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THE CHARGE-TRANSFER INTERACTION OF 7,7,8,8-TETRACYANOQUINODIMETHANE WITH *trans*-BIS(TRIALKYLPHOSPHINE)DIALKYNYLPLATINUM(II) AND RELATED COMPLEXES

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SUMMARY

7,7,8,8-Tetracyanoquinodimethane** (TCNQ) showed charge-transfer interaction with *trans*-bis(trialkylphosphine)dialkynylplatinum(II), *trans*-$[(R'_3P)_2Pt(C{\equiv}CR)_2]$, ($R' = Me$, Et, Pr, Bu, and $R = H$, Me, $CH_2{=}CH$, $CH_3C{\equiv}C$ or Ph), and their palladium(II) and nickel(II) derivatives. The following 1/1 adducts were isolated as stable purple-black crystals:

$[(Me_3P)_2Pt(C{\equiv}CH)_2]$ [TCNQ] $[(Me_3P)_2Pt(C{\equiv}CCH_3)_2]$ [TCNQ]
$[(Et_3P)_2Pt(C{\equiv}CH)_2]$ [TCNQ] $[(Et_3P)_2Pt(C{\equiv}CCH_3)_2]$ [TCNQ]

These adducts showed a characteristic absorption band in the visible region (λ_{max}; 506–555 nm in CH_2Cl_2).

From the study of their formation constants and consideration of the molecular geometry of component molecules, it was deduced that electron was donated from the alkynyl groups to TCNQ. This characteristic property of the alkynyl group which coordinates to transition-metal atom is regarded as the consequence of the back-donation of electrons from the central metal which increases the electron density on the alkynyl groups and enhances their donor properties.

INTRODUCTION

In our studies of properties of the square-planar dialkynyl complex, *trans*-$[L_2M(C{\equiv}CR)_2]$, where M is nickel(II), palladium(II) or platinum(II), and L is tertiary phosphine or tertiary stibine, the important role of d_π–p_π interaction in the metal–carbon bond has been examined by means of infrared[1] and electronic[2,3] spectroscopies. In those studies, the electronic spectrum of the alkynyl complex showed a considerable solvent effect in alcohols[2]. The effect was considered to be the result of the formation of a hydrogen bond between alcohols and the alkynyl complex.

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** Chemical Abstracts name: 3,6-bis(dicyanomethylene)-1,4-cyclohexadiene.

Since a proton acceptor sometimes behaves as a good electron donor, we have studied the reaction of the alkynyl complex with some organic π-acceptors. Amongst these acceptors, 7,7,8,8-tetracyanoquinodimethane (TCNQ) showed a striking change of color in solution, which suggests the existence of a charge-transfer (CT) interaction, and very stable CT complexes were isolated in some cases.

In this paper, we discuss the structure of the CT complex and the property of the bond between the alkynyl group and the central metal. Earlier workers have shown that some organometallic complexes interact with the organic electron acceptors, *e.g.* $[(\pi\text{-}C_5H_5)_2M][TCNE]$, (M = Fe, Co or Ni, TCNE = tetracyanoethylene), $[(C_6H_5CH_3)_2Cr]^+[TCNQ]^-[TCNQ]$[4,5]. In these complexes, interaction takes place between the ligands and the acceptors. In our case, the CT interaction was considered also to take place between the alkynyl group coordinated to the central metal and TCNQ as discussed below.

RESULTS

Charge-transfer complexes and their infrared and visible spectra

When a dichloromethane solution of TCNQ was mixed with a solution of the alkynyl complex, *trans*-$[(R'_3P)_2M\text{-}(C{\equiv}CR)_2]$, in dichloromethane at room temperature, the initially pale yellow color of the solution turned to deep red or purple in the case of the palladium and platinum complexes, and to violet in the nickel complex within 5 h. In the former case, the color was maintained at least for 2 days, but it faded away within 30 min in the latter case.

In some platinum complexes, the interaction with TCNQ is particularly strong, and the following 1/1 adducts were isolated as stable, purple-back crystals:

$[(Me_3P)_2Pt(C{\equiv}CH)_2][TCNQ]$ $[(Me_3P)_2Pt(C{\equiv}CCH_3)_2][TCNQ]$
$[(Et_3P)_2Pt(C{\equiv}CH)_2][TCNQ]$ $[(Et_3P)_2Pt(C{\equiv}CCH_3)_2][TCNQ]$

The donor–acceptor ratio was determined by elemental analyses. The infrared spectra of the above complexes are shown in Fig. 1 and Table 1. In general, the infrared spectra of the weak CT complexes show small differences, compared with the summation of the spectra of the two components. The spectra of the above adducts also involve only slight modification of that of the components, except the C=C

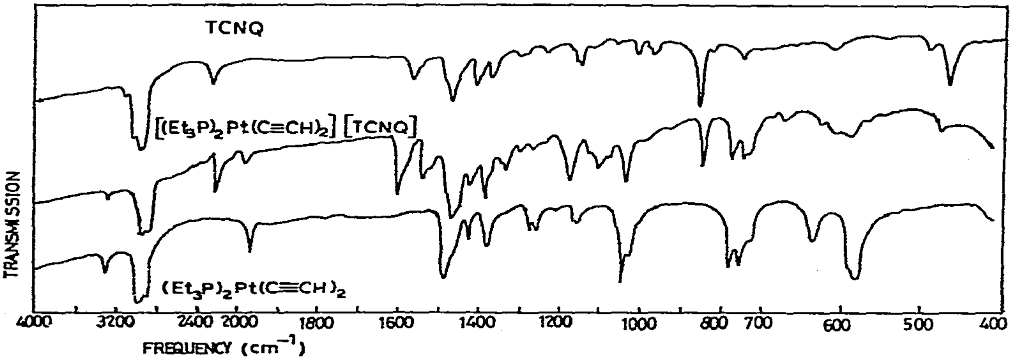

Fig. 1. Infrared spectra of $[(Et_3P)_2Pt(C{\equiv}CH)_2][TCNQ]$ and its component compounds (In Nujol).

TABLE 1

INFRARED SPECTRA[a] OF THE CT COMPLEXES, $[L_2Pt(C{\equiv}CR)_2][TCNQ]$ AND RELATED COMPOUNDS

TCNQ	3050 w, 2210 m, 1548(sh), 1538 m, 1520(sh), 1355 m, 1285 w, 1205 w, 1126 w, 1115 w, 1092 w, 1045 w, 999 w, 962 w, 861 vs, 805 w, 620 w, 498 w, 475 s
trans-$(PMe_3)_2Pt(C{\equiv}CH)_2$ (I)	3275 m, 1964 s, 1430 m, 1422 m, 1413 m, 1399 w, 1367(sh), 1340(sh), 1302 w, 1286 s, 1208 w, 1170 w, 1147 m, 965 vs, 955 vs, 870 m, 858 m, 847 vs, 680 m, 607 s, 566 s
(I) (TCNQ)	3270 m, 2195 s, 1971 m, 1591 s, 1530(sh), 1518 m, 1510 m, 1418 m, 1408 m, 1367(sh), 1337 w, 1327 w, 1305 w, 1287 m, 1260 w, 1170 m, 1160(sh), 1124 w, 1113 w, 1100 m, 1017 w, 945 vs, 920 w, 861 m, 840 s, 742 m, 720 m, 675 m, 670 m, 630 w, 615 w, 600 s, 572 s, 562 m, 475 w, 460 w
trans-$(PEt_3)_2Pt(C{\equiv}CH)_2$ (II)	3260 m, 1956 s, 1410 s, 1250 m, 1238 m, 1140 m, 1032 vs, 1010 s, 762 s, 712 s, 633 m, 580 s
(II) (TCNQ)	3280 m, 2200 m, 1975 m, 1595 vs, 1530 s, 1525(sh), 1510(sh), 1418 s, 1410 w, 1332 m, 1290 m, 1260 m, 1238 w, 1170 s, 1122 m, 1112 m, 1100 m, 1075 m, 1032 s, 992 w, 978 w, 920 w, 842 s, 768 s, 740 s, 730 m, 673 m, 626 m, 603 s, 589 s, 570 m, 552 w, 478 s

[a] In cm^{-1}, in Nujol.

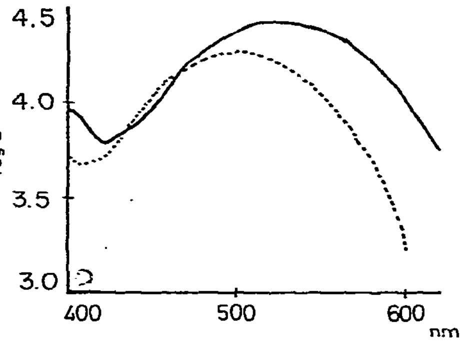

Fig. 2. Spectra of $[(Et_3P)_2Pt(C{\equiv}CCH_3)_2]$ [TCNQ] in CH_2Cl_2 (solid line) and in cyclohexane (dotted line).

stretching vibration (ring) of TCNQ component, which is infrared inactive (A_g) in TCNQ[12] and show a strong absorption at 1600 cm^{-1} in the adducts. This observation was interpreted in terms of a lowering of symmetry from D_{2h} (TCNQ) to C_{2v}. A similar situation is shown in the case of benzene/iodine solutions where an increase in the intensity of the A_{1g} fundamental at 992 cm^{-1} and of the E_{1g} fundamental at 850 cm^{-1} occurs[13].

These adducts showed one broad and intense absorption which lay in the region 500–530 nm in dichloromethane. The spectrum of $[(Et_3P)_2Pt(C{\equiv}CCH_3)_2]$-[TCNQ] in cyclohexane showed a remarkable blue shift ($\Delta\lambda$ 24 nm), compared with that in dichloromethane (Fig. 2), which is one of the features of CT complexes. Although the definition of the term, "charge-transfer (CT) complex", is somewhat ambiguous, these adducts may be called "CT complexes"*.

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* We adopted Foster's definition in this work[6].

No other π-acceptors, *e.g.*, TCNE, chloranil, bromanil or pyromellitic dianhydride, showed such interaction with the alkynyl complex under the same conditions.

Determination of the formation constants

Since the formation constant (K_c) is sometimes used as a convenient criterion for the estimation of the strength of the CT interaction, we determined spectrophotometrically the K_c value of the following system (using the Foster–Hammick–Wardley equation)[7] in dichloromethane at 29–32°, unless otherwise stated (Table 2).

$$trans\text{-}[(R'_3P)_2Pt(C{\equiv}CR)_2] + TCNQ \underset{K_c}{\rightleftharpoons} [(R'_3P)_2Pt(C{\equiv}CR)_2]\,[TCNQ]$$

The CT interaction of the nickel alkynyl complex with TCNQ was too weak to enable determination of the formation constant and for the same reason the formation constant was determined for only one palladium complex system (Table 2).

TABLE 2

FORMATION CONSTANTS OF THE SYSTEM, $[L_2M(C{\equiv}CR)_2]/TCNQ$, IN CH_2Cl_2 AT 29–32°[a]

M	L	R	λ_{max} (nm)	log ε	log K_c
Pt	Me_3P	H	555	4.31	∞
		CH_3	506	4.47	4.77
		$CH_2{=}CH$	538	3.86	4.02
		Ph	504	4.45	2.12
	Et_3P	H	525	4.37	∞
		CH_3	524	4.45	∞
		$CH_2{=}CH$	556	4.15	∞
		$CH_3C{\equiv}C$	546	4.62	3.71
		Ph	518	4.70	2.81
	Pr_3P	Ph	520	4.75	2.75
	Bu_3P	Ph	522	4.59	3.21
Pd	Et_3P	CH_3	506	4.60	2.80

[a] λ_{max} of the system, $[(Et_3P)_2Ni(C{\equiv}CH_3)_2]/TCNQ$, was 570 nm, log ε and log K_c were not determined.

In platinum complexes, K_c values decreased as the following order of R's, which is parallel to the increasing order of their electron withdrawal resonance effect:

$$R{=}H > CH_3 > CH_2{=}CH > CH_3C{\equiv}C > Ph$$

This is a good criterion for discussion of the structure of the CT complex and the nature of metal–carbon bond.

The phosphine had also influence on the formation constant, though the influence of R is superior to that of the phosphine (Table 2). Plots of log $K_c(R')/K_c(CH_3)$ against the sum of the σ^*-value of each $R'(3\sigma^*)$ showed a considerably good linear correlation (Fig. 3), where $K_c(R')$ is the formation constant of the system, *trans*-$[(R'_3P)_2Pt(C{\equiv}CPh)_2]/TCNQ$, $K_c(CH_3)$ is that of the trimethylphosphine complex, and σ^* is Taft's[8] polar substituent constant of R'.

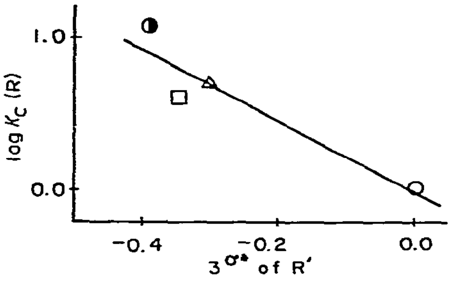

Fig. 3. Plots of log $K_c(R')/K_c(CH_3)$ against $3\sigma^*$-values, log $K_c(R)$; log $K_c(R')/K_c(CH_3)$: ○, $R'=CH_3$; △, $R'=C_2H_5$; □, $R'=n\text{-}C_3H_7$; ◐, $R'=n\text{-}C_4H_9$.

DISCUSSION

Structure of CT complexes

The result that no acceptors except TCNQ take part in an interaction with the alkynyl complex suggests the significant role of molecular shape and size of acceptors in addition to their electron affinities. The more remarkable influence of the alkynyl group than that of phosphines indicates that the CT interaction presumably takes place between TCNQ and the alkynyl group of the donor complex rather than the phosphine group.

The molecule of TCNQ belongs to the D_{2h} symmetry group which is the same group as that of the alkynyl complex, and its acceptor orbital is b_{3g}, when the coordinate system is taken as in Fig. 4[9]. Therefore, overlap between these two orbitals is possible and the structure shown in Fig. 4 is most probable for the CT complex. The distance between carbon atoms 7 and 8 (5.65 Å) is essentially equal to that between two alkynyl bonds (ca. 5 Å) in the alkynyl complex[10,11]. For this reason, the CT interaction between TCNQ and alkynyl groups of the donor complex may be possible.

The reason that the other π-acceptors, *e.g.* TCNE, chloranil, bromanil and pyromellitic dianhydride, which belong to the D_{2h} group and have b_{3g} acceptor orbitals[9], are incapable of the CT interaction, may be related to their smaller molecular size which makes the interaction impossible.

d_π–p_π interaction between the alkyl group and the central metal

Only a few instances have ever been reported of CT complexes in which alkynyl groups play the part of an electron donor. Since the alkynyl group is, in general, not

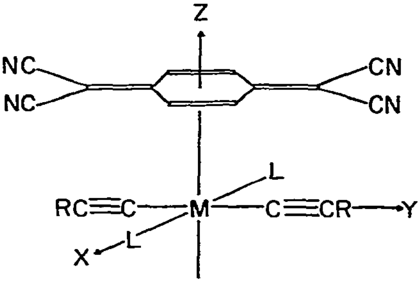

Fig. 4. Structure of the CT complex.

considered a good electron donor, our examples are regarded as a characteristic property of the alkynyl group which coordinates to a transition metal atom.

These properties are probably the consequence of back-donation of electron density from the central metal which increases the electron density on the alkynyl groups, enhancing their donor properties. That the more electron-withdrawing substituent of the alkynyl group gave smaller K_c-value is explained by the delocalization of electrons caused by the substituent.

The contribution of the phosphine group did not indicate the primary importance for the interaction, but the result that the phosphine group bearing the more electron-releasing alkyl group increased the formation constant is one of the most remarkable examples of *cis*-influence. When the donor property of the phosphine group increases, the electron density on the central metal may increase. Consequently, back-donation to the alkynyl group increases to give a larger value of the formation constant.

The central metal has the role of an electron donor to the alkynyl group through the back-donation. To discuss the influence of the central metal, we attempted to determine the formation constant of the system, *trans*-$[(Et_3P)_2M(C\equiv CCH_3)_2]$/TCNQ, (M=Ni, Pd or Pt), (Table 2). Unfortunately, the constant of the nickel complex was not determined because of instability of the system, which probably came from the small value of the formation constant. The constant decreased as follows;

$$Pt > Pd\ (> Ni)$$

This order shows that the degree of back-donation from the central metal decreases in this order.

It is concluded that back-donation, which reinforces the metal-alkynyl bond[1], increases the electron density on alkynyl groups. The electron withdrawal substituent of the alkynyl group decreases the electron density and reduces the donor property of the alkynyl groups[2]. The more basic phosphine increases the ability of the central metal for the back-donation.

EXPERIMENTAL

The isolation of CT complexes

$[(Et_3P)_2Pt(C\equiv CCH_3)_2]$ [TCNQ]. *trans*-$[(Et_3P)_2Pt(C\equiv CCH_3)_2]$ (0.3 g) was

TABLE 3

CT COMPLEXES, $[L_2Pt(C\equiv CR)_2][TCNQ]$[a]

L	R	Found (%)			Calcd. (%)			Yield
		C	H	N	C	H	N	(%)
Et_3P	CH_3	50.50	5.66	8.00	50.48	5.65	7.85	17
	H	49.01	4.81	7.82	49.05	5.29	8.17	11
Me_3P	CH_3	45.51	4.55	9.11	45.79	4.48	8.90	43
	H	43.75	4.25	8.93	43.93	4.02	9.32	10

[a] These complexes were stable below 100°.

dissolved in 20 ml of dichloromethane containing 0.2 g of TCNQ. Immediately, the color of the solution was turned to deep red. The solution was left overnight, and then the solvent was removed under reduced pressure. The residue was extracted by 100 ml of carbon tetrachloride. After the removal of the carbon tetrachloride, the residue was continuously extracted by n-hexane for 48 h. An analytically pure sample (0.07 g) was obtained as purple-black needles. λ_{max}524 nm (log ε 4.43) in dichloromethane, λ_{max} 500 nm (log ε 4.29) in cyclohexane. analytical data are listed in Table 3.

The other CT complexes. The other CT complexes listed in Table 3 are prepared by the same procedure described above.

Preparation of trans-$[(Pr_3P)_2Pt(C{\equiv}CPh)_2]$

cis-$[(Pr_3P)_2PtCl_2]$ (0.5 g) was reacted with PhC≡CNa in liquid ammonia by the same procedure reported in the previous paper[1].

Yellow crystals (0.390 g) of *trans*-$[(Pr_3P)_2Pt(C{\equiv}CPh)_2]$ were obtained from n-pentane at −25°; m.p. 85–86°. (Found: C, 57.00; H, 7.14. $C_{34}H_{52}P_2Pt$ calcd.: C, 56.89; H, 7.30%.)

trans-$[(Bu_3P)_2Pt(C{\equiv}CPh)_2]$

trans-$[(Bu_3P)_2Pt(C{\equiv}CPh)_2]$ was prepared from 0.4 g of *cis*-$[(Bu_3P)_2PtCl_2]$ by the same procedure. Yellow crystals (0.27 g), m.p. 88–92°. (Found: C, 59.82; H, 8.84. $C_{40}H_{64}P_2Pt$ calcd.: C, 59.90; H, 8.04%.)

Estimation of formation constants (K_c)

Method. Since both donor complexes and TCNQ showed no absorption in the region, 450–600 nm, K_c values were estimated by Foster–Hammick–Wardley equation[7];

$$A/[D]_0 = -K_c \cdot A + K_c \cdot [A]_0 \cdot \varepsilon$$

In the equation, $[A]_0$ and $[D]_0$ are initial concentration of TCNQ and donor complexes respectively, and A is absorbance of the CT spectrum. K_c value and ε_{max} were evaluated by least-square treatment.

Measurement. Visible spectra were recorded using a Hitachi EPS-3T Recording Spectrophotometer with a 10 mm cell at 29–32°. Range of $[D]_0$ was taken between 10^{-3}–10^{-4} mol/l and $[A]_0$ was taken as a constant of the order of 10^{-5} mol/l.

Interaction with the other π-acceptors

trans-$[(Et_3P)_2Pt(C{\equiv}CCH_3)_2]$ was reacted with TCNE, chloranil, bromanil and pyromellitic dianhydride in dichloromethane. However, no CT interaction was observed.

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