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CARBENE COMPLEXES

IV*. FAR INFRARED AND ^{31}P NMR SPECTRA OF PALLADIUM AND PLATINUM CARBENE COMPLEXES

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Summary

Infrared bands mainly associated with ν(M—X$_2$) stretching modes (M = Pd or Pt, and X = Cl, Br, or P) have been identified in the spectra of 35 carbene complexes. Based on these results and on $|^1J|$(^{31}P—^{195}Pt) the *trans*-influence of the carbene ligands is assessed.

Introduction

A series of palladium and platinum carbene complexes of the ligand 1,3-dimethylimidazolidine-2-ylidene and related carbenes has been prepared. Preparative details [2, 3], chemical properties [4, 5], IR, ^{1}H NMR [5], and ^{13}C NMR [1] spectra have been published. We now report other spectroscopic studies (far IR and ^{31}P NMR) which in addition to providing structural information, afford further data concerning the *trans*-influence of the new carbene ligands.

Infrared spectra

Carbene complexes of the series *cis*- or *trans*-L$_2$MCl$_2$, where L = tertiary phosphine or arsine and M = Pd or Pt, show strong infrared absorptions in the range 270—350 cm^{-1} (see Table 1). These bands are tentatively attributed to ν(M—Cl$_2$) vibrational modes. In order to confirm this assignment a number of analogous bromo complexes was prepared: these (*cis*-isomers) showed strong absorptions at 175—205 cm^{-1} [ν(M—Br$_2$)] and the bands previously assigned to metal—chlorine vibrations were absent (see Tables 1 and 2). However, bands associated with ν(M—Br$_2$) were not sufficiently strong for most of the *trans*-

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[*] For part I see ref. 3; part II, ref. 5; part III, ref. 1.

TABLE 1

METAL—CHLORINE STRETCHING VIBRATIONS IN THE SERIES *cis*- AND *trans*-L_2MCl_2 (L = TERTIARY PHOSPHINE OR ARSINE, OR CARBENE, M = Pd OR Pt)

Formula	*trans*-Series		*cis*-Series	
	Compound	$\nu(M{-}Cl_2)^a$	Compound	$\nu(M{-}Cl_2)^a$
$PtCl_2(\overline{CNPhCH_2CH_2N}Ph)(PEt_3)$	(I)	341 s	(II)	308 s, 277 s
$PtCl_2(\overline{CNPhCH_2CH_2N}Ph)(PBu_3)$	(III)	337 s	(IV)	305 s, 275 m
$PtCl_2(\overline{CNPhCH_2CH_2N}Ph)(PMe_2Ph)$	(V)	340 s	(VI)	312 s, 285 s
$PtCl_2(\overline{CNPhCH_2CH_2N}Ph)(AsEt_3)$	(VII)	340 vs	(VIII)	312 s, 285 s
$PtCl_2(\overline{CNMeCH_2CH_2N}Me)(PEt_3)$	(IX)	339 vs	(X)	312 vs, 288 vs
$PtCl_2(\overline{CNMeCH_2CH_2N}Me)(PPr_3)$	(XI)	340 vs	(XII)	359 vs, 286 s
$PtCl_2(\overline{CNMeCH_2CH_2N}Me)(PBu_3)$	(XIII)	340 vs	(XIV)	308 vs, 285 s
$PtCl_2(\overline{CNMeCH_2CH_2N}Me)(PMe_2Ph)$	(XV)	*b*	(XVI)	311 s, (305 sh), 283 s
$PtCl_2(\overline{CNMeCH_2CH_2N}Me)(AsEt_3)$	(XVII)	338 vs	(XVIII)	310 vs, 295 vs
$PtCl_2(\overline{CNMeC_6H_4S}\text{-}o)(PEt_3)$	(XIX)	347 s (320 sh)	(XX)	310 s, (302 sh), 281 s
$PtCl_2(\overline{CNMeC_6H_4S}\text{-}o)(PBu_3)$	(XXI)	348 s, 325 s ^{c}	(XXII)	310 s, (302 sh), 285 s
$PtCl_2(\overline{CNMeC_6H_4S}\text{-}o)(PMe_2Ph)$	(XXIII)	*b*	(XXIV)	315 s, (310 sh), 285 s
$PdCl_2(\overline{CNPhCH_2CH_2N}Ph)(PEt_3)$	(XXV)	351 s (318 m)	(XXVI)	302 s, 272 s
$PdCl_2(\overline{CNPhCH_2CH_2N}Ph)(PBu_3)$	(XXVII)	350 s	(XXVIII)	306 s, 275 m
$PdCl_2(\overline{CNMeCH_2CH_2N}Me)(PEt_3)$	(XXIX)	*b*	(XXX)	309 s, (302 sh), 285 s
$PdCl_2(\overline{CNMeCH_2CH_2N}Me)(PBu_3)$	(XXXI)	*b*	(XXXII)	305 s, 292 s
$PdCl_2(\overline{CNMeC_6H_4S}\text{-}o)(PEt_3)$	(XXXIII)	*b*	(XXXIV)	311 s, (303 sh), 280 s
$PdCl_2(\overline{CNMeC_6H_4S}\text{-}o)(PBu_3)$	(XXXV)	*b*	(XXXVI)	312 s, (307 sh), 447 s

[a] Spectra run as Nujol mulls using KBr discs. [b] Data not available; *trans* → *cis* isomerisation too facile. [c] Also shoulders in spectrum at 330 and 320 cm^{-1}. All peaks in the appropriate region are quoted, but the shoulders (in parentheses) are not necessarily associated with $\nu(M{-}Cl_2)$.

isomers that any *reliable* assignments could be made, and, for these, figures have been omitted from Table 1. In common with most other square planar dihalides the *trans*-isomers in the present compounds show only one strong $\nu(M{-}Cl_2)$ band whereas there are invariably two major absorptions associated with $\nu(M{-}X_2)$ in the *cis*-series.

Far infrared frequencies, and especially $\nu(M{-}Cl_2)$ have also been useful in assessment of ligand *trans*-influence [6]. In the present series we have already noted [2, 4], based on X-ray structural data, that the carbenes exert a *trans*-influence for platinum(II) very close to that of tertiary phosphines. Infrared spectra, however, are less simple to interpret for this series, in which the *cis*-complexes are *unsymmetrical.* However, if instead of using mean $\nu(Pt{-}X_2)$ values (see e.g., ref. 6) we consider both frequencies a trend is clearly discernible; e.g., compare [(compound), $\nu(Pt{-}Cl_2)$ cm^{-1}]: (I) 308, 277; (IX) 312, 288; and (XIX) 310, 281; with *cis*-$PtCl_2(PEt_3)_2$ 305, 283 [7]. The values clearly suggest a very similar *trans*-influence for the three carbenes and triethylphosphine. Analogous

TABLE 2

METAL—BROMINE STRETCHING VIBRATIONS IN THE SERIES *cis*- AND *trans*-L_2MBr_2

Formula	*trans*-Series		*cis*-Series	
	Compound	ν(M—Br_2)[a]	Compound	ν(M—Br_2)[a]
$PtBr_2(\overline{CNPhCH_2CH_2N}Ph)(PEt_3)$	(XXXVII)	248 m	(XXXVIII)	195 vs, 203 s
$PtBr_2(\overline{CNMeCH_2CH_2N}Me)(PEt_3)$	(XXXIX)	b	(XL)	192 vs, 203 s
$PtBr_2(\overline{CNMeC_6H_4S}\text{-}o)(PEt_3)$	(XLI)	b	(XLII)	197 s, 187 s
$PdBr_2(\overline{CNPhCH_2CH_2N}Ph)(PEt_3)$	(XLIII)	b	(XLIV)	b
$PdBr_2(\overline{CNPhCH_2CH_2N}Ph)(PBu_3)$	(XLV)	b	(XLVI)	197, 179 s

[a] Samples ground with polythene, and spectra run on polythene-based discs. [b] Bands not sufficiently well resolved to make reliable assignments.

comparisons may be made for other groups of compounds, including the bromo and palladium complexes.

Metal—phosphorus vibrations for the *trans*-compounds are not subject to the same difficulties, and are shown in Table 3, together with metal—arsenic data. However in this case coupling, of ν(M—P) or ν(M—As) with internal modes of the ligand [e.g., δ(PCC)], is a serious drawback [8].

In the present context assignment of the bands having largely ν(M—P) character is relatively straightforward. Thus we have an extensive series of closely related derivatives, for which arsine analogues are available for comparison,

TABLE 3

METAL—PHOSPHORUS AND —ARSENIC VIBRATIONS IN THE SERIES *cis*- AND *trans*-L_2MX_2 (L = TERTIARY PHOSPHINE OR ARSINE, OR CARBENE; X = Cl or Br; M = Pd or Pt)

trans-Series		*cis*-Series	
Compound	ν(M—P) or ν(M—As)[a]	Compound	ν(M—P) or ν(M—As)[a]
(I)	422 w	(II)	439 m
(III)	455 w	(IV)	475 w
(V)	442 m	(VI)	452 w
(VII)		(VIII)	306 w
(IX)	421 m	(X)	435 m
(XI)	443 m	(XII)	447 s
(XIII)	445 w	(XIV)	442 s
(XV)		(XVI)	437 s
(XVII)	436 w	(XVIII)	440 m
(XIX)	435 s, 425 sh	(XX)	435 m, 430 sh
(XXI)	435 s	(XXII)	430 s
(XXIII)		(XXIV)	437 w
(XXV)	415 w	(XXVI)	435 w
(XXVII)		(XXVIII)	472 w
(XXIX)		(XXX)	435 w, 425 w
(XXXI)		(XXXII)	440 m
(XXXIII)		(XXXIV)	430 s
(XXXV)		(XXXVI)	447 s
(XXXVII)	420 s	(XXXVIII)	438 w
(XXXIX)	432 m	(XL)	447 s
(XLI)	431 s	(XLII).	437 m
(XLIII)	412 w	(XLIV)	412 m
(XLV)	452 w	(XLVI)	468 w

[a] Spectra run as nujol mulls between KBr discs.

and the region [7, 9] of the spectrum for ν(M—P) exhibits only a single band. It should be pointed out that the free ligands also exhibit a single weak band (unassigned) in this region; however, this band is not present in metal complexes which do not contain phosphines, and moreover the present complexes show but a single absorption within the ν(M—P) range. As a means of assessing *trans*-influence, ν(M—P) data are clearly unreliable, but at least do not conflict with our general conclusion; note: (I) has ν(Pt—P) at 422 cm^{-1}, *trans*-$PtCl_2(PEt_3)_2$, at 419 cm^{-1} [9].

ν(M—C) has proved difficult to assign in complexes of the present type. All these compounds exhibit a medium-weak band in the region 500—550 cm^{-1} which may be associated with the M—C_{carb} stretching mode, but the parent olefins also show a band in the same region. Moreover, the Pt^{IV} complexes $PtCl_4(CHNMe_2)PEt_3$ and $PtCl_4(CHNMe_2)PBu_3$, show no absorptions between 480 and 600 cm^{-1} [10]. Those in the present series at 510—540 cm^{-1} may therefore arise from internal modes of the carbene ligands.

^{31}P NMR spectra

Data for the carbene complexes are presented in Table 4. The *cis*-complexes invariably exhibit larger $|^1J|(^{31}P—^{195}Pt)$, which confirms other stereochemical assignments. Variations in J(P—Pt) in the *trans*-complexes can be interpreted in terms of the appropriate form of the Pople and Santry expression for coupling [11], and can be used as a measure of the *trans*-influence of the ligand *trans* to P. In this procedure a high $J(^{31}P—^{195}Pt)$ implies a low *trans*-influence for the appropriate ligand. Once again we note the general similarity to tertiary phosphines, [compare $|^1J|(^{31}P—^{195}Pt)$ for (I), 2.44 kHZ, with that of *trans*-$PtCl_2(PBu_3)_2$, 2.39 kHz], but the method is sensitive enough to make distinctions possible between the different carbene ligands. We should thus have the *trans*-influence order: $Et_3P \approx$ 1,3-dimethylimidazolidinylidene > *N*-methylbenzothiazolinylidene ≥ 1,3-dimethylimidazolidinylidene:

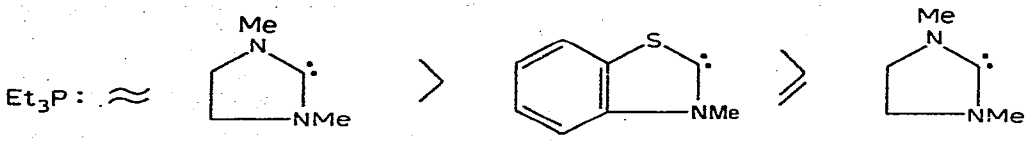

TABLE 4

^{31}P CHEMICAL SHIFTS AND $|J|(^{31}P—^{195}Pt)$ FOR THE SERIES *cis*- AND *trans*-L_2MX_2 (L = TERTIARY PHOSPHINE OR CARBENE: X = Cl or Br; M = Pd or Pt).

trans-Series			*cis*-Series		
Compound	$\delta^{31}P$ [b]	$|J|(^{31}P—^{195}Pt)$ [a]	Compound	$\delta^{31}P$ [b]	$|J|(^{31}P—^{195}Pt)$ [c]
(I)	+110.8	2.44	(II)	[d]	
(IX)	+110.0	2.35	(X)	+136.2	3.72
(XI)	+119.1	2.34	(XII)	+114.8	3.75
(XIII)	+ 80.2	2.35	(XIV)	+ 46.3	3.26
(XIX)	+107.2	2.44	(XX)	[d]	
(XXXVII)	+114	2.47	(XXXVIII)	[d]	
(XXXIX)	+121	2.36	(XL)	+114	4.08

[a] Measured in chloroform solution. [b] In ppm from external (capillary) P_4O_6. [c] In kHz. [d] *cis*-Isomer too insoluble for measurements.

Experimental

The preparations of the complexes have been previously reported [2, 3]. IR spectra were recorded using a Perkin Elmer model 457 grating instrument, and ^{31}P NMR spectra were obtained using a Perkin Elmer model R10 spectrometer operating a 24.29 MHz, with a Northern Electronics C.A.T. Far infrared spectra were measured using an R.I.I.C. FS 620 Fourier transform spectrometer, and samples were made up as polythene discs.

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