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Reactions of rhodium(II) and iridium(III) complexes bearing a P,O-coordination with tetracyanoethylene in the presence of KPF₆

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Abstract

Reactions of Cp*M(MDMPP-*P*,*O*)Cl (1a: M = Rh, 1b: M = Ir; MDMPP-*P*,*O* = *P*Ph₂(2-*O*-6-MeOC₆H₃)) with tetracyanoethylene (tcne) in the presence of KPF₆ gave Cp*MCl[*P*Ph₂{2-*O*-3-(C(CN)₂CH(CN)₂)-6-MeOC₆H₂}] (2), [{Cp*MPPh₂{2-*O*-3-(C(CN)= C(CN)₂)-6-MeOC₆H₂}]₂(CN)](PF₆) (3), [{Cp*Ir*P*Ph₂{2-*O*-3-(C(CN)=C(CN)₂)-6-MeOC₆H₂}](CN){Cp*Ir(MDMPP-*P*,*O*}](PF₆) (4b) and [{Cp*Ir(MDMPP-*P*,*O*)}₂(CN)](PF₆) (5b), depending on the reaction conditions. Reaction of **2** with KPF₆ or AgOTf in the absence and presence of xylyl isocyanide (XylNC) gave **3** or [Cp*MCl{*P*Ph₂(2-*O*-3-(C(CN)₂-CH(CN)₂)-6-MeOC₆H₂)}(Xy-INC)](OTf) (6). The structure of **3a** (M = Rh) was confirmed by X-ray crystal analysis. © 2004 Elsevier B.V. All rights reserved.

Keywords: Tetracyanoethylene; Pentamethylcyclopentadienyl; Rhodium(III); Iridium(III); C-CN bond cleavage

1. Introduction

Tetracyanoethylene (tcne) affords a variety of charge transfer and organometallic complexes as a result of its strong electrophilicity [1]. Among them, the reactions with metal-acetylide complexes are particularly interesting: (i) insertion into M–C bonds [2]; (ii) [2 + 2] addition to acetylide groups to give cyclobutene-metal complexes [3]; (iii) addition of dicyanomethylene fragments, derived from cleavage of the double bond of tcne, to an acetylide group [4]. In all cases except for (i), tcne is reactive to strongly activated unsaturated groups on the ligands.

Pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes with the P,O chelating coordination derived from demethylation of tertiary aromatic phosphine ligands bearing the methoxy groups at the *ortho*-

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positions have activated small molecules such as alkynes and alkyl amines. For example, when complexes were treated with 1-alkyne or disubstituted alkyne in the presence of KPF₆, novel single or double insertion of alkyne into the Rh (or Ir)–O bond gave six- or sevenmembered metallacycles [5]. Reactions with tertiary or secondary amines in the presence of KPF₆ led to cleavage of the C–N bond, generating the corresponding primary alkyl amine complexes [6].

We have reported that the aforementioned complexes were treated with electron-deficient olefins such as tone or 7,7,8,8-tetracyano-*p*-quinodimethane (tonq), generating the complexes that the olefin inserted into weakly activated C–H bonds on the phenyl ring of the phosphine ligand (Scheme 1) [7]. When they were treated with an anion radical of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-tonq), spontaneous substitution of the H atom adjacent to the metal–O bond with the F₄-tonq anion radical and subsequent aromatization of a quinodimethane ring occurred, followed by the final formation of binuclear complexes by its dimerization (Scheme 1) [8]. When these reactions were carried out in the presence of KPF₆ or AgOTf, we found an insertion

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Scheme 1. Reactions of $[Cp*MCl{PRPh(2-O-6-MeOC_6H_3)}]$ (M = Rh, Ir; R = Ph, 2,6-(MeO)₂C₆H₃) with tone or Li[F₄-tonq].

of tcne into a C–H bond and a subsequent α , β elimination from the C(CN)₂–CH(CN)₂ group to give complexes bearing the 1-cyano-2,2'-dicyanoethylene moiety. In these reactions, we could isolate cyanometal complexes by capture of an eliminated cyano group. Insertion of tcne and subsequent dehydrocyanation have been noted in the furanyl and thienyl platinum complexes, however a fate of cyano group has not been described [9]. Recently, Bruce et al. [10] have reported an unusual formation of cyanoruthenium complex, Cp*Ru(PPh₃)[C(CH=CHPh)=CPhC{CPh=C(CN)₂}-C(CN)₂}-C(CN)(\eta^2-CN)] (Cp*=C₅Me₅), from tcne and an allylic complex, Cp*Ru(PPh₃)[η^3 -CHPhCHC=CPh-(CCPh)].

2. Results and discussion

2.1. Reactions

When **1a** was treated with an equivalence of tcne in the presence of KPF₆, **2a** and **3a** were isolated in 59.3% and 4.1% yields, respectively (Scheme 2). Orange brown complex (**2a**) has the structure that tcne inserted into the C–H bond adjacent to the Rh–O bond by comparison with the spectroscopic data of the known complex [7]. The IR spectrum of **3a** showed $v(C\equiv N)$ bands at 2224 and 2152 cm⁻¹ together with a PF₆ anion at 841 cm⁻¹. The molecular peak of m/z 1318 corresponded to the value of [{Cp*Rh(MDMPP-P,O)(tcne)}₂]-[HCN+H]



Scheme 2. Reactions of 1 with tone in the presence of KPF₆; the PF₆ anion was omitted for clarity.

 $(MDMPP-P, O = PPh_2(2-O-6-MeOC_6H_3))$. In the ¹H NMR spectrum, the Cp* protons appeared as two sets $(3a_1: \delta 1.03 \text{ and } 1.08, \text{ and } 3a_2: \delta 1.21 \text{ and } 1.28)$ with two kinds of resonances consisting of a 1:1 intensity ratio, suggesting the presence of isomers. The isomer ratio of $3a_1$ and $3a_2$ is 1:5. The detailed structure was confirmed by X-ray analysis of $3a_2$ (Fig. 1). The molecule has a structure that two [Cp*RhPPh₂{2-O-3-(C(CN)=C- $(CN)_2$)-6- $(MeO)C_6H_2$] moieties were connected by a $C \equiv N$ ligand, in which each of C and N atoms has an occupancy of 0.5. Since the molecule has a crystallographically imposed inversion center in the middle of the C(N)-N(C) bond, the complex has an *anti*-form to the C-N triple bond. Complex $(3a_2)$ has two chiral centers at the Rh atoms and the priority order of the ligands at the Rh center is $Cp^* > P > O > C(N)$. Fig. 1 shows the anti-structure with an R_{Rh}S_{Rh*}/S_{Rh}R_{Rh*} pair. Thus, complex $(3a_1)$ is assumed to be an *anti*-structure with an

 $R_{Rh}R_{Rh*}/S_{Rh}S_{Rh*}$ pair. The PM3 model calculation showed to prefer the *anti*-structure (**3a**₁) with an $R_{Rh}R_{Rh*}/S_{Rh}S_{Rh*}$ to the *anti*-structure (**3a**₂) with an $R_{Rh}S_{Rh*}/S_{Rh}R_{Rh*}$ pair. Less stable complex (**3a**₂), however, was preferably formed, probably being a result of steric requirements.

When a similar reaction was performed for the iridium analog **1b**, complexes (**2b**, **3b** and **4b**) were isolated in 62.2%, 3.8% and 5.5% yields, respectively. The IR spectrum of **4b** showed the presence of a C–N triple bond and a PF₆ anion. X-ray analysis of **4b** was carried out. Only a cationic molecular structure was found and an anionic part (PF₆ anion) could not be clearly detected, because of poor single crystals. The cationic part was solved as a structure in which [Cp*IrPPh₂ $\{2-O-3-(C(CN)=C(CN)_2)-6-(MeO)C_6H_2\}$] and [Cp*Ir-(MDMPP-*P*,*O*)] moieties were connected by a C=N ligand. Since the molecular peak of *m/z* 1396



Fig. 1. Molecular structure of 3a: (a) one molecular structure and (b) two independent molecular structures. The PF₆ anions were omitted for clarity.

corresponded to the value of the cationic molecule, the cationic molecular structure was assumed to be true. Thus, **4b** is an *anti*-form with an $R_{Ir}S_{Ir*}/S_{Ir}R_{Ir*}$ pair.

In the reaction of **1b** with tone in a 2:1 molar ratio, **3b**, **4b** and **5b** were isolated. The IR spectrum of **5b** showed the presence of the C–N triple bond at 2158 cm⁻¹ and the PF₆ anion at 841 cm⁻¹. In the FAB mass spectrometry, the value of m/z 1296 accorded with the value of [{Cp*Ir(MDMPP-*P*,*O*)}₂(CN)] (1297.5). The ¹H NMR spectrum showed the presence of two diastereomers (**5b**₁ and **5b**₂) with a 1:4 molar ratio; the Cp* protons appeared as singlets at δ 1.02 and 1.11 for **5b**₁ and at δ 0.91 and 0.98 for **5b**₂, respectively. Based on the structures of **3a** and **4b**, **5b**₂ was assumed to be the *anti*- structure with an $R_{Ir}S_{Ir*}/S_{Ir}R_{Ir*}$ pair and the diastereomer **5b**₁ was the *anti*-form with an $R_{Ir}R_{Ir*}/S_{Ir}S_{Ir*}$ pair.

Complex (2) reacted readily with KPF₆ to eliminate HCN, generating 3 in relatively high yields (Scheme 3). Elimination of HCN from the HC(CN)₂–C(CN)₂–L (L= organic group bearing a metal) moiety on treatment with alumina has been noted in platinum complexes [9]. A similar reaction was carried out in the presence of AgOTf instead of KPF₆, generating an OTf anion complex. Reaction of 2 with xylyl isocyanide (XylNC) in the presence of AgOTf afforded 6 formulated as [Cp*MPPh₂{2-O-3-(C(CN)CH(CN)₂)-6-MeO-C₆H₂}(XylNC)](OTf) (6a: M=Rh; 6b: M=Ir) (Scheme 3).



Scheme 3. Reactions of 2 with KPF₆ or AgOTf in the absence and presence of xylyl isocyanide; the PF₆ or OTf anion was omitted for clarity.



Scheme 4. A possible route for the reactions of 1 with tone in the presence of KPF₆.

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Table 1 Selected bond lengths (Å) and angles (°) for [{Cp*RhPPh₂{2-O-3-(C(CN)=C(CN)₂)-6-MeO-C₆H₂}₂(CN)](PF₆) $3a_2$

Bond lengths					
Rh(1) - P(1)	2.309(3)	Rh(1)–O(1)	2.106(7)	Rh(1)–C(1) (N7)	2.057(9)
C(1)–C(1*) (N7)	1.10(2)	C(9)–C(10)	1.37(1)	N(1)–C(11)	1.12(2)
N(2)–C(12)	1.13(2)	N(3)-C(13)	1.13(2)	Rh(2)–P(2)	2.317(3)
Rh(2)–O(3)	2.103(8)	Rh(2)–N(8)	2.059(9)	N8–N8*(C)	1.13(2)
C(44)–C(45)	1.33(2)	N(4)-C(46)	1.15(2)	N(5)-C(47)	1.13(2)
N(6)-C(48)	1.07(2)				
Rond angles					
$\mathbf{D}(1) \mathbf{D}\mathbf{b}(1) \mathbf{O}(1)$	02 0(2)	$\mathbf{P}(1)$ $\mathbf{P}\mathbf{h}(1)$ $\mathbf{N}(\mathbf{C})$	96 6(2)	O(1) P h(1) N (C)	84 0(2)
P(1) = KII(1) = O(1)	02.0(2)	P(1) = Ril(1) = N(C)	80.0(2)	O(1) = KII(1) = N(C)	64.9(5) 124.2(0)
Rh(1) - P(1) - C(3)	96.7(1)	P(1)-C(3)-C(2)	113.6(7)	O(1) - C(2) - C(3)	124.2(9)
Rh(1)-C(N)-N(C)	174(1)	C(7)-C(9)-C(10)	124(1)	C(7)-C(9)-C(11)	118.9(9)
C(10)–C(9)–C(11)	116(1)	C(9)–C(10)–C(12)	119(1)	C(9)–C(10)–C(13)	124(1)
C(12)-C(10)-C(13)	116(1)	N(1)-C(11)-C(9)	170(1)	N(2)-C(12)-C(10)	178(1)
N(3)-C(13)-C(10)	178(1)	P(2)–Rh(2)–O(3)	82.1(2)	P(2)-Rh(2)-C(N)	92.4(3)
O(3)-Rh(2)-N(C)	84.3(4)	Rh(2)–P(2)–C(38)	99.1(4)	P(2)-C(38)-C(37)	113.6(8)
O(3)-C(37)-C(38)	121(1)	Rh(2)-C(N)-N(C)	176(1)	C(42)-C(44)-C(45)	127(1)
C(42)-C(44)-C(46)	113(1)	C(45)-C(44)-C(46)	119(1)	C(44)–C(45)–C(47)	123(1)
C(44)-C(45)-C(48)	120(1)	C(47)-C(45)-C(48)	115(1)	N(4)-C(46)-C(44)	173(1)
N(5)-C(47)-C(45)	175(1)	N(6)-C(48)-C(45)	174(1)		

A possible route was assumed from the reaction products (Scheme 4). The UV–Vis spectrum of a mixture of 1 with KPF₆ is similar to that of 1, suggesting no extraction of a Cl anion by KPF₆. Thus, 2 was initially generated by insertion of tcne into the C–H bond, accompanied by the formation of an intermediate A. Since in the PM3 model calculation the electron density at the 5-position of the aromatic group in the metallacycle is greater than that at the 3-position, ² the substitution reaction is expected to occur preferably at the 5-position. It is assumed to be responsible for steric requirement of the methoxy group that the reaction occurred at the 3-position.

The reaction of A with 1 and KPF₆ generated 4, and the reaction with 2 and KPF₆ led to the formation of 3. The CN anion eliminated in this process reacted with 1 to afford an intermediate **B**, followed by the formation of 5 from the reaction of **B** with 1 and KPF₆. In these reactions, intermediates **A** and **B** could not be isolated.

2.2. Crystal structure of 3a

A perspective drawing with atomic numbering schemes is given in Fig. 1 and selected bond lengths and angles are listed in Table 1. Complex (**3a**) consists of two independent molecules and each of them has two chiral centers (two Rh atoms). Fig. 1 shows that the molecule is an $R_{Rh}S_{Rh*}/S_{Rh}R_{Rh*}$ pair. The adoption of the *anti*form is responsible for steric demand of the bulky P,O-chelating ligand. The presence of the C(CN)=C(CN)₂ groups was confirmed by the C10 (or C*10) (molecule 1) and C45 (or C*45) (molecule 2) atoms with the sp² carbon atoms; C12–C10–C13 (116°), C9–C10–C12

(119°), C9–C10–C13 (124°) for the molecule 1, C44– C45-C47 (123°), C44-C45-C48 (120°) and C47-C45-C48 (115°) for the molecule 2. The C9-C10 and C44–C45 bond lengths are 1.37 and 1.33 Å, respectively, being in usual double bonding values. The C(CN)= $C(CN)_2$ moieties deviate somewhat from their planes as shown in the torsion angles, for example, C11-C9-C10- $C12 = 174(1)^{\circ}, C11 - C9 - C10 - C13 = -10(1)^{\circ}, C46 - C44 C45-C47 = 1(2)^{\circ}$ and $C46-C44-C45-C48 = -167(1)^{\circ}$. In the furanyl complex the olefinic part $(C(CN)=C(CN)_2)$ is nearly coplanar with the furan ring [9], whereas in **3a**, the dihedral angles between the aromatic ring and the $C(CN)=C(CN)_2$ plane are ca. 40°, relieving steric repulsion between two moieties. The average Rh-P bond length of 2.313 A and Rh–O bond length of 2.105 A are not significantly different from those found in the related complexes bearing P,O-coordination [11]. The average Rh–C(N) bond length of 2.058(9) A is in usual M–C(N) bond lengths, compared with that (2.077(8) A) found in $[Cp*Rh{P(2,6-(MeO)_2C_6H_3)}{2-O-3-(1,4-{C(CN)_2}_2 C_6F_4$)-6-MeOC₆H₂}]₂ [8]. The average P-Rh-O bite angle of 82.5° is similar to those found in rhodium, iridium and ruthenium bearing this type of ligands [5,7,11-13]. The average Rh–C(N)–N(C) angle of 175° is linear and the average C(N)-N(C) length is in the value of the typical triple bond lengths.

3. Experimental

3.1. General considerations

All reactions were carried out under a nitrogen atmosphere. Dichloromethane was distilled from CaH_2 and diethyl ether was distilled from $LiAlH_4$. Complexes Cp*MCl(MDMPP-*P*,*O*) (M = Rh [11], Ir [12] and

 $^{^{2}}$ The charges on the carbon atoms of the 3- and 5-positions are -0.230 and -0.285, respectively, in the PM3 calculation of **1a**.

 $[Cp*MCl{PPh_2(2-O-3-(C(CN)CH(CN)_2)-6-(MeO)-C_6H_2)}]$ (M = Rh, Ir) [7] were prepared according to the literature. The infrared and electronic absorption spectra were measured on FT/IR-5300 and U-best 30 instruments, respectively. The ¹H NMR spectra were measured on a JEOL EPC400 instrument at 400 MHz.

3.2. Reaction of Cp*RhCl(MDMPP-P,O) (1a) with TCNE in the presence of KPF_6

A mixture of **1a** (113.4 mg, 0.195 mmol) and KPF₆ (107.9 mg, 0.585 mmol) was stirred in CH₂Cl₂ (10 ml) and acetone (10 ml) for 0.5 h at room temperature. TCNE (25.7 mg, 0.195 mmol) was added to the reaction mixture and stirred for 48 h. The solvent was removed under reduced pressure and the residue was extracted with CH₂Cl₂. The CH₂Cl₂ solution was dried and the residue was washed with diethyl ether. Recrystallization of the residue from CH₂Cl₂ and diethyl ether gave the reddish violet crystals of **3a** (5.5 mg, 4.1%) and orangebrown crystals of the known complex (**2a**) (77.7 mg, 59.3%). The population between **3a**₁ and **3b**₁ is 1:5. Spectroscopic data are shown in Section 3.3.

3.3. Reaction of 2a with KPF_6

A mixture of 2a (133.1 mg, 0.188 mmol) and KPF₆ (172.8 mg, 0.936 mmol) was stirred in CH_2Cl_2 (10 mL) and acetone (10 mL) at room temperature. After 24 h, the solvent was removed under reduced pressure and the residue was extracted with CH₂Cl₂. Removal of the solvent and recrystallization of the residue from CH₂Cl₂ and hexane gave reddish violet complex of 3a (42.0 mg, 83.9%). FAB mass: m/z 1318 ([M]⁺) (M = cationic molecule). UV–Vis (CH₂Cl₂): λ_{max} 521, 367, 328 nm. IR(nujol): 2224, 2152 (C≡N), 841 (PF₆) cm⁻¹. ¹H NMR (CDCl₃): δ 1.03 (d, J_{PH} = 3.7 Hz, Cp*, 15H)^{a1}, 1.08 (d, $J_{\rm PH} = 3.6$ Hz, Cp*, 15H)^{a1}, 1.21 (d, ${}^{2}J_{\rm PH} = 3.3$ Hz, Cp*, $(15H)^{a2}$, 1.28 (d, ${}^{2}J_{PH} = 3.3$ Hz, Cp*, $(15H)^{a2}$, 3.67 (s, Me)^{a1 + a2}, 3.69 (s, Me)^{a1 + a2}, 5.27 (s, CH₂Cl₂), 9.95–8.12 (m, Ph, 24H). Anal. Calc. for C₆₉H₆₀F₆N₇O₄P₃Rh ₂. 2CH₂Cl₂: C, 52.19; H, 3.95; N, 6.00. Found: C, 51.94; H, 4.10; N, 6.04%.

Analogously, the complex bearing an OTf anion was obtained from 2a and AgOTf, identifying in comparison with spectroscopic data of 3a.

3.4. Reaction of Cp*IrCl(MDMPP-P,O) (1b) with TCNE in the presence of KPF_6

In a 1:1 ratio, similarly to the preparation of 3.2, **2b** (76.6 mg, 62.2%), **3b** (5.6 mg, 3.8%) and **4b** (8.2 mg, 5.5%) were obtained from a mixture of **1b** (130.7 mg, 0.195 mmol), tcne (25.7 mg, 0.195 mmol) and KPF₆ (179.5 mg, 0.975 mmol). **4b**: FAB mass: m/z 1396 ([M – 1]⁺)

(M = cationic molecule).UV–Vis (CH₂Cl₂): λ_{max} 520, 365, 236 nm. IR(nujol): 2197, 2145 (N≡C), 842 (PF₆) cm⁻¹. *Anal.* Calc. for C₆₄H₆₁F₆Ir₂N₄O₄ P₃: C, 49.86; H, 3.99; N, 3.63. Found: C, 50.39; H, 3.97; N, 3.46%. Spectroscopic data of **3b** are shown in Section 3.5.

In a 1:0.5 ratio, similarly to the preparation of 3.2, 3b (3.1 mg, 3.6%), 4b (5.3 mg, 6.6%) and 5b (23.0 mg, 30.7%) were obtained from 1b (70.8 mg, 0.104 mmol), tcne (7.9 mg, 0.052 mmol) and KPF₆ (97.0 mg, 0.52 mmol). Complex (5b) was isolated by fractional recrystallization from CH₂Cl₂ and hexane. The population between $5b_1$ and $5b_2$ is 1:4. 5b: FAB mass: m/z 1296 $([M-1]^+)$ (M = cationic molecule). UV–Vis (CH₂Cl₂): λ_{max} 523, ca. 300 nm. IR(nujol): 2158, 2145 (N=C), 841 $(PF_6) \text{ cm}^{-1}$. ¹H NMR (CDCl₃): 0.91 (d, ²*J*_{PH} = 2.0 Hz, Cp^* , 15H)^{*2}, 0.98 (d, ${}^{2}J_{PH} = 2.0$ Hz, Cp^* , 15H)^{*2}, 1.02 $(d, {}^{2}J_{PH} = 2.0 \text{ Hz}, \text{ Cp*}, 15\text{H})^{*1}, 1.11 (d, {}^{2}J_{PH} = 2.0 \text{ Hz},$ Cp*, 15H)*1, 3.46 (s, MeO, 3H)*1, 3.47 (s, MeO, 3H)*1, 3.58 (s, MeO, 6H)^{*2}, 6.6–8.2 (m, Ph, 24H)^{*1+2}. Anal. Calc. for C₅₉H₆₄F₆Ir₂NO₄P₃: C, 49.13; H, 4.47; N, 0.97. Found: C, 48.78; H, 4.29; N, 1.17%.

3.5. Reaction of 2b with KPF₆

Similarly to the preparation of 3.3, complex (**3b**) (15.7 mg, 52.8%) was obtained from the reaction of **2b** (23.3 mg, 0.036 mmol) and KPF₆ (20.0 mg, 0.11 mmol). FAB mass: m/z 1498 ([M]⁺) (M = cationic molecule). UV–Vis (CH₂Cl₂): λ_{max} 519, 374, 328 nm. IR(nujol): 2216, 2148 (N=C), 839 (PF₆) cm⁻¹. ¹H NMR (CDCl₃): δ 1.57 (d, ²*J*_{PH} = 1.8 Hz, Cp*, 30H)*¹, 1.70 (d, ²*J*_{PH} = 1.8 Hz, Cp*, 15H)*², 3.50 (s, Me, 3H)*¹, 3.53 (s, Me, 3H)*², 6.1-7.9 (m, Ph, 24H)*¹⁺². *Anal.* Calc. for C₆₉H₆₀F₆Ir₂N₇O₄ P₃: C, 50.45; H, 3.68; N, 5.97. Found: C, 50.39; H, 3.97; N, 6.46%.

3.6. Reaction of **2a** with xylyl isocyanide in the presence of AgOTf

A mixture of 2a (70.1 mg, 0.099 mmol) and AgOTf (52.7 mg, 0.205 mmol) was stirred in CH₂Cl₂ (10 mL) and acetone (10 mL) at room temperature. After 1 h, xylyl isocyanide (19.1 mg, 0.152 mmol) was added to the reaction mixture. After the mixture was stirred for 24 h, the solvent was removed under reduced pressure and the residue was extracted with CH₂Cl₂. The solvent was removed and the residue was washed with diethyl ether. Recrystallization of the residue from CH₂Cl₂ and diethyl ether gave an orange complex of 6a (54.7 mg, 58.1%). FAB mass: m/z 804 ([M]⁺) (M = cationic molecule). UV–Vis (CH₂Cl₂): λ_{max} 350, 319 nm. IR(nujol): 2179 (N≡C, C≡N), 1261, 1155, 1030 (OTf) cm⁻¹. ¹H NMR (CDCl₃): δ 1.87 (d, ²*J*_{PH} = 3.0 Hz, Cp*, 15H), 1.95 (s, o-Me 6H), 3.56 (s, MeO, 3H), 5.28 (s, CH₂Cl₂), 6.46 (s, CH=, 1H), 7.24-7.80 (m, Ph, 15H). Anal. Calc. for C₄₅H₄₀F₃N₅O₅PRhS · 0.25CH₂Cl₂: C, 55.74; H, 4.19; N, 7.18. Found: C, 55.59; H, 4.26; N, 7.13%.

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3.7. Reaction of **2b** with xylyl isocyanide in the presence of AgOTf

Similarly to the preparation of **6a**, orange complex **(6b)** (14.0 mg, 17.3%) was obtained from the reaction of **2b*** (50.0 mg, 0.078 mmol), xylyl isocyanide (15.8 mg, 0.116 mmol) and AgOTf (39.9 mg, 0.155 mmol). FAB mass: m/z 894 ([M]⁺) (M = cationic molecule). UV–Vis (CH₂Cl₂): λ_{max} 312 nm. IR(nujol): 2179 (N=C, C=N), 1261, 1155, 1032 (OTf) cm⁻¹. ¹H NMR (CDCl₃): δ 1.95 (d, ²*J*_{PH} = 2.5 Hz, Cp*, 15H), 2.10 (s, *o*-Me 6H), 3.60 (s, MeO, 3H), 6.40 (s, CH=, 1H), 7.1–8.0 (m, Ph, 15H). *Anal.* Calc. for C₄₅H₄₀F₃IrN₅O₅PS: C, 51.82; H, 3.87; N, 6.71. Found: C, 51.54; H, 3.93; N, 6.48%.

3.8. Data collection

Complex (3a) was recrystallized from CH₂Cl₂/hexane. The measurement was made on a Rigaku/MSC Mercury CCD diffractometer, using Mo K α radiation at 20 °C. Four preliminary data frames were measured at 0.5° increments of ω , in order to assess the crystal quality, and preliminary unit cell parameters were calculated. The cell parameters were refined using all reflections measured in the range $2.8^{\circ} < 2\theta < 55^{\circ}$. The intensity images were measured at 0.5° intervals of ω for a duration of 20 s. The frame data were integrated using a D*TREK program package and the data sets were corrected for absorption using a REQAB program.

The crystal parameters along with data collections are summarized in Table 2. Intensities were collected for

Table 2

Crystal data for [{Cp*RhPPh₂{2-O-3-(C(CN) = C(CN)₂)-6-(MeO)-C₆H₂}₂(CN)](PF₆) $3a_2^a$

Formula	$C_{90}H_{90}Cl_2F_6N_4 O_4P_2Rh_2$		
Formula weight	1744.38		
Crystal system	triclinic		
Space group	<i>P</i> 1 (No. 2)		
Lattice parameters			
a (Å)	13.616(4)		
b (Å)	14.616(6)		
<i>c</i> (Å)	19.845(9)		
α (°)	83.00(2)		
β (°)	76.69(2)		
γ (°)	64.53(2)		
$V(Å^3)$	3468(2)		
Ζ	2		
D_{calc} (g/cm ³)	1.670		
μ (Mo K α) (cm ⁻¹)	6.77		
$2\theta_{\rm max}$	55.0		
No. measured (uniqueness)	15154		
No. observed	8578 $(I > 3.0\sigma(I))$		
No. variables	857		
$R; Rw^{\mathrm{b}}$	0.107; 0.146		
Goodness-of-fit	2.08		

^a Measured by Rigaku/MSC Mercury CCD at 20°.

 ${}^{b}R = \sum |F_{o}| - |F_{c}| / \sum |F_{o}|$ and $Rw = [\sum w(|F_{o}| - |F_{c}|)^{2} / \sum wF_{o}^{2}]^{1/2}$.

Lorentz and polarization effects. Atomic scattering factors were taken from the usual tabulation of Cromer and Waber [14]. Anomalous dispersion effects were included in F_{calc} [15]; the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [16]. All calculations were performed using the TEXSAN crystallographic software package [17].

3.9. Determination of the structure

Complex was solved by Patterson methods (DIR-DIF94 PATTY). The non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F values. All hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.97 Å. The complex consists of two independent molecules. Each crystal unit has a crystallographically imposed inversion center in the middle of the C(N)–N(C) bond. The C(N) and N(C) atoms were refined as the occupancy of 0.5. The CN group for the molecule 1 was calculated as the C atoms and that for the molecule 2 as the N atoms.

4. Conclusion

Pentamethylcyclopentadienylrhodium(III) and -iridium(III) complexes bearing a P,O-coordination reacted readily with electron-withdrawing olefins, generating various kinds of complexes under different reaction conditions. For example, the reaction of **1** with neutral tcne or tcnq led to insertion of olefin into the C–H bond adjacent to the M–O bond, affording **2** [5]. Reactions with Li[F₄-tcnq] gave binuclear macrocyclic complexes (Scheme 1) [8].

In this paper, the reactions with tone in the presence of KPF₆ led to cleavage of the C–CN bond, generating complexes (3–5) bearing CN and C(CN)–C(CN)₂ moieties. These reactions were found to proceed via an initial formation of **2**. Reactions described here are added to the chemistry of electron withdrawing tone.

Reactions of **1** with tone in the presence of KPF₆ are not clean and the formation of various complexes except isolated complexes should be considered. Thus, we could not isolate all complexes that would be formed in these reactions. Reactions of **2** with KPF₆ generated **3** in relatively high yields, but we could not confirm the fate of HCN.

5. Supplementary materials

Table listing detailed crystallographic data, atomic positional parameters and bond lengths and angles an be obtained from the authors upon request. CCDC: 224536 for 3a.

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