Journal of Organometallic Chemistry, 67 (1974) 315—320

FAR INFRARED SPECTRA OF ZEROVALENT PLATINUM—ACETYLENE COMPLEXES

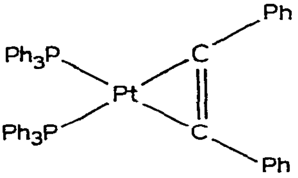
A. FURLANI, P. CARUSI and M.V. RUSSO
Istituto di Chimica Generale ed Inorganica, Università di Roma (Italy)
(Received July 19th, 1973)

Summary

The low frequency IR spectra of a series of $(Ph_3P)_2Pt(HC{\equiv}CR)$ complexes have been measured in the range 600—300 cm^{-1}. Pt—P and Pt—C stretching frequencies have been assigned by comparison with spectra of similar platinum complexes.

Introduction

The synthesis of platinum(0)—acetylene complexes of general formula $(Ph_3P)_2Pt(ac)$ (ac = acetylene or acetylene derivative) was first carried out by Chatt et al. [1]. Later workers synthesized other complexes of this type [2 - 9], and numerous papers have been published [10 - 15] on the nature of the acetylene—platinum bond. IR spectra have shown that the stretching frequencies of the triple bond of acetylene is reduced by about 500 cm^{-1} on coordination [1,4,5,8].

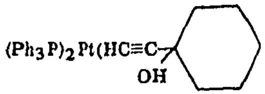
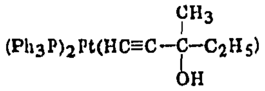
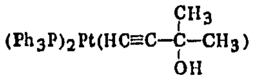
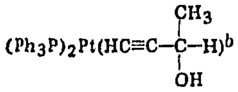
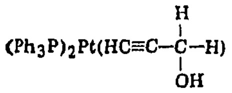


(A)

X-ray diffraction studies have shown that the complex (A) is nearly planar, and that the axis of the multiple bond forms an angle of about 14° with the plane containing the platinum and the phosphorus atoms [16]. This structure is similar to that of analogous complexes of Ni^0 and Pt^0 with acetylenes and olefins [15]. X-ray measurements have confirmed that the triple bond is lengthened on coordination; the C—C bond distance is about 1.30 Å, i.e. in the

TABLE 1

ELEMENTAL ANALYSES AND PHYSICAL PROPERTIES OF $(Ph_3P)_2Pt(HC\equiv CR)$ COMPLEXES

Complex		IR spectrum $\nu(C\equiv C)$ (cm^{-1})[a]	M.p.(°C)	Analysis found (calcd.) (%)	
				C	H
(I)	$(Ph_3P)_2Pt(HC\equiv C-Ph)$	1690m	153 - 155	64.3 (64.2)	4.39 (4.4)
(II)	$(Ph_3P)_2Pt[HC\equiv C-C(CH_3)=CH_2]$[b]	1680m, 1720m	133 - 135	62.56 (62.8)	4.6 (4.6)
(III)		1690m, 1720(sh)	142 - 143	62.20 (62.63)	4.99 (4.98)
(IV)	 $(Ph_3P)_2Pt(HC\equiv C-\overset{CH_3}{\underset{OH}{C}}-C_2H_5)$	1690m, 1720(sh)	144 - 147	61.77 (61.69)	4.85 (4.90)
(V)	 $(Ph_3P)_2Pt(HC\equiv C-\overset{CH_3}{\underset{OH}{C}}-CH_3)$	1690m, 1720(sh)	148 - 150	61.16 (61.27)	4.62 (4.73)
(VI)	 $(Ph_3P)_2Pt(HC\equiv C-\overset{CH_3}{\underset{OH}{C}}-H)$[b]	1700m	135 - 138	61.15 (60.71)	4.70 (4.56)
(VIII)	 $(Ph_3P)_2Pt(HC\equiv C-\overset{H}{\underset{OH}{C}}-H)$	1720m	124 - 127	60.10 (60.39)	4.55 (4.39)

[a] m = Medium intensity, (sh) = shoulder. [b] New complex.

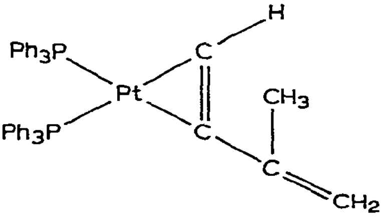
region of the C=C distance in olefins. We have now examined the low frequency IR spectra of a series of $(Ph_3P)_2Pt(ac)$ complexes, and compared them with those of similar platinum complexes.

Low frequency IR spectra of *cis*- and *trans*-$(R_3P)_2PtX_2$ (R = alkyl; X = halogen) have been extensively studied by Goodfellow et al. [17 - 19], Park et al. [20,21], and Chatt et al. [22,23] and assignments made on the basis of group theory. Very extensive series of complexes were examined, and IR and Raman spectra were compared. The *trans*-$(R_3P)_2PtX_2$ complexes could be classified in the point group C_{2h}, taking the ligands as point masses. The validity of this assumption was supported by experimental data: only a single PtP_2, and a single PtX_2 stretching vibration were observed, as predicted by the theory, and it was assigned to the B_u asymmetric mode. The symmetric vibrations are Raman-active only. The symmetry of the *cis* complexes is C_{2v}, and both symmetric and antisymmetric Pt—P_2 and Pt—X_2 stretching vibrations are IR active.

The Pt—P_2 modes of platinum complexes with PEt_3 ligands are observed between 450 - 420 cm^{-1}. Adams et al. [24] have examined the low frequency IR spectra of complexes containing Pt—C bonds, viz. *cis*-$(R_3P)_2PtL_2$ (L = CH_3, C_2H_5 or C_3H_7). As predicted by symmetry arguments, two Pt—C stretching modes were found in the range 600 - 500 cm^{-1}. The intensity of the Pt—C band decreases in the order: $CH_3 > C_2H_5 > C_3H_7$. Recent studies confirm that the Pt—C stretching modes appear in the 600 - 500 cm^{-1} region and that they are often of low intensity [25 - 28].

Results and discussion

The compounds examined, some of which are new, are listed in Table 1.



(B)

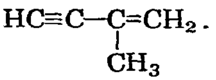
We have assigned the structure (B) to complex (II), on the basis of its IR spectrum in the 4000 - 600 cm^{-1} region and by comparison with the spectrum of the ligand  $HC{\equiv}C{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH_2$. The band at 895 cm^{-1}, characteristic of the $R_1R_2C{=}CH_2$ group, is still present in the spectrum of the complex, while that of the alkynyl group expected to be at 2110 cm^{-1}, is absent. Two bands, of nearly the same intensity, are observed at 1720 and 1680 cm^{-1}. The former is also present in the spectrum of the ligand, whilst the latter is in the range in which C≡C stretching vibrations of monosubstituted acetylenes bound to the platinum atom are normally found [5 - 8]. Other complexes (see Table 1) nor-

TABLE 2

IR ABSORPTION FREQUENCIES^{a} (cm^{-1}) FOR $(Ph_3P)_2Pt(HC{\equiv}CR)$ COMPLEXES (NUJOL MULLS)

Complex	R								
(I)	C_6H_5	583 vw[b]		555 ms		535 ms	529 w (sh) (531 ms)[a]	516 s	510 s (513 ms)
(II)	$C(CH_3)=CH_2$			559 ms	551 w (551 ms)	541 ms	532 w (sh) (529 m)	519 s	512 s
(III)	$C_6H_{10}OH$		568 (sh)	553 m (553 m)		539 m		521 s (523 ms)	510 s
(IV)	$C(CH_3)(OH)C_2H_5$	583 w		562 m	(556 ms)	540 ms		521 s	510 s
(V)	$C(CH_3)_2OH$	595 vw		(566 ms)	(559 ms)	540 m		522 s	511 s
(VI)	$CH(OH)CH_3$			555 m	(554 ms)	542 ms		523 s	513 s
(VII)	CH_2OH					542 ms	533 w		513 s
PPh_3						541 m		513 s	499 s

[a] The frequencies of free acetylenes are given in parentheses. [b] s, Strong; m, medium; w, weak; vw, very weak; (sh), shoulder.

mally show a single band (sometimes with a shoulder) in this region. The splitting of the C≡C band of acetylenes coordinated to platinum has also been observed by Greaves et al. [4] in the spectra of some platinum complexes with disubstituted acetylenes.

The IR frequencies (600 - 400 cm^{-1} region) of the complexes discussed here are given in Table 2. No significant bands were observed below 400 cm^{-1}. The bands of the triphenylphosphine and of the ligands are also given. It can be seen that the IR spectrum of triphenylphosphine exhibits several bands in the ranges in which Pt—P and Pt—C stretching frequencies are normally found. Since ligand bands also lie in the same spectral regions, only tentative assignments of the $Pt—P_2$ and $Pt—C_2$ modes are suggested.

Since there are no crystallographic data available, we have made the assumption that the $(Ph_3P)_2Pt(ac)$ molecules examined are nearly planar, as is known to be the case for the complex $(Ph_3P)_2Pt(PhC{\equiv}CPh)$ [16]. As for *cis*-$(R_3P)_2PtL_2$, of C_{2v} symmetry, the lower symmetry so produced will give both IR allowed symmetric and antisymmetric stretching modes.

All complexes show a band of medium intensity at about 560 cm^{-1}, which can be assigned to one of the Pt—C vibrations. The other may lie under the band at 540 cm^{-1}, which is of higher intensity than the corresponding band for triphenylphosphine. However, weak bands are observed in the range 580 - 595 cm^{-1} in the spectra of three of the complexes. Consequently, another explanation may be that the second Pt—C band is so weak as not to be observed in all cases. Thus, for example, Ruddick et al. [25,26] failed to find any Pt—C band in the spectra of $PtX_3CH_3L_2$ complexes ($L = PMe_2Ph$; X = halogen).

The triplet at about 500 cm^{-1} is slightly shifted to higher frequencies on coordination, and the band at 520 cm^{-1} increases in intensity. The three bands are of decreasing intensity in the spectra of the complexes, while they are of about the same intensity in the spectrum of uncoordinated triphenylphosphine. Deacon et al. [29] report that the doublet at 433 - 423 cm^{-1} is also shifted to

498 s		478 (sh)	461 (sh)	452 m	440 m		425 (sh)	419 m
499 s				453 m	437 m		424 m	
500 s	493 (sh)		467 (sh)	458 ms (453 w)	443 (sh)	434 (sh) (431 w)	425 ms	
501 s		480 (sh)		455 ms	443 (sh) (443 m)	436 m	424 ms	
499 s		480 (sh)		456 ms	443 (sh)	436 m	423 ms (420 w)	
501 s				458 ms	440 m		428 ms	
499 s	495 (sh)			453 m	437 m		425 (sh)	418 m
491 s						433 m	423 m	

higher frequencies on coordination. In the region 500 - 400 cm^{-1} we observed several bands the most intense of which lies at 423 ± 5 cm^{-1}. Adams et al. [30] reported that the Pt(PPh$_3$)$_4$ complex shows a very intense band at 424 cm^{-1}, and they suggested that it might be assigned to ν(Pt—P). The similarity of our spectra confirm this suggestion. The common band in the spectra of these complexes, at 455 cm^{-1}, is probably due to the other ν(Pt—P). In the light of the discussions by Goodfellow et al. [19] and Chatt et al. [23] of the IR and Raman spectra of PEt$_3$ complexes, and making the assumption that the Pt—P stretching frequencies follow the same trend in the spectra of triethyl and triphenylphosphine complexes, we can assign the 455 cm^{-1} band to the symmetric Pt—P mode and that at 425 cm^{-1} to the asymmetric one. No significant influence of the R radicals of the coordinated acetylene on the IR spectra was observed. Similar conclusions were made by Roundhill et al. [8], who investigated some analogous Pt complexes and observed that the difference in $\Delta\nu$(C≡C) values is also extremely small, even when the radicals on the coordinated acetylenes are of very different electron-withdrawing power (R = CF$_3$, C$_6$H$_5$ or CH$_2$OH). However, when R is a tertiary alcohol group, the Pt—C band is at 566 cm^{-1}, whilst for a secondary alcohol group it is shifted to 555 cm^{-1}. When R is CH$_2$OH the band at ≈ 560 cm^{-1} is not observed and a new band at 533 cm^{-1} appears, which may be the Pt—C band shifted to lower frequencies. This behaviour may be due to the different distribution of electron density in the Pt—C bonds caused by the electron donor properties of the methyl groups.

Experimental

Complexes were prepared by reducing *cis*-(Ph$_3$P)$_2$PtCl$_2$ with hydrazine in the presence of the substituted acetylene [1 - 5]. Elemental analyses were carried out by A. Bernhardt, W. Germany.

IR spectra were run on Perkin—Elmer model 521 (600 - 300 cm^{-1}) and Beckman IR 20 (4000 - 600 cm^{-1}) spectrophotometers. Spectra were recorded with Nujol mulls supported on NaCl discs or KRS-5 (R11C) discs. The resolution of the spectra was greatly enhanced by very fine grinding of the complexes.

References

1 J. Chatt, G.A. Rowe and A.A. Williams, Proc. Chem. Soc., (1957) 208.
2 A.D. Allen and C.D. Cook, Can. J. Chem., 41 (1963) 1235.
3 A.D. Allen and C.D. Cook, Can. J. Chem., 42 (1964) 1063.
4 E.O. Greaves, J.L. Lock and P.M. Maitlis, Can. J. Chem., 46 (1968) 3879.
5 J.H. Nelson, H.B. Jonassen and D.M. Roundhill, Inorg. Chem., 8 (1969) 2591.
6 J.H. Nelson, J.J.R. Reed and H.B. Jonassen, J. Organometal. Chem., 29 (1971) 163.
7 S. Cenini, R. Ugo and G. La Monica, J. Chem. Soc. A, (1971) 409.
8 P.B. Tripathy and D.M. Roundhill, J. Organometal. Chem., 24 (1970) 247.
9 D.A. Harbourne, D.T. Rosevear and F.G.A. Stone, Inorg. Nucl. Chem. Lett., 2 (1966) 247.
10 H. Nelson, K.S. Wheelock, L.C. Cusachs and H.B. Jonassen, Chem. Commun., (1969) 1019.
11 J.P. Collman and J.W. Kang, J. Amer. Chem. Soc., 89 (1967) 844.
12 S. Wheelock, J.H. Nelson, L.C. Cusachs and H.B. Jonassen, J. Amer. Chem. Soc., 92 (1970) 5110.
13 J.H. Nelson, K.S. Wheelock, L.C. Cusachs and H.B. Jonassen, Inorg. Chem., 11 (1972) 422.
14 M.N. Chisholm, H.C. Clark, L.E. Manzer and J.B. Stothers, J. Amer. Chem. Soc. 94 (1972) 5087.
15 F.R. Hartley, Angew. Chem., Int. Ed. Engl., 11 (1972) 596.
16 J.O. Glanville, J.M. Stewart and S.O. Grim, J. Organometal. Chem., 7 (1967) P9.
17 P.L. Goggin and R.J. Goodfellow, J. Chem. Soc. A, (1966) 1462.
18 R.J. Goodfellow, J.G. Evans, D.L. Goggin and D.A. Duddell, J. Chem. Soc. A, (1968) 1604.
19 D.A. Duddell, P.L. Goggin, R.J. Goodfellow, M.G. Norton and J.G. Smith, J. Chem. Soc. A, (1970) 545.
20 P.J.D. Park and P.J. Hendra, Spectrochim. Acta, Part A, 25 (1969) 227.
21 P.J.D. Park and P.J. Hendra, Spectrochim. Acta, Part A, 25 (1969) 909.
22 D.M. Adams, J. Chatt, J. Gerratt and A.D. Westland, J. Chem. Soc., (1964) 734.
23 J. Chatt, G.J. Leigh and D.M. Mingos, J. Chem. Soc. A, (1969) 2972.
24 D.M. Adams, J. Chatt and B.L. Shaw, J. Chem. Soc., (1960) 2047.
25 J.D. Ruddick and B.L. Shaw, J. Chem. Soc. A, (1969) 2801.
26 J.D. Ruddick and B.L. Shaw, J. Chem. Soc. A, (1969) 2964.
27 H. Masai, K. Sonogshira and N. Hagigara, J. Organometal. Chem., 26 (1971) 271.
28. D.E. Clegg, J.R. Hall and J.A. Swile, J. Organometal. Chem., 38 (1972) 403.
29 G.B. Deacon and J.H.S. Green, Chem. Ind. (London), (1965) 1031.
30 D.M. Adams and P.J. Chandler, J. Chem. Soc. A, (1969) 588.