)Cl

Compound	IR (cm^{-1}), CH_2Cl_2 soln.		NMR δ (ppm), $CDCl_3$ soln.
	νC≡O	νC—O—C	
$C_8H_{12}OCH_3PtClCO$ (Ib$_1$)	2105vs	1087vs, 1074(sh)	5.68[b] 2H, s(br); 3.50 1H, m; 3.30 OCH_3, s; 3.10 1H, m; 2 90-1.60 8H, m
$C_8H_{12}O(CH_2)_2CH_3PtClCO$ (Ib$_2$)	2105vs	1080vs	
$C_8H_{12}OCH(CH_3)_2PtClCO$ (Ib$_3$)	2110vs	1038vs	
$C_{10}H_{12}OCH_3PtClCO$ (IIb)	2100vs	1088vs, 1077(sh)	7.00[c] 1H, s(br); 6.64[c] 1H, s(br); 3.60 2H, m; 3.23 OCH_3, s; 3.10-2.15 6H, m; 1.72 1H, d; 1.51 1H, d
$C_6H_{10}OCH_3PtClCO$ (IIIb)	2097vs	1085vs	
$C_9H_{14}OCH_3PtClCO$ (IVb)	2103vs	1088vs	
$C_{10}H_{14}OCH_3PtClCO$ (Vb)	2098vs	1100(sh), 1080vs	5.05[d] 1H, s(br); 3.92 2H, m; 3.28 OCH_3, s; 2.17 CH_3, s; 2.70-1.60 8H, m

[a] NMR data of Ib$_2$, Ib$_3$, IIIb, and IVb are not reported since the spectra consisted of unresolvable overlapping multiplets, except for the resonances of methyl and methoxyl protons. [b] Two ^{195}Pt satellite peaks are observable (^2J(H—Pt) 78 Hz). [c] Two ^{195}Pt satellite peaks are observable (^2J(H—Pt) 64 Hz). [d] Two ^{195}Pt satellite peaks are observable (^2J(H—Pt) 74 Hz).

pressure, giving colourless solutions (Ib-Vb) which are stable for weeks when stored at low temperature (—30 to —70°) and when traces of alcohols in the solvent are avoided*. IR and NMR spectra of the solutions (see Table 1) suggest that they contain monomeric species of the type B, formed through the splitting of the chlorine bridges of Ia-Va by carbon monoxide. In the IR spectra of the species B the very strong absorption band in the neighbourhood of 2100 cm^{-1} indicates the presence of a terminal coordinated carbonyl group. In the NMR spectra the presence of the ^{195}Pt satellite olefinic peaks indicates that the double bonds are still coordinated to the metal.



B

We were not able to isolate compounds Ib-Vb in the solid state, because any attempt to remove the solvent or precipitate the solute resulted in loss of CO and reformation of the starting dimers Ia-Va.

Alkoxycarbonyl complexes

If solutions of compounds Ib-Vb are allowed to react with an alcohol at low temperature, an addition reaction to the coordinated carbonyl group may occur, together with the expulsion of the alkoxyl group from the dienyl moiety and the resulting formation of the alkoxycarbonyl complex (diene)PtClCOOR (C). In Table 2 some of these reactions are concisely described.

TABLE 2

REACTIONS OF THE CARBONYL COMPLEXES Ib-Vb WITH ALCOHOLS

(Temp. -40°, time 36 h, solvent CH_2Cl_2)

Carbonyl compound	Alcohol (1 mol/mol Pt)	Product
$C_8H_{12}OCH_3PtClCO$ (Ib_1)	CH_3OH	$C_8H_{12}PtClCOOCH_3$ (Ic_1)
$C_{10}H_{12}OCH_3PtClCO$ (IIb)	CH_3OH	no reaction
$C_6H_{10}OCH_3PtClCO$ (IIIb)	CH_3OH	decomposition (Pt, $C_6H_{10}PtCl_2$)
$C_9H_{14}OCH_3PtClCO$	CH_3OH	$C_9H_{14}PtClCOOCH_3$ (IVc)
$C_{10}H_{14}OCH_3PtClCO$ (Vb)	CH_3OH	$C_{10}H_{14}PtClCOOCH_3$ (Vc)
$C_8H_{12}O$-n-$C_3H_7PtClCO$ (Ib_2)	n-C_3H_7OH	$C_8H_{12}PtClCOO$-n-C_3H_7 (Ic_2)
$C_8H_{12}O$-i-$C_3H_7PtClCO$ (Ib_3)	i-C_3H_7OH	no reaction
$C_8H_{12}OCH_3PtClCO$ (Ib_1)	C_2H_5OH	$C_8H_{12}PtClCOOCH_3$ (Ic_1)
$C_8H_{12}OCH_3PtClCO$ (Ib_1)	n-C_3H_7OH	$C_8H_{12}PtClCOOCH_3$ (Ic_1)
$C_8H_{12}OCH_3PtClCO$ (Ib_1)	i-C_3H_7OH	no reaction
$C_8H_{12}O$-n-$C_3H_7PtClCO$ (Ib_2)	C_2H_5OH	$C_8H_{12}PtClCOOC_2H_5$ (Ic_4)
$C_8H_{12}O$-i-$C_3H_7PtClCO$ (Ib_3)	C_2H_5OH	$C_8H_{12}PtClCOOC_2H_5$ (Ic_4)

---

* If commercial chloroform or dichloromethane which contain small amounts of ethanol as a stabilizing agent are used, results identical to those reported in Table 2 are obtained.

TABLE 3

SELECTED DATA FROM THE IR AND NMR SPECTRA OF ALKOXYCARBONYL COMPLEXES (diene)PtClCOOR

Compound	Mp	IR (cm^{-1}), Nujol		NMR δ (ppm), $CDCl_3$ soln.
		$\nu C\equiv O$	$\nu C-O-C$	
$C_8H_{12}PtClCOOCH_3$ (Ic$_1$)	126-130° dec.	1666 vs	1095 vs	5.82^b 2H, s(br); 5.04^b 2H, s(br); 3 68^b OCH_3, s; 2 46 8H, m(br)
$C_8H_{12}PtClCOOC_2H_5$ (Ic$_4$)	117-119° dec.	1665 vs	1100 vs	5.79^c 2H, s(br); 4.99^c 2H, s(br); 4.15^c OCH_2, q; 2.44 8H, m(br); 1.21 CH_3, t
$C_8H_{12}PtClCOO$-n-C_3H_7 (Ic$_2$)	93-94° dec	1665 vs	1105 vs	5.76^c 2H, s(br); 4.97^c 2H, s(br); 4.02^c OCH_2, t; 2.42 8H, m(br); 1.6 $-CH_2-$, m; 0.91 CH_3, t;
$C_9H_{14}PtClCOOCH_3$ (IVc)	102-106° dec	1662 vs	1100 vs	5.46 1H, m; 4.95^d 2H, s(br); 3.68^d OCH_3, s; 2.5 8H, m(br); 2.07 CH_3, s
$C_{10}H_{14}PtClCOOCH_3$ (Vc)		1665 vs	1100 vs^a	5.59 3H, m, 3.67^c OCH_3, s; 2.19 CH_3, s; 2.60-1.60 8H, m

[a] CH_2Cl_2 soln. [b] Two ^{195}Pt satellite peaks are observable ($^2J(H-Pt)$ 35 Hz, $^2J(H-Pt)$ 76 Hz, $^4J(H-Pt)$ 6 Hz respectively. [c] Two ^{195}Pt satellite peaks are observable ($^2J(H-Pt)$ 37 Hz, $^2J(H-Pt)$ 75 Hz, $^4J(H-Pt)$ 6 Hz respectively). [d] Two ^{195}Pt satellite peaks are observable ($^2J(H-Pt)$ 73 Hz, $^4J(H-Pt)$ 6 Hz respectively). [e] Two ^{195}Pt satellite peaks are observable ($^4J(H-Pt)$ 6 Hz).

TABLE 4

SELECTED DATA FROM NMR SPECTRA OF IVa AND Va δ (ppm) IN $CDCl_3$ SOLUTION (60 MHz)

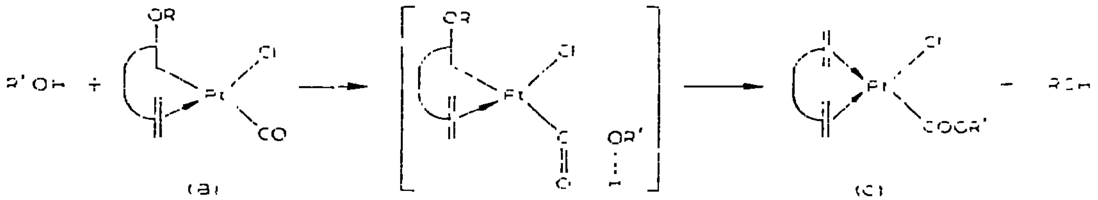
$[C_9H_{14}OCH_3PtCl]_2$ (IVa)	4.50[a] 1H, s(br); 3.23 OCH_3, s; 1.78 CH_3, s; 4.0-3.0 2H, m; 2.9-1.2 8H,
$[C_{10}H_{14}OCH_3PtCl]_2$ (Va)	4.39[b] 1H, s(br); 4.10-3.50 2H, m; 3.15 OCH_3, s, 3.05 1H, d, 1.86 CH_3, 2.40-1.10 7H, m

[a] Two ^{195}Pt satellite peaks are observable (^2J(H—Pt) 90 Hz). [b] Two ^{195}Pt satellite peaks are observable (^2J(H—Pt) 89 Hz).

Alkoxycarbonyl complexes Ic_1, Ic_2, Ic_3 ($R' = C_2H_5$) and IVc were isolated and characterized by elemental analysis, molecular weight determination, IR an NMR spectroscopy (see Table 3). Compound Vc, which could not be isolated in the solid state because of its facile decomposition, was detected only in solution by IR and NMR spectroscopy.

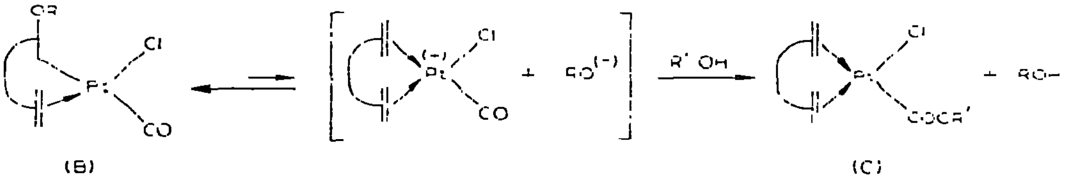
A spontaneous migration of the alkoxyl group from the organic moiety to the coordinated carbonyl group is not observed if the solution is alcohol-free It follows that the formation of alkoxycarbonyl compounds proceeds via a nucleophilic addition of the alcohol present in solution to the coordinated carbonyl group. On the basis of these observations two different mechanisms appear to be possible. The first one involves attack of the alcohol at the neutral carbonyl complex, and subsequent (or simultaneous) rearrangement of the organic moiety with expulsion of the alkoxyl group (Scheme 1); the second

SCHEME 1



requires a dissociation equilibrium of the neutral carbonyl complex, with subsequent nucleophilic attack at the cationic carbonyl complex (Scheme 2).

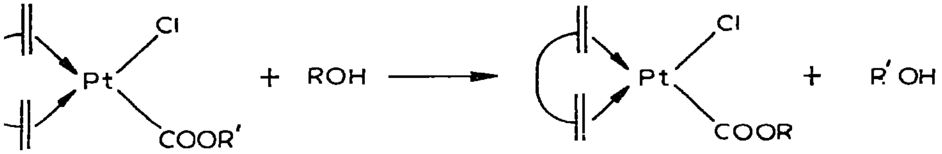
SCHEME 2



By inspection of Table 2 it can be seen that a further possible reaction is exchange of alkoxyl groups on the alkoxycarbonyl function. The data in Table 2, supported by alcohol-exchange experiments carried out on the alkoxycarbonyl complexes Ic, show also that the stability of the alkoxycarbonyl complexes decreases with steric hindrance of the alcohol involved, in the following order:

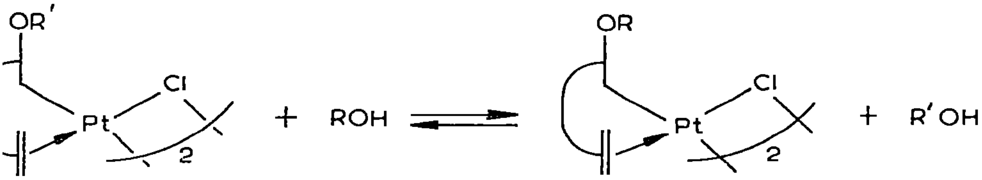
$H_3OH > C_2H_5OH > n\text{-}C_3H_7OH > i\text{-}C_3H_7OH$. This is in agreement with the sults reported by Byrd and Halpern [7] for the addition of alcohols to *trans*-'tCl(phosphine)$_2$CO]$^+$ cations. Moreover, we found that the exchange in

HEME 3



heme 3 only occurs when R is a group lighter than R', whereas the alkoxyl change readily occurs on the alkoxydienyl dimers Ia even when R is heavier an R' (Scheme 4). In a typical experiment the methoxycarbonyl complex Ic$_1$

HEME 4



as recovered unaltered after refluxing for 6 h, in n-propanol (at 50° under duced pressure to prevent decomposition), whereas the n-propoxycarbonyl mplex Ic$_2$ was completely converted to Ic$_1$ by simple dissolution in methanol room temperature. On the other hand, the methoxydienyl dimer Ia$_1$ was nverted to Ia$_2$ or Ia$_3$ by refluxing for 5 min with n-propanol or i-propanol, spectively, and storing at room temperature overnight. Thus the nature of the koxyl group appears to effect more the stability of the alkoseylcarbonyl comexes Ic than the stability of the alkoxydienyl dimers Ia.

The formation of the alkoxycarbonyl complexes consists then in the dition of a nucleophile to a coordinated carbonyl group, together with the mination of the same nucleophile (when R = R' in Scheme 1 and 2) from the enyl moiety, with formation of a coordinated double bond. Therefore it folws that, in the cases reported, carbon monoxide is a stronger electrophilic e than a coordinated carbon—carbon double bond. However, this cannot be nsidered as a general characteristic of alkoxydienylcarbonyl complexes. The rmation of the (diene)PtClCOOR complex does not in fact occur for the diclopentadiene derivative. IIb, even under more favourable conditions than ose quoted in Table 2, i.e. at much higher concentration (about 40%) of ethanol in dichloromethane. Since the electronic environment of the platinum om in all the carbonyl compounds Ib-Vb is very similar, a different intrinsic ectrophilicity of the coordinated carbonyl group seems rather unlikely. This nclusion is strongly supported by the C≡O stretching frequencies, which are arly the same for all the carbonyl complexes (see Table 1), pointing to the me charge density, and thence the same electrophilicity, for the carbonyl oup [8, 1, 4a]. A reasonable explanation of the different behaviour of comund IIb can be found in the particular unfavourable dienyl—diene rearrangent involved in the formation of a hypothetical (dicyclopentadiene) PtClCOOR complex. In fact, the considerable strain in the norbornenyl skeleton of the diene is confirmed by the high first heat of hydrogenation of dicyclopentadiene: 33.4 kcal/mol versus 27 kcal/mol for the second heat of hydrogenation [9]. This strain is lacking in the dienyl structure, which is then the favoured one fc the dicyclopentadiene derivative IIb.

In conclusion, our results, within the limits of the small number of syster studied, reveal the stronger electrophilic character of coordinated carbon mon with respect to coordinated olefins. However, we should note that the differer in electrophilicity between the two sites is not great and that particular steric situations, either in the alkoxyl or in the olefinic moiety, may well reverse this behaviour.

Experimental

Materials

All solvents were distilled after treatment with suitable drying agents and stored under nitrogen. 1,5-cyclooctadiene, 1,5-hexadiene and dicyclopentadien were commercial products; 1-methyl-1,5-cyclooctadiene and 3a, 4, 7, 7a-tetrahydro-6-methyl-indene were kindly supplied by Montecatini—Edison S.p.A., Milan. The diolefin complexes were obtained by a known method [6a].

Instrumentation

Infrared spectra were recorded with a Perkin—Elmer 457 spectrophotometer or a Perkin—Elmer 720 spectrophotometer. NMR spectra were recorded with Perkin—Elmer R 12 and Varian HA100-15 spectrometers. Molecular weights were determined in chloroform solution with a Hitachi—Perkin—Elmer Model 115 apparatus.

Synthesis and characterization of the starting compounds Ia-Va

$[C_8H_{12}OCH_3PtCl]_2$ (Ia_1), $[C_8H_{12}O(CH_2)_2CH_3PtCl]_2$ (Ia_2), $[C_8H_{12}OCH(CH_3)_2PtCl]_2$ (Ia_3), $[C_{10}H_{12}OCH_3PtCl]_2$ (IIa) and $[C_9H_{14}OCH_3PtCl]_2$ (IVa) were prepared using published procedures [6]. Ia_2. 78% yield, white prisms, m.p. 127-142° dec. (Anal. found: C, 33.1; H, 4.71; Pt, 48.8 calcd.: C, 33.2; H, 4.82; Pt. 49.1%). Ia_3. 73% yield, white plates, m.p. 153-170°C dec. (Anal. founc C, 33.0; H, 4.68; Pt, 48.9 calcd.: C, 33.2; H, 4.82; Pt, 49.1%). IVa. 65% yield, white needles, m.p. 150-210° slowly dec. (Anal. found: C, 30.8; H, 4.39; Pt, 50.4 calcd.: C, 31.3; H, 4.47; Pt, 50.8%).

$[C_6H_{10}OCH_3PtCl]_2$ (IIIa). A mixture of 2.0 g (5.7 mmol) of dichloro(1,5-hexadiene)platinum(II) and 0.51 g (6.1 mmol) of sodium bicarbonate was suspended in 100 ml of methanol and stirred for 30 min at room temperature. The solvent was evaporated in vacuo, and the residue was recovered with 50 ml of chloroform and filtered. The chloroform solution was concentrated to a small volume, then 100 ml of ether were added. The colourless precipitate which formed was collected on a filter, washed with ether, and dried to afford 1.6 g of IIIa. 81% yield, white powder, m.p. 99-101° dec. (Anal. found: C, 23.8; H, 3.64; Pt, 57.1 calcd.: C, 24.4; H, 3.81; Pt, 56.8). $[C_{10}H_{14}OCH_3PtCl]_2$ (Va), was prepared using the same procedure described for IIIa. 2.0 g of dichloro(methyltetrahydroindene)platinum(II) afforded 1.5 g of Va. 76% yield, white prisms, m.

38-143° dec. (Anal. found: C, 33.3; H, 4.28; Pt, 49.2 calcd.: C, 33.4; H, 4.33; t, 49.3.

All relevant NMR data of compound IVa and Va are reported in Table 4. The NMR spectrum of IIIa is an unresolvable complex of multiplets, except for the methoxyl group protons, which give rise to two close singlets (δ 3.27 and δ 3.25 ppm respectively) of nearly equal intensity. The two peaks coalesce into a singlet on adding a bridge-splitting reagent such as triphenylphosphine, pyridine or carbon monoxide. This phenomenon has been interpreted assuming that the dimer IIIa is a mixture of two diastereoisomers, one with the two monomeric units having the same absolute configuration, the other with the two monomeric units having the opposite absolute configuration. This isomerism is obviously removed by the bridge-splitting and the formation of monomeric species.

General procedure for the reaction of the alkoxydienylcomplexes with CO

0.50 g of the alkoxydienyl dimer, partially dissolved in 4 ml of anhydrous dichloromethane, was allowed to absorb CO from a gas burette under magnetic stirring at 0°. Within a few minutes 1 mol CO/mol Pt was absorbed, and the solid was completely dissolved, giving a colourless solution, which rapidly darkened if not stored below −30° (dry ice is needed for the hexadiene derivative IIIb). Evaporation of the solution, as well as precipitation with n-heptane (even in a CO atmosphere) led to the starting dimer in all cases.

General procedure for the reaction of the carbonyl complexes with alcohols

To a cold solution of the carbonyl complex, containing 0.50 g of the starting dimer in 4 ml of absolute dichloromethane, a small amount (20-50 μl) of the alcohol was added under a carbon monoxide atmosphere. The solution was then kept at −40° during 48 h. Some decomposition leading to metallic platinum occurred in all cases. The solution was then treated with charcoal, filtered, and the filtrate concentrated to a small volume (2 ml). Treatment with n-heptane afforded, in the cases where the reaction occurred (see Table 2), the alkoxycarbonyl complex in form of white, air-stable needles, with a yield ranging between 40 and 70%. The solution of IIb afforded instead 0.40 g of the starting dimer IIa after the same treatment. The solution of IIIb extensively decomposed, giving, besides metallic platinum, a small amount (0.10 g) of the parent complex dichloro(1,5-hexadiene)platinum(II). $C_8H_{12}PtClCOOCH_3$ (Ic_1): (Anal. found: C, 29.7; H, 3.70; Pt, 49.3; mol. wt. 395 calcd.: C, 30.2; H, 3.80; Pt, 49.1: mol. wt. 398). $C_8H_{12}PtClCOOC_3H_7$ (Ic_2): (Anal. found: C, 33.4; H, 4.46; Pt, 45.3; mol. wt. 410 calcd.: C, 33.8; H, 4.50; Pt, 45.8; mol. wt. 426). $C_8H_{12}PtClCOOC_2H_5$ (Ic_4): (Anal. found: C, 32.1; H, 4.11; Pt, 47.3; mol. wt. 407 calcd.: C, 32.1; H, 4.16; Pt, 47.4; mol. wt. 412). $C_9H_{14}PtClCOOCH_3$ (IVc): (Anal. found: C, 31.6; H, 3.60; Pt, 47.9; mol. wt. 394 calcd.: C, 32.1; H, 4.16; Pt, 47.4; mol. wt. 412).

A slightly more convenient procedure for the synthesis of compound Ic_1 was realised by adding an equal volume of methanol to the solution of Ib_1, and keeping the solution in dry ice for three days. In this way decomposition reactions were minimized and yields up to 93% were obtained. The same procedure applied to the solution of the 1,5-hexadiene derivative IIIb which gave rise to a solution whose IR spectrum showed a terminal coordinated carbonyl band at 2100 cm^{-1}, as well as an acylic carbonyl band at 1660 cm^{-1}. Any attempts to isolate a product from this solution were frustrated by extensive decomposition

Acknowledgement

I am indebted to Professor G. Paiaro for valuable discussions and suggestio This work was supported by the Italian Research Council (C.N.R.), Grant no. 73.01054.03.

References

1 R.J. Angelici, Accounts. Chem. Res., 5 (1972) 335 and refs. therein.
2 L. Busetto, G. Dolcetti, A. Palazzi and D. Pietropaolo, J. Organometal. Chem., 66 (1974) 453 and refs. therein.
3 L. Busetto, M. Graziani and U. Belluco, Inorg. Chem., 10 (1971) 78.
4 (a) R.J. Angelici, P.A. Christian, B. Douane Dombek and G.A. Pfeffer, J. Organometal. Chem., 67 (197 287; (b) L. Busetto, A. Palazzi and G. Dolcetti, Proc. VI Conv. Naz. Chim. Inorg., A.I.C.I., Florence Sept 1973, p. 105.
5 A. Vitagliano and G. Paiaro, J. Organometal. Chem., 49 (1973) C49.
6 (a) J. Chatt, L.M. Vallarino and L.M. Venanzi, J. Chem. Soc., (1957) 2436; (b) J.K. Stille and R.A. Morgan, J. Amer. Chem. Soc., 88 (1966) 5135.
7 J.E. Byrd and J. Halpern, J. Amer. Chem. Soc., 93 (1971) 1634.
8 D.J. Darensbourg and M.Y. Darensbourg, Inorg. Chem., 9 (1970) 1691.
9 G. Becker and W.A. Roth, Chem. Ber. 67 (1934) 627.