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The Preparation and Spectroscopic Properties of Fumaronitrile Complexes of Palladium(0) and Platinum(0)

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Fumaronitrile complexes, $M(FMN)(AsPh_3)_2$ ($M=Pd$, Pt and FMN=fumaronitrile), have been prepared. Various chelating agents replaced $AsPh_3$ in the complexes, giving $M(FMN)L$ (L is a chelating agent containing N, P, or As as donor atoms). The chemical shift of the methine protons of these complexes increased in the order:

$$\text{Pd–As} < \text{Pd–P} < \text{Pt–As} < \text{Pt–P}.$$

This is probably the increasing order of the π-back donation in these complexes. The UV spectra of the complexes are also described.

In recent years, olefin complexes of transition metals in the low oxidation state have been the subjects of many studies.[1] These investigations have established that stable complexes are formed with olefins containing electronegative substituents (activated olefin). Fumaronitrile is a typical activated olefin and is expected to give stable complexes of Pd(0) and Pt(0). However, only two complexes, $Pd(FMN)(PPh_3)_2$[2] and $Pt(FMN)(PPh_3)_2$,[3] have been reported so far. In this paper we will describe the preparation, spectroscopic properties, and some ligand-exchange reactions of fumaronitrile complexes of zero-valent Pd and Pt. The effect of a donor atom, N, P, or As, on the metal-olefin bonding will also be discussed.

Results and Disucssion

Preparation and Ligand-exchange Reactions. The complex $Pt(FMN)(AsPh_3)_2$ was prepared by the reac-

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[1] B. Nelson and H. B. Jonassen, *Coord. Chem. Rev.*, **6**, 27 (1971) and refs. therein.

[2] G. L. McClure and W. H. Baddley, *J. Organometal. Chem.*, **27**, 155 (1971).

[3] G. La Monica, G. Navazio, P. Sandorini, and S. Cenini, *ibid.*, **31**, 89 (1971).

tion of $Pt(AsPh_3)_4$ with FMN in benzene. A corresponding palladium complex, $Pd(FMN)(AsPh_3)_2$, was synthesized by the reduction of $PdCl_2(AsPh_3)_2$ with hydrazine monohydrate in the presence of FMN. The similar reduction of $PdCl_2(PPh_3)_2$ also gave the complex $Pd(FMN)(PPh_3)_2$ reported by MaClure *et al.*[2]

The reactivities of these two arsine complexes towards bidentate ligands are very similar except for the reaction with the ligands (N–N) containing two nitrogen donor atoms. As is shown in the Scheme, all of the ligands (N–N) studied here replaced $AsPh_3$ in $Pd(FMN)(AsPh_3)_2$, thus forming Pd(FMN)(N–N), but only ethylenediamine (en) and cyclohexanediamine (cyhn) could react with $Pt(FMN)(AsPh_3)_2$. The other three ligands failed to replace $AsPh_3$ in the complex. Two factors are conceivable to explain the difference in their reactivities: the p*K* values and the steric factors of the bidentate ligands(N–N). Steric factors do not seem to be serious in the present case, because cyhn reacts with both palladium and platinum complexes; also two ligands, bipy and o-phen, replace $AsPh_3$ in $Pt(CF_2{=}CF_2)(AsPh_3)_2$, thus giving $Pt(CF_2{=}CF_2)L$ (L is bipy, o-phen), as has been reported by Kemmitt and Moore.[4] As is clear from Table 1, the p*K* values of en and cyhn are larger than those of the other three ligands. Thus, it may be reasonable to assume that the p*K* values of the ligands (N–N) are important in the ligand-exchange reactions studied here. The replacement of $AsPh_3$ in the perfluoroolefin complex may be due to the strong *trans*-effect of perfluoroolefin, which weakens the Pt–As bond and makes the substitution of $AsPh_3$ by the ligand with a small p*K* value possible.

Table 1. The p*K* values of bidentate ligands (N–N)[a]

	en	cyhn	o-phen	2,9-phen	bipy
pK_1	9.87	9.99(*trans*) 9.89(*cis*)	4.92	6.15	4.49

a) L. G. Sillen and A. E. Martell ed., "Stability Constants," Special Publication No. 17, The Chemical Society, London (1964).

$Pd(FMN)(EPh_3)_2$ (E=P, As) reacts with $SbPh_3$ to give white precipitates. The porduct of E=P was identified as $Pd(SbPh_3)_2(PPh_3)_2$ as reported by Takahashi *et al.*[5] on the basis of its analytical data and decomposition point. The analytical data of the compound of E=As corresponds to $Pd(SbPh_3)_3(AsPh_3)$, and the presence of $SbPh_3$ and $AsPh_3$ in the complex was confirmed by its far-infrared spectrum, which gave absorptions at 455(s), 270(s), and 260(s) cm^{-1} assignable to $SbPh_3$ and 472(m), 325(m), and 315(m) cm^{-1} assignable to $AsPh_3$.

PMR Spectra. The PMR spectra of fumaronitrile complexes were measured in $CDCl_3$, with TMS as the internal standard; the data are summarized in Table 2. Unfortunately, the spectra of the complexes formed with a bidentate ligand (N–N) were not obtained because of their low solubility in common organic solvents. As is clear from Table 2, the olefinic protons show the large high-field shift which is characteristic of the olefin coordinated to a transition metal in the low-oxidation state. The chemical shifts increased in the order:

Pd-As < Pd-P < Pt-As < Pt-P

for both monodenate ligands (PPh_3 and $AsPh_3$) and bidentate ligands (P–P and As–As), although the shifts of the complexes with monodentate ligands are always larger than those of the corresponding chelates. Cenini *et al.*[6] related this shift to the amount of π-back donation from the metal to the ligand. Therefore, the order seems to indicate the increasing ability of π-back donation of the ME_2 system (M=Pd, Pt and E=P, As).

Table 2. The PMR spectral data of the CH of fumaronitrile (FMN) and its complexes in $CDCl_3$ (23°C)

Complex	τ(CH)(ppm)	*J*(P-H)(Hz)	*J*(Pt-H)(Hz)
FMN	3.70(s)		
$Pd(FMN)(PPh_3)_2$	7.01(d)	4.5	
Pd(FMN)(P-P)	6.71(d)	6.8	
$Pd(FMN)(AsPh_3)_2$	6.65(s)		
$Pd(FMN)(As\text{-}As)_2$	6.10(s)		
$Pt(FMN)(PPh_3)_3$	7.54(dt)	6.4	59
Pt(FMN)(P-P)	7.23(dt)	7.8	62
$Pt(FMN)(AsPh_3)_2$	7.19(t)		68
Pt(FMN)(As-As)	6.93(t)		70

s=singlet, d=doublet, dt=doublet of triplet, t=triplet.

In the complexes containing fumaronitrile and two phosphorus atoms, the PMR spectra showed that only

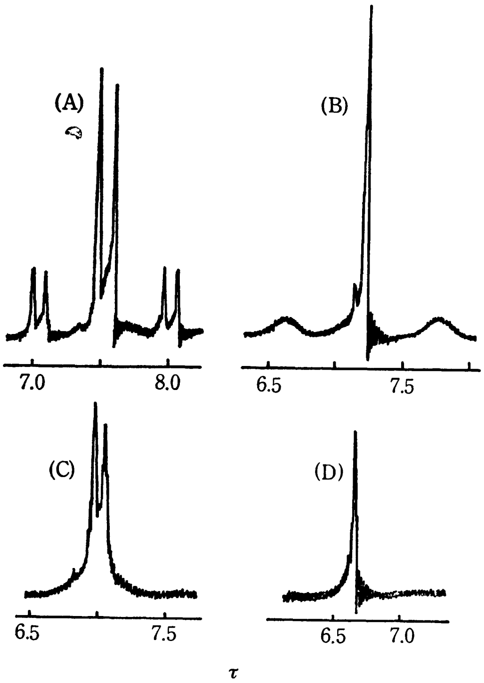

Fig. 1. The PMR spectra of the CH of the complexes M(FMN)L.
(A) $Pt(FMN)(PPh_3)_2$, (B) $Pt(FMN)(AsPh_3)_2$,
(C) $Pd(FMN)(PPh_3)_2$, (D) $Pd(FMN)(AsPh_3)_2$.

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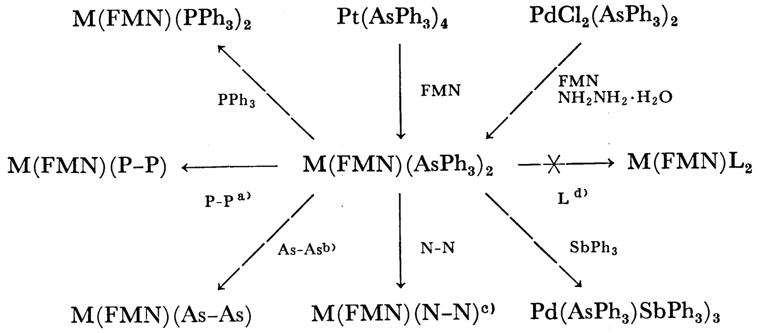

a) P-P $=Ph_2PCH_2CH_2PPh_2$

b) As-As $=Ph_2AsCH_2CH_2AsPh_2$

c) M$=$Pd N-N$=\alpha\alpha'$-bipyridyl (bipy), 1,10-phenanthroline (o-phen), 2,9-dimethyl-1,10-phenanthroline (2,9-phen), ethylenediamine (en), cyclohexanediamine (cyhn)
M$=$Pt N-N$=$en, cyhn

d) L$=$pyridine, SPh_2, $S(CH_3)_2$

Scheme.

one phosphorus atom is coupled with the methine protons, as is shown in Fig. 1, although the coupling of two phosphorus atoms to ^{19}F or ^1H has been reported in the complexes $Pt(CF_2{=}CF_2)(PPh_3)_2$[7], $Pt(CH_2{=}CH_2)(PPh_3)_2$[8], and $Pt(RC{\equiv}CH)(PPh_3)_2$.[1] Similar results are also obtained for $Pt(FMN)(PPh_3)_2$[3] and some other olefin complexes.[6] The phosphorus atom which couples with a methine proton is probably *trans* to the carbon atom of the methine group, as has been suggested by Cenini *et al.*[6] It is likely that the appearance of a doublet in our complexes is due to the small coupling constant of a *cis*-phosphorus atom with the olefinic proton, since Greaves *et al.*[9] observed that the 60 MHz spectrum of the methyl protons of $Pt(MeC{\equiv}CPh)(PPh_3)_2$ gave only a doublet, while the 100 MHz spectrum split the methyl doublet into symmetrical doublets.

The satellites of the complex $Pt(FMN)(AsPh_3)_2$ are very broad, but its central peak is sharp, as is shown in Fig. 1. A similar phenomenon is also observed in the PMR spectrum of $Pt(CH_2{=}CClCN)(AsPh_3)_2$.[10] Recently Mann *et al.*[11] reported the complex behaviour of the satellites of Pt_2Cl_2(2-methylallyl)$_2$ with the temperature; they suggested the possibility of a partial contribution of a relaxation phenomenon of the platinum-195 nucleus. A similar consideration might explain the phenomenon observed here.

In the platinum complexes, J(Pt–H) was *ca.* 60 Hz for the phosphine complexes and ca. 70 Hz for the arsine complexes (Table 2). A decrease in J(Pt–H) with the change from As to P has also been reported for *trans*-$[Pt(Me)L(PMe_2Ph)_2]$ (L$=PPh_3$, $AsPh_3$).[12] This order is expected on the basis of the fact that J(Pt–C–H) seems to have a close relation with the s-character of Pt,[13] and the Pt(6s) character in the Pt–olefin bond will be decreased by the coordination of a better σ-donor atom, as has been discussed by Church and Mays,[14] although Nelson and Jonassen[1] suggested that the contributions from terms other than the Fermi contact term are important.

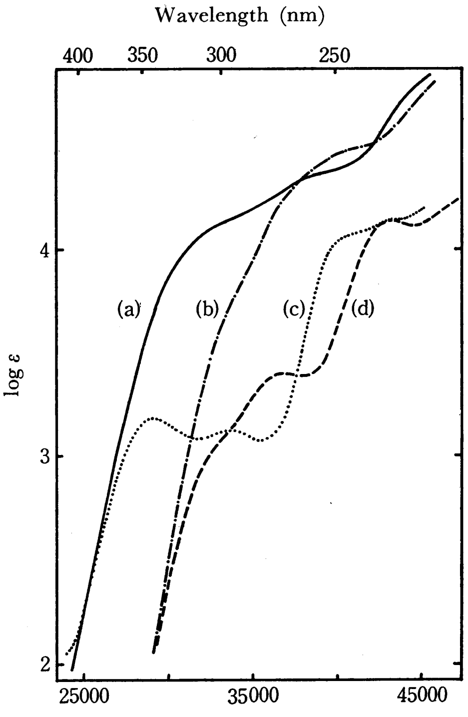

Fig. 2. The UV spectra of the complexes M(FMN)L.
(a) $Pd(FMN)(PPh_3)_2$, (b) $Pt(FMN)(AsPh_3)_2$,
(c) Pd(FMN)(cyhn), (d) Pt(FMN)(cyhn).

UV Spectra. The UV spectra of M(FMN)(cyhn) (M$=$Pd, Pt) are shown in Fig. 2. Similar spectra are also obtained for the complexes M(FMN)(en). The bands in the 25000—38000 cm^{-1} region arise from the complex formation, because FMN do not show strong

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TABLE 3. ANALYTICAL DATA

M(FMN)L		Mp(dp) (°C)	Found (%)			Required (%)		
M	L		C	H	N	C	H	N
Pd	$(PPh_3)_2$	130—140	67.3	4.6	4.0	67.8	4.6	4.0
Pd	$(AsPh_3)_2$	155—165	60.1	4.1	3.5	60.3	4.1	3.5
Pd	(P-P)	170—185	61.6	4.7	4.6	61.8	4.5	4.8
Pd	(As-As)	190—205	53.7	3.8	4.0	53.7	3.9	4.2
Pd	bipy	155—165	47.9	2.7	15.7	49.4	3.0	16.5
Pd	o-phen	225—235	52.4	2.6	15.1	52.7	2.8	15.4
Pd	2,9-phen	235—245	54.8	3.7	14.2	55.1	3.6	14.3
Pd	en	120—130	29.3	4.1	22.6	29.5	4.1	22.9
Pd	cyhn	150—158	40.7	5.2	18.0	40.2	5.4	18.8
Pt	$(PPh_3)_2$	200—210	59.5	3.9	2.9	60.2	4.0	3.5
Pt	$(AsPh_3)_2$	179—185	53.7	3.6	2.6	54.3	3.6	3.2
Pt	(P-P)	250—255	53.5	3.8	4.1	53.7	3.9	4.2
Pt	(As-As)	200—210	47.8	3.7	4.3	47.4	3.5	3.7
Pt	en	230—242	22.6	3.2	17.5	21.6	3.0	16.8
Pt	cyhn	226—241	31.8	4.2	14.5	31.0	4.2	14.5

absorptions below 42000 cm^{-1}. Since the formal charge of Pd and Pt in the complexes is zero, these bands are probably due to charge transfer from the metal d-orbitals to the FMN π^*-orbital. In their spectroscopic study of *trans*-[(ol)$PtCl_2L$] (ol=olefin), Denning *et al.*[15] also reported that the transitions from metal d-orbitals to olefin π^* are observed in the 31000—45000 cm^{-1} range. The molar extinction coefficients of M(FMN)(cyhn) also support the above assignment, because they are $\sim 10^3$ and comparable to those reported for *trans*-[(ol)$PtCl_2L$].[15,16] For the other complexes studied here we could not find any bands assignable to charge transfer from metal d-orbitals to FMN π^* or vacant d-orbitals of a phosphorus atom[17] because of the strong absorption of the ligand other than FMN (Fig. 2).

Experimental

The PMR spectra were recorded with a JEOL-C-60H spectrometer. The UV spectra were recorded with a HITACHI 323 spectrophotometer, using acetonitrile as the solvent. All the reagents were commercially available and were used without further purification. The $Pd(PPh_3)_4$,[18] $Pt(PPh_3)_4$,[19] and $Pt(AsPh_3)_4$[20] were prepared by the methods reported in the literature.

Fumaronitrilebis(triphenylarsine)palladium(O). To an ethanol solution of $AsPh_3$ (3.2 g) we added an aqueous solution of K_2PdCl_4 (1.6 g) at 50—60°C. Fumaronitrile (0.5 g) and then 10 m*l* of an ethanol solution of $NH_2NH_2 \cdot H_2O$ (10%) were added slowly to the mixture at 50—60°C. About 20 min later, the pale yellow products were filtered off and washed with water, ethanol, and diethyl ether.

Fumaronitrilebis(triphenylarsine)platinum(O). $Pt(AsPh_3)_4$ (2.1 g) was stirred into a benzene solution (100 ml) of FMN (0.2 g). After the complete dissolution of the Pt-$(AsPh_3)_4$, the solution was filtered and concentrated to about 10 ml *in vacuo*. The white precipitates formed by adding methanol were filtered off and washed with diethyl ether.

Fumaronitrile-1,2-bis(diphenylarsino)ethanepalladium(O). A solution of 1,2-bis(diphenylarsino)ethane (0.6 g) in benzene (20 ml) was added to a solution of Pd(FMN)$(AsPh_3)_2$ (0.8 g) in benzene (50 ml) at room temperature. The solution turned pale yellow; by adding ethanol to the concentrated solution, pale yellow materials were precipitated. Recrystallization from chloroform-diethyl ether gave pale yellow crystallines.

In a similar manner, Pd(FMN)(P–P), Pt(FMN)(As–As), and Pt(FMN)(P–P) were prepared.

Fumaronitrile(α,α′-bipyridyl)palladium(O). To a solution of Pd(FMN)$(AsPh_3)_2$ (0.8 g) in benzene (60 ml), we added a solution of α,α′-bipyridyl (0.3 g) in benzene (40 ml) at room temperature. The solution turned yellow-green and then gave pale yellow precipitates. It was filtered and washed with benzene. By analogous methods, Pd(FMN)L was prepared (L is o-phen and 2,9-phen).

Fumaronitrile(ethylendiamine)palladium(O). To a solution of Pd(FMN)$(AsPh_3)_2$ (0.8 g) in benzene (60 ml), we added a solution of ethylenediamine (0.1 ml) in benzene (40 ml). White materials started to precipitate in a few minutes. After the mixture had been stirred for 1 hr, the precipitates were filtered off and washed with benzene. Pt(FMN)(en), Pd(FMN)(cyhn) and Pt(FMN)(cyhn) were prepared in a similar way.

Triphenylarsinetris(triphenylantimony)palladium(O). A solution of triphenylantimony (1.4 g) in benzene (40 ml) was added to a solution of Pd(FMN)$(AsPh_3)_2$ (0.8 g) in benzene (60 ml) at room temperature. The solution turned yellow and then gave white precipitates. After 1 hrs' stirring, the precipitates were filtered off and washed with benzene and ether. Found: C, 58.0; H, 3.8.% Calcd for $C_{72}H_{60}$-$AsPdSb_3$: C, 58.8, H, 4.1%.

The analytical data for the fumaronitrile complexes are summarized in Table 3.

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