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THE INFRARED SPECTRA OF THE SQUARE-PLANAR DIALKYNYL COMPLEXES OF NICKEL(II), PALLADIUM(II) AND PLATINUM(II)

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SUMMARY

The stability of the metal–carbon bond in bis(triethylphosphine)dialkynyl complexes of Ni^{II}, Pd^{II} and Pt^{II} was investigated through the substituent effect exerted on metal–carbon stretching frequencies, and a linear relationship was established between the square of the frequencies and Taft's polar constants of the substituents on alkynyl groups.

The relationship was interpreted in terms of $d\pi$–$p\pi$ interaction between central metal and alkynyl groups. The interaction is considered to reinforce the metal–carbon bond.

INTRODUCTION

The chemistry of organic derivatives of transition metals has made brilliant progress during the past two decades and much effort has been expended on the consideration of bonding and structure. Among many kinds of complexes, alkyl derivatives are interesting ones, since the derivatives are considered to play significant role in various reactions as intermediates or active species of the catalyst[1]. However, our knowledge about properties of the metal–alkyl bond seems still insufficient.

We have prepared and measured the IR spectra (4000–200 cm^{-1}) of a series of square-planar dialkynyl complexes of nickel(II), palladium(II) and platinum(II), namely *trans*-$[L_2M(C{\equiv}CR)_2]$, where L is tertiary phosphine or stibine. It was found that asymmetric metal–carbon stretching frequencies were sensitive to the change of R. Through the relation, the bond properties will be discussed below.

RESULTS AND DISCUSSION

The IR spectra of the alkynyl complexes, *trans*-$[L_2M(C{\equiv}CR)_2]$, were recorded from 4000 to 200 cm^{-1}, where M is Ni^{II}, Pd^{II} or Pt^{II}, L is trimethylphosphine, triethylphosphine, triphenylphosphine or triethylstibine and R is listed in Table 1.

These complexes have D_{2h} molecular configuration (Fig. 1) around the central metal. The IR active metal–carbon stretching is B_{2u} mode. The A_g mode is only Raman active.

From the reported spectra of Pd^{II}[2], Pt^{II}[3,4] and Pt^{IV}[5] alkyl complexes, the

TABLE 1

IR SPECTRA OF *trans*-$L_2M(C{\equiv}CR)_2$

M	L	R	ν(C–M) (cm^{-1})	ν(P–M) (cm^{-1})	ν(C≡C)[a] (cm^{-1})
Ni	Et_3P	Me	557	405	2105
		$CH{=}CH_2$	550	405	2080
		Ph	570	405	2085
		CH_2F	566	405	2100
		C≡CPh	578	405	2040, 2170
		C≡CH	585	405	1985, 2100
Pd	Et_3P	$CH{=}CH_2$	543	405	2070
		Ph	545	405	2070
		CH_2F	560	405	2115
		C≡CPh	578	405	2050, 2170
		C≡CH	597	405	1990, 2120
	Me_3P	$CH{=}CH_2$	544	340	2090
		Ph	547	337	2080
	Ph_3P	Ph	548		2110
Pt	Et_3P	$CH{=}CH_2$	544	405	2050
		Ph	549	405	2107
		CH_2F	561	405	2120
		C≡CPh	578	405	2050, 2160
		C≡CH	580	405	1996, 2140
	Me_3P	$CH{=}CH_2$	545	346	2100
		Ph	551	346	2090
	Ph_3P	$CH{=}CH_2$	537		2100
		Ph	551		2090
	Et_3Sb	Ph	547		2080
		C≡CPh	578		2030, 2140

[a] ν(C≡C) of free alkynes RC≡CH : R = Me 2123 cm^{-1} (ref. 20), R = $CH{=}CH_2$ 2101 cm^{-1} (ref. 21), R = Ph 2115 cm^{-1} (ref. 20) and R = CH_2F 2149 cm^{-1} (ref. 20).

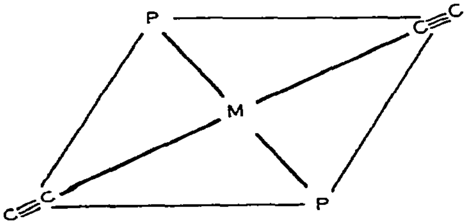

Fig. 1. Molecular configuration of the square-planar dialkynyl complexes.

metal–carbon stretching is expected to be observed in the region, 600–500 cm^{-1}, for the alkynyl complexes of Pd^{II}, Pt^{II} and probably Ni^{II}. The IR spectra of the bis(trialkylphosphine)dihalo complexes of these metals[6,7] showed no absorption in this region.

The IR spectra (600–500 cm^{-1}) of *trans*-$[(Et_3P)_2M(C{\equiv}CR)_2]$, (M = Ni, Pd or Pt), are shown in Fig. 2.

These complexes exhibit one absorption in this region, which was sensitive to the change of R (Figs. 2, 3 and Table 1). The phenylethynyl derivatives showed three

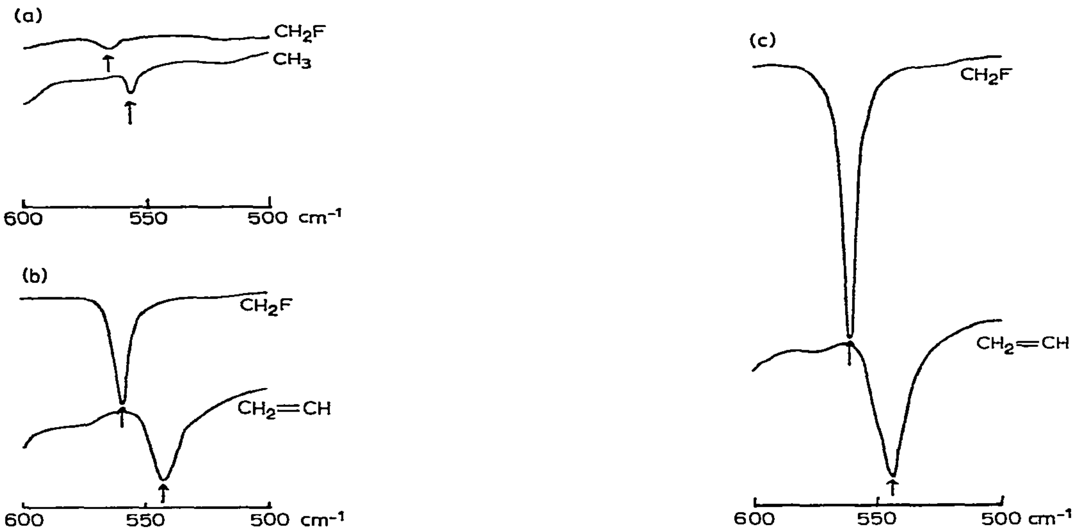

Fig. 2. IR spectra of *trans*-[(Et$_3$P)$_2$M(C$\equiv$CR)$_2$]; arrowed absorptions are ν(M–C); (a) M = Ni, (b) M = Pd, (c) M = Pt.

absorptions, but two of them, about 520 and 530 cm^{-1}, are due to the deformation of mono-substituted phenyl ring[8] (Fig. 3). Hence, these absorptions are considered to be the B_{2u} mode metal–carbon stretching vibration. The assignment for other complexes was made by comparison.

The frequencies of the metal–carbon, metal–phosphorus and carbon–carbon stretchings are listed in Table 1.

In the series of triethylphosphine complexes, the plots of the square of the metal–carbon stretching frequencies (ν^2) against Taft's polar substituent constants

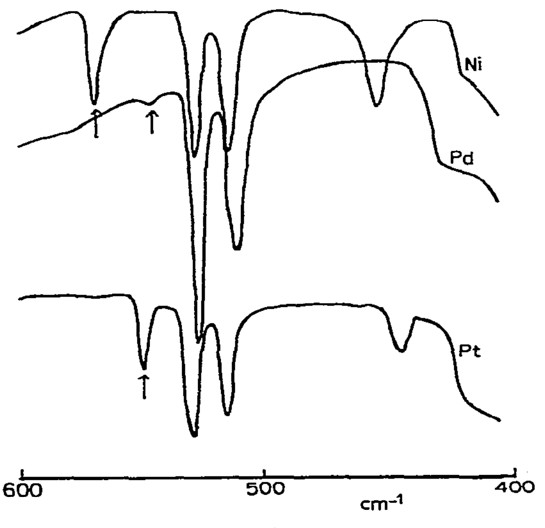

Fig. 3. IR spectra of *trans*-[(Et$_3$P)$_2$M(C$\equiv$CPh)$_2$]; arrowed absorptions are ν(M–C).

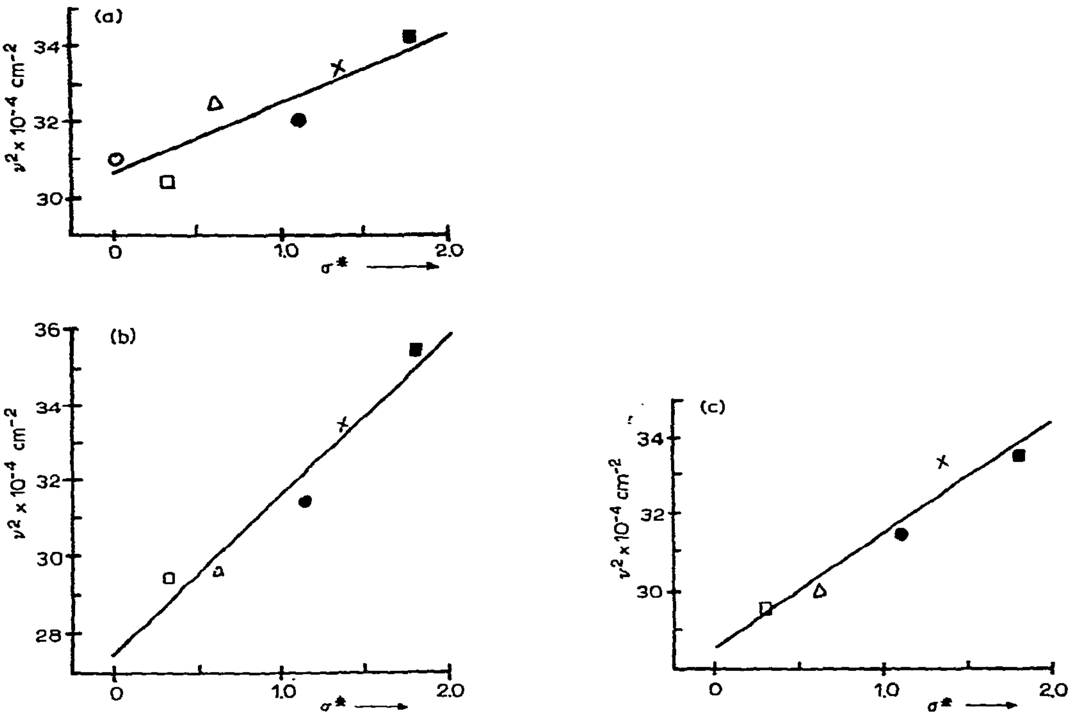

Fig. 4. Plots of ν^2 vs. Taft's polar constants (σ^*); ○ CH_3, □ CH_2=CH, △ Ph, ● CH_2F, x PhC≡C, ■ HC≡C; (a) M=Ni, (b) M=Pd, (c) M=Pt.

(σ^*)[9] of R showed considerably good linear relationship (Fig. 4). The least square treatment gave following correlation coefficients; 0.91 for the series of Ni complexes, 0.97 for Pd and Pt complexes, respectively.

The interaction of the metal–carbon stretching with other vibrations in same symmetry such as carbon–carbon stretching or metal–phosphorus rocking will be small enough to neglect, because of the large difference in the frequencies among them. Therefore, the ν^2 closely relates to the force constant of the stretching vibration which reflects the bond strength[3c].

It is considered that the metal–carbon bonds are reinforced in the complexes associated with R's of larger σ^*-value, namely the more electronegative groups. For such substituents afforded low π-antibonding (π^*) levels[10] of the alkynyl groups, the energy difference between the π^* levels and d-levels (d_{xy} and d_{yz}) of the central metal may become smaller. The $d\pi$–$p\pi$ interaction will be facilitated under such situation. Hence, the alkynyl groups are more tightly bound to the metal atom through the $d\pi$–$p\pi$ interaction.

The stretching frequencies of carbon–carbon triple bonds in the complexes were significantly reduced from those of free alkynes (Table 1). This is considered to be another evidence for the existence of $d\pi$–$p\pi$ interaction.

Our interpretation is in agreement with earlier presumption[11], the results of Chatt *et al.*[3,12] and Calvin *et al.*[2] and the interpretation of X-ray study of the phenylethynyl complex of Ni^{II}[13].

The effect of the ligands *cis* to alkynyl groups was also investigated (Table 1). However, no appreciable influence on the metal–carbon bond was conceivable from our results. This means that the *cis* effect is negligible in the square-planar dialkynyl complexes, as already pointed out[14].

EXPERIMENTAL

Infrared spectra

The IR spectra of the alkynyl complexes were recorded as nujol mull and KBr tablets using Model DS-402G IR Spectrophotometer of Japan Spectroscopic Co., Ltd. by Miss H. Morimoto.

Materials

The following alkynes, 3-fluoro-1-propyne[15], 1,3-butadiyne[16], 4-phenyl-1,3-butadiyne[16] and vinylacetylene[18], were prepared by the reported procedure. The latter three compounds were prepared by the action of sodium amide in liquid ammonia and used without isolation for further step.

The complexes listed in Table 2 were prepared by the reaction of the chloro- or bromo-complexes of Ni^{II}, Pd^{II} and Pt^{II} with sodium salt of appropriate alkynes in liquid ammonia in good yields.

TABLE 2

ANALYSES AND MELTING POINTS OF *trans*-$L_2M(C{\equiv}CR)_2$

M	L	R	Found (%) C	Found (%) H	Calcd. (%) C	Calcd. (%) H	M.p.[a] (°C)
Ni	Et_3P	$CH{=}CH_2$	60.32	9.23	60.48	9.14	43–45
		CH_2F	53.01	8.68	52.84	8.38	60–62
		$C{\equiv}CPh$	70.64	7.32	70.48	7.39	130d
		$C{\equiv}CH$	61.24	8.20	61.10	8.21	140d
Pd	Et_3P	CH_2F	47.10	7.72	47.33	7.50	74–75.5
		$C{\equiv}CPh$	64.83	6.67	64.81	6.80	170d
		$C{\equiv}CH$	54.92	7.50	54.49	7.32	100d
	Me_3P	$CH{=}CH_2$	46.46	7.00	46.62	6.71	110–112md
		Ph	57.63	6.15	57.34	6.12	160d
	Ph_3P	Ph	74.84	4.93	74.96	4.84	118–120 md
Pt	Et_3P	CH_2F^b					
		$C{\equiv}CPh$	56.34	5.93	56.38	5.91	218–221md
	Me_3P	$CH{=}CH_2$	37.31	5.51	37.42	5.38	138–140
		Ph	48.00	5.41	48.09	5.14	244d
	Ph_3P	Ph	67.69	4.35	67.75	4.37	82–87
	Et_3Sb	Ph	41.15	4.91	41.25	4.95	154–159md
		$C{\equiv}CPh$	44.63	4.78	44.52	4.67	180d

[a] d : decomposes above the temperature; md : melts with decomposition. [b] Partly isomerized to $(Et_3P)_2PtF_2$ in solution.

The vinylethynyl complexes of bis(triethylphosphine)palladium, -platinum and bis(triphenylphosphine)platinum, and the butadiynyl complex of bis(triethylphosphine)platinum were kindly presented by Mr. I. Kaneko, which were prepared by dehalohydrogenation method[19].

Other complexes were prepared by the reported procedure[2,3,12].

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REFERENCES

1 R. Ugo, *Chim. Ind. (Milan)*, 51 (1969) 1319 and references cited therein.
2 G. Calvin and G. E. Coates, *J. Chem. Soc.*, (1960) 2008.
3 (a) R. J. Cross, *Organometal. Chem. Rev.*, 2 (1967) 97;
  (b) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1959) 4020;
  (c) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1960) 2047.
4 C. R. Kistner, J. H. Hutchinson, J. R. Doyle and J. C. Storlie, *Inorg. Chem.*,2 (1963) 1255.
5 D. E. Clegg and J. R. Hall, *J. Organometal. Chem.*, 17 (1969) 175.
6 P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc. A*, (1966) 1462.
7 G. E. Coates and C. Parkin, *J. Chem. Soc.*, (1963) 421.
8 J. C. Evance and R. A. Nyquist, *Spectrochim. Acta*, 16 (1960) 918.
9 (a)R. W. Taft, Jr., *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, p. 556;
  (b) P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, 82 (1960) 795;
  (c) W. Drenth and A. Hogervorst, *Recl. Trav. Chim. Pays-Bas*, 87 (1968) 41.
10 H. Kato, H. Konishi, H. Yamabe and T. Yonezawa, *Bull. Chem. Soc. Jap.*, 40 (1967) 2761.
11 H. H. Jaffe and G. O. Doak, *J. Chem. Phys.*, 21 (1953) 196.
12 (a) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1959) 705;
  (b) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1960) 1718.
13 W. A. Spofford, III, P. D. Carfagna and E. L. Amma, *Inorg. Chem.*, 6 (1967) 1553.
14 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 2nd ed., 1967, p. 382.
15 R. E. Job and J. Sheridan, *Nature*, 193 (1962) 677.
16 M. Nakagawa and T. Inui, *Nippon Kagaku Zasshi*, 73 (1952) 143.
17 V. A. Andnevskii, I. L. Kotlyarevskii and M. S. Shvartberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1966) 882; *Chem. Abstr.*, 62 (1966) 13580a.
18 T. F. Rutledge, *Acetylenic Compounds*, Reinhold, New York, 1968, p. 28.
19 I. Kaneko and N. Hagihara, to be published.
20 B. Wojtowiak and R. Queignec, *C. R. Acad. Sci., Paris, Ser. B*, 262 (1966) 811.
21 A. J. Saggiomo, *J. Org. Chem.*, 22 (1957) 1171.