Unprecedented Formation of Dinuclear Macrocyclic Complexes by Insertion of 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-Tcnq) into a C−H Bond and Subsequent Coordination to Metal Atoms

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The complexes [Cp*RhCl{PPh[C_6H_3-2,6-$(MeO)_2$](C_6H_3-2-O-6-OMe)-*P,O*}] (**1a**) and [Cp*MCl{PPh_2(C_6H_3-2-O-6-MeO)-*P,O*}] (**1b**: M = Rh; **3b**: M = Ir) with P,O chelating coordination react readily with lithium 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane [Li(F_4-tcnq)] to form the dimeric complexes **2a**, **2b** and **4b** by substitution of the H atom adjacent to the metal-O bond with F_4-tcnq and coordination through the nitrogen atom of a cyano group to another metal. The X-ray crystal structure of **2a** is described. Reaction of **1b** with F_4-tcne proceeds by an insertion into the C–H bond adjacent to the Rh–O bond.

Introduction

Aromatic phosphanes bearing the two methoxy groups at the *ortho* positions have extreme nucleophilicity and large cone angles.[1,2] Previously we reported that one of the *ortho*-methoxy groups in (2,6-dimethoxyphenyl)diphenylphosphane and bis(2,6-dimethoxyphenyl)phenylphosphane were demethylated upon treatment with bis[dichloro(η^6-arene)ruthenium(II)] or bis[dichloro(η^5-pentamethylcyclopentadienyl)rhodium(III) (or iridium(III))] to give ruthenium(II),[3,4] rhodium(III)[5] and iridium(III)[6] complexes with P,O chelating phosphane ligands, as shown in Scheme 1. The rhodium and iridium complexes (**1a**: M = Rh, R = C_6H_3-2,6-$(MeO)_2$; **1b**: M = Rh, R = Ph; **3b**: M = Ir, R = Ph) reacted with mono- or disubstituted alkyne in the presence of KPF_6 or $NaPF_6$ to give novel six- or seven-membered metallacycles arising from a single or double insertion of alkyne into the Rh−O or P−C bond.[7−9] When complexes **1b** and **3b** were treated with electron-deficient olefins such as tetracyanoethylene (tcne) or 7,7,8,8-tetracyano-*p*-quinodimethane (tcnq), the olefin inserted into weakly activated C−H bond on the phenyl ring of the phosphane ligand (Scheme 1).[10,11]

A similar insertion of an electron-deficient olefin into the C−H bond has been documented for 2-furanyl- and 2-thienylplatinum complexes.[12] We also reported that the reaction of [Cp*IrCl{PPh_2(C_6H_3-2-*O*-6-MeO)}] (**3b**) with Li(tcnq) afforded the green charge-transfer complex [Cp*Ir{PPh_2(C_6H_3-2-*O*-6-MeO)}(tcnq)].[11]

During our research on interactions of the aforementioned complexes with lithium 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane [Li(F_4-tcnq)], we found that the F_4-tcnq molecule underwent a substitution reaction at the position adjacent to the M−O bond and coordination to another metal atom of a cyano group, forming a dinuclear macrocyclic complex. This type of compounds provides a new entry into the family of inorganic macrocycles.

Results and Discussion

When compound **1a** was treated with Li(F_4-tcnq) at room temperature (Scheme 2), the orange yellow complex **2a** was formed. Its FAB mass spectrum shows peaks at *m*/*z* = 1761 (26.5%) and *m*/*z* = 881 (100%). The former is the molecular peak with a mass corresponding to a dimer [Cp*Rh{PPh[C_6H_2-2,6-$(MeO)_2$](C_6H_3-2-O-6-MeO)-*P,O*}-(F_4-tcnq)]$_2$ (mol. wt. = 1761.3). The base peak of the spectrum corresponds to half of the molecular peak value ([M/2] = 880.6). This result suggested that **2a** has a dimeric structure. The electronic spectrum shows a strong absorption band at 332 nm (Figure 1a). The IR spectrum has absorptions at 2194 and 2164 cm^{-1} due to a C-N triple bond. The ^{1}H NMR spectrum shows broad resonances at δ = 1.59, 3.20 and 3.46 ppm, the former being assignable to Cp*

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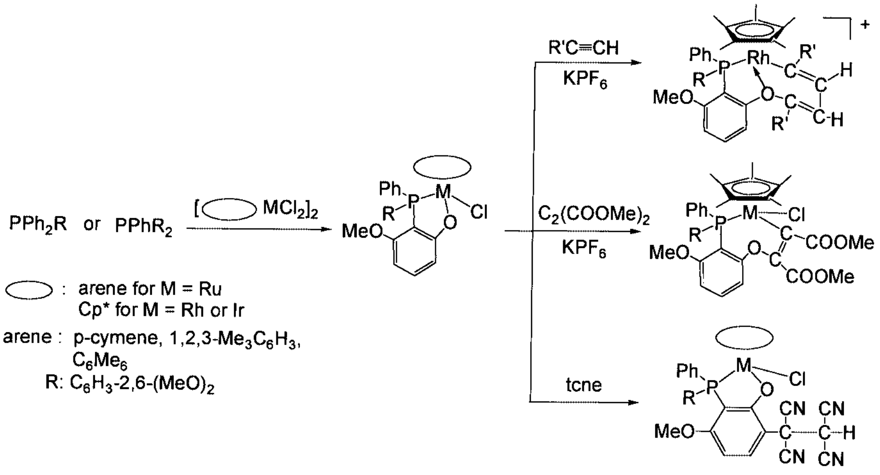
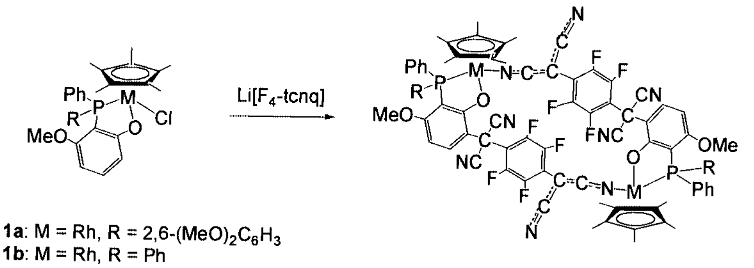


Scheme 1



1a: M = Rh, R = 2,6-(MeO)$_2$C$_6$H$_3$
1b: M = Rh, R = Ph
3b: M = Ir, R = Ph

2a: M = Rh, R = 2,6-(MeO)$_2$C$_6$H$_3$
2b: M = Rh, R =Ph
4b: M = Ir, R = Ph

Scheme 2

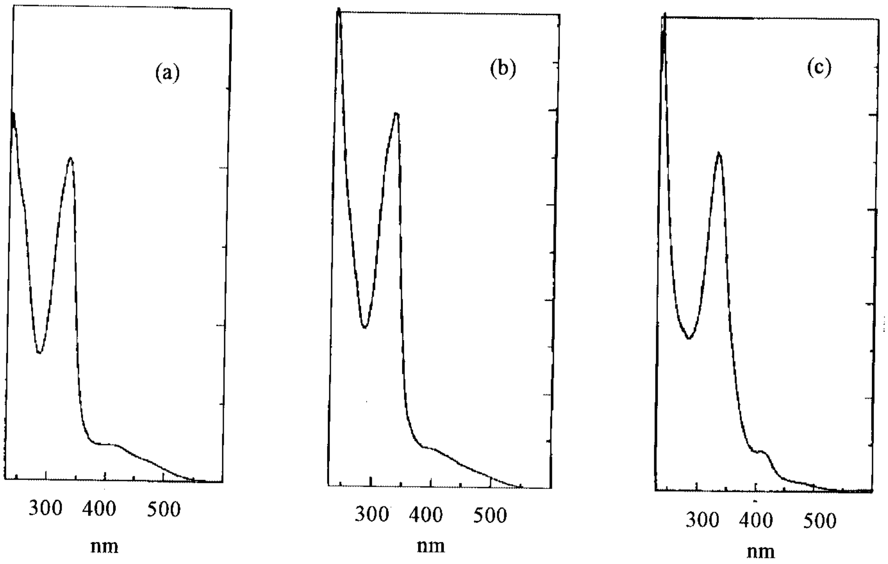


Figure 1. Electronic spectra of: (a) **2a**, (b) **2b** and (c) **4b**

protons and the others to methoxy protons, indicating that the molecule has a symmetric structure.

The detailed structure was confirmed by X-ray analysis (Figure 2 and Table 1). The molecule constructs of a macrocyclic structure with two Cp*Rh{PPh[C_6H_3-2,6-$(MeO)_2$](C_6H_2-2-*O*-6-MeO)-*P*,*O*} moieties connected by two F_4-tcnq molecules. Each F_4-tcnq molecule has undergone the aromatization of a quinone ring to a benzene one by the substitution of an H atom adjacent to an ether-O coordination, and one of the C-N triple bonds is coordinated to another Rh center. The dihedral angles between the benzene rings bearing F atoms (C35-C36-C37-C38-C39-

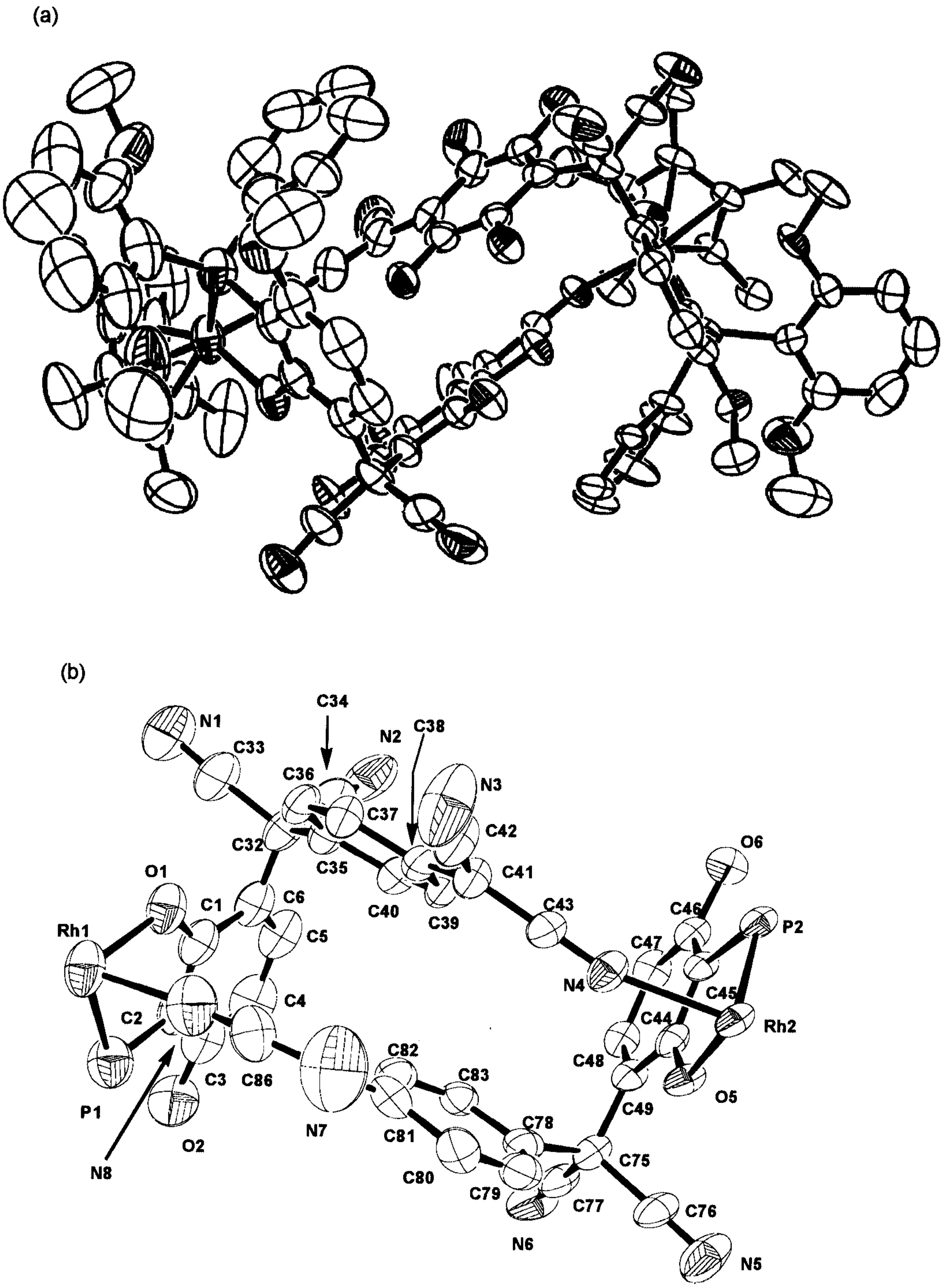


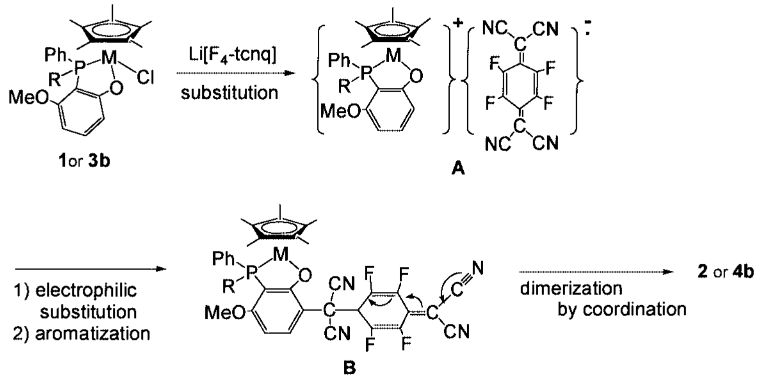
Figure 2. (a) Molecular structure of **2a**; the C84 and C85 atoms sit behind the N7 atom; displacement ellipsoids are shown at the 30% probability level; (b) framework for a core of **2a**; the Cp*, PF_6 anions, F and some other atoms have been omitted for clarity

C40 and C78-C79-C80-C81-C82-C83) and the six-membered rings (C1-C2-C3-C4-C5-C6 and C44-C45-C46-C47-C48-C49) containing the P,O coordination are nearly perpendicular in the range 81−99°. The dihedral angles between two opposite benzene rings are 142.5° and 20.1°, respectively, forming a distorted-rectangular cavity with the dimensions of about 3.5 × 7.0 Å.

The average angles around the C41 and C84 atoms are 120.0°, compared to the more normal bond angles of 109.4° and 109.5° around the C32 and C75 atoms, respectively. These data suggest that the C41 and C84 atoms are sp^2 hybridized. The average C−C and C≡N bond lengths in the inner C-C≡N groups containing the C32 and C75 atoms are 1.49 and 1.13 Å, respectively, and are therefore

Table 1. Selected bond lengths (Å) and angles (°) for **2a**

Rh(1)−P(1)	2.322(3)	Rh(1)−O(1)	2.081(6)	Rh(1)−N(8)	2.076(9)
Rh(2)−P(2)	2.325(2)	Rh(2)−O(5)	2.079(4)	Rh(2)−N(4)	2.078(6)
N(1)−C(33)	1.14(1)	C(33)−C(32)	1.49(1)	N(2)−C(34)	1.15(1)
C(34)−C(32)	1.47(1)	N(3)−C(42)	1.17(1)	C(41)−C(42)	1.39(1)
N(4)−C(43)	1.147(8)	C(43)−C(41)	1.388(9)	N(5)−C(76)	1.122(9)
C(75)−C(76)	1.497(10)	N(6)−C(77)	1.134(9)	C(75)−C(77)	1.492(10)
N(7)−C(85)	1.16(1)	C(84)−C(85)	1.39(1)	N(8)−C(86)	1.16(1)
C(84)−C(86)	1.37(1)				
P(1)−Rh(1)−O(1)	82.1(2)	P(1)−Rh(1)−N(8)	90.6(2)	O(1)−Rh(1)−N(8)	86.3(3)
P(2)−Rh(2)−O(5)	81.5(1)	P(2)−Rh(2)−N(4)	87.9(2)	O(5)−Rh(2)−N(4)	85.2(2)
Rh(1)−P(1)−C(2)	100.2(3)	Rh(1)−O(1)−C(1)	120.8(6)	P(1)−C(2)−C(1)	114.4(6)
O(1)−C(1)−C(2)	122.0(8)	Rh(2)−P(2)−C(45)	100.2(2)	Rh(2)−O(5)−C(44)	120.1(4)
P(2)−C(45)−C(44)	114.0(4)	O(5)−C(44)−C(45)	122.5(5)	Rh(1)−N(8)−C(86)	174.1(9)
N(8)−C(86)−C(84)	179(1)	C(85)−C(84)−C(86)	117.0(8)	C(81)−C(84)−C(85)	117.0(8)
C(81)−C(84)−C(86)	119.7(8)	Rh(2)−N(4)−C(43)	166.2(6)	N(4)−C(43)−C(41)	177.4(7)
C(43)−C(41)−C(38)	122.7(6)	C(42)−C(41)−C(43)	113.5(6)	C(38)−C(41)−C(42)	123.7(6)



Scheme 3

similar to normal C-C single and C-N triple bonds. However, the average C−C bond length of 1.39 Å in the C-C≡N groups containing the C81 and C84 atoms is shorter by 0.1 Å than that in the inner C-C≡N groups, falling in the region of a C-C double bond, and the N7−C85 bond length of 1.16 Å is slightly long than those in the inner C-C≡N groups. These bond lengths suggest the presence of electron delocalization through the N3−C42−C41−C43−N4 and N7−C85−C84−C86−N8 bonds. The average Rh−P and Rh−O bond lengths are 2.323 Å and 2.080 Å, respectively [those found in the parent complex **1a** are 2.323(2) Å and 2.050(5) Å].[9] The average Rh−N bond length of 2.077 Å is normal for a Rh−N bond.

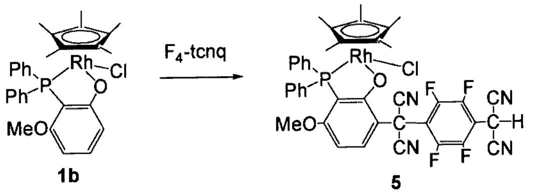
A similar reaction occurred for **1b** to give the dimeric complex **2b** as yellow crystals, which showed an electronic spectrum very similar to that of **2a** (Figure 1b).

The iridium complex **3b** reacts readily with Li(F_4-tcnq) to generate a brown complex **4b**, which has a molecular peak of $m/z = 1819$, corresponding to a binuclear complex. The IR spectrum of **4b** has absorptions at 2218 and 2170 cm^{-1} due to C-N triple bonds and at 1640 cm^{-1} due to C-N or C-C double bonds. The UV/Vis spectrum shows a sharp absorption band at 330 nm and has a similar pattern to those of **2a** and **2b** (Figure 1c). These results suggested that **4b** has a macrocyclic structure similar to **2**.

Previously, we have reported that a similar reaction of **3b** with Li(tcnq) affords the green charge-transfer complex [Cp*Ir{$PPh_2(C_6H_3$-2-O-6-MeO)-*P,O*}(tcnq)] (a tcnq analogy of intermediate A in Scheme 3) without generating the corresponding dinuclear complex.[11] The difference in electrophilicity between F_4-tcnq and tcnq is assumed to be the driving force leading to the formation of the dinuclear complex.

This reaction consists of the initial formation of a charge-transfer complex A, followed by an electrophilic substitution of a F_4-tcnq radical to the carbon atom adjacent to the ether-O atom, forming an intermediate species B. In the reaction with Li(tcnq), a tcnq analog of the charge transfer complex A was isolated. In the case of Li(F_4-tcnq), the reaction proceeds further and completes by aromatization of the quinone ring and coordination to the metal atom of another molecule to generate the dimeric complex **2** or **4** (Scheme 3).

Finally, the reaction of **1b** with F_4-tcnq led to insertion of F_4-tcnq into a C−H bond adjacent to the ether-O rhodium bond to generate the mononuclear complex **5**



Scheme 4

(Scheme 4). This type of insertion has already been reported.[10,11]

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Dichloromethane was distilled from over CaH_2 and diethyl ether was distilled from over $LiAlH_4$. The pentamethylcyclopentadienyl complexes of rhodium and iridium [Cp*MCl{$PPh_2(C_6H_3$-2-O-6-MeO)-*P,O*}] (**1b**: M = Rh;[5] **3b**: M = Ir[6]) and [Cp*RhCl{$PPh(C_6H_3$-2,6-$(MeO)_2)(C_6H_3$-2-O-6-MeO)-*P,O*}}][5] (**1a**) were prepared according to literature procedures. Lithium 2,3,5,6-tetracyanotetrafluoroquinodimethane [Li(F_4-tcnq)] was prepared by modification of a literature method.[13] 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 Bruker AC250 instrument at 250 MHz, and $^{31}P\{^1H\}$ NMR spectra were measured at 101 MHz using 85% H_3PO_4 as an external reference. Elementary analyses were preformed by the Analytical Center, School of Pharmaceutical Science, Toho University.

Reaction of 1a with Li(F_4-tcnq): Li(F_4-tcnq) (33.8 mg, 0.123 mmol) was added at room temperature to a solution of **1a** (65 mg, 0.101 mmol) in CH_2Cl_2 (20 mL). After 5 h, the solvent was removed. The residue was washed with diethyl ether and recrystallized from CH_2Cl_2 and diethyl ether, giving **2a** as an orange solid (13.2 mg, 14.8%). FAB MS: *m/z* (%) = 1761 (26) $[M]^+$, 881 $[M/2]^+$. IR (Nujol): $\tilde{\nu}$ = 2194, 2164 (C≡N), 1647 (C=N) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 400 (sh), 331 nm. ^1H NMR ($CDCl_3$): δ = 1.59 (br. s, Cp*, 30 H), 3.20 (s, MeO, 3 H), 3.45 (s, MeO, 3 H), 5.27 (s, CH_2Cl_2), 6.9−7.9 (m, Ph, 11 H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 69.5 (s) ppm. $C_{86}H_{68}F_8N_8O_8P_2Rh_2\cdot CH_2Cl_2$ (1864.2): calcd. C 56.60, H 3.82, N 6.07; found C 56.32, H 4.01, N 5.92.

Reaction of 1b with Li(F_4-tcnq): According to the above-mentioned procedure, the binuclear macrocycle **2b** (yellow, 40.5 mg, 38.0%) was obtained from **1b** (75.5 mg, 0.130 mmol) and Li(F_4-tcnq) (37.0 mg, 0.131 mmol). FAB MS: *m/z* (%) = 1641 $[M]^+$. IR (Nujol): $\tilde{\nu}$ = 2202, 2156 (C≡N), 1643 (C=N) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 410 (sh), 330 nm. $C_{82}H_{60}F_8N_8O_4P_2Rh_2$ (1641.5): calcd. C 60.01, H 3.68, N 6.82; found C 59.31, H 3.80, N 6.74.

Reaction of 1b with F_4-tcnq: A mixture of **1b** (71.7 mg, 0.123 mmol) and F-tcnq (34.7 mg, 0.126 mol) was stirred in CH_2Cl_2 (15 mL) at room temperature. After 5 h, the solvent was removed in vacuo. The residue was washed with diethyl ether and recrystallized from CH_2Cl_2 and diethyl ether to afford reddish brown crystals of **5** (38.4 mg, 36.3%). FAB MS: *m/z* = 857 $[M]^+$. IR (Nujol): $\tilde{\nu}$ = 2156 (C≡N) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 333, 260 nm. $C_{41}H_{31}ClN_4O_2F_4PRh$ (857.0): calcd. C 57.46, H 3.65, N 6.54; found C 57.18, H 3.85, N 6.44.

Reaction of 3b with Li(F_4-tcnq): According to the above-mentioned procedure, the iridium macrocycle **4b** (yellow, 39.1 mg, 40.2%) was obtained from **3b** (71.6 mg, 0.107 mmol) and Li(F_4-tcnq) (31.03 mg, 0.111 mmol). IR (Nujol): $\tilde{\nu}$ = 2189, 2137 (C≡N), 1641 (C=N) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 410(h), 330 nm. $C_{82}H_{60}F_8Ir_2N_8O_4P_2$ (1819.8): calcd. C 54.12, H 3.32, N 6.15; found C 52.10, H 3.44, N 5.91.

X-ray Crystallography: Complex **2a** was recrystallized from CH_2Cl_2/diethyl ether. A crystal was mounted at the top of a quartz fiber using perfluoro(polyoxopropylene ethyl ether), which was set on a MSC/ADSC Quantum CCD/Rigaku AFC8(ultraX 18) diffractometer. The measurement was made using Mo-K_α radiation at 0 °C under a cold nitrogen stream. 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 the reflections measured in the range $2.8° < 2\theta < 40°$. The intensity images were measured at 0.5° intervals of ω for a duration of 20 s. The frame data were integrated using the d*TREK program package, and the data sets were corrected for absorption with the REQAB program. The crystal parameters along with data collection are summarized in Table 2. The data were corrected for Lorentz and polarization effects. Atomic scattering factors were taken from Cromer and Waber with the usual tabulation.[14] Anomalous dispersion effects were included in F_c;[15] the values of Δf′ and Δf′′ were those of Creagh and McAuley.[16] All calculations were performed using the teXsan crystallographic software package.[17] The structure was solved by direct methods (SIR92). The positions of all non-hydrogen atoms were refined with anisotropic thermal parameters by using full-matrix least-squares methods. All hydrogen atoms were calculated at the ideal positions with a C−H distance of 0.97 Å.

Table 2. Crystal data for **2a**

Formula	$C_{86}H_{68}O_8P_2N_8F_8Rh_2$
Molecular weight	1761.26
Crystal system	monoclinic
Space group	$P2_1/c$ (No14)
a Å	22.755(1)
b Å	16.109(1)
c Å	25.0019(4)
β °	113.3895(6)
V Å^3	8412.0(6)
Z	4
D_{calc} g/cm^3#1.419	
μ (Mo-K_α) cm^{-1}	5.38
Reflections (< 2θ°)	80.0
Reflections observed ($I > 2\sigma(I)$]	10276
Parameters	1027
R/*Rw* [a]	0.070/0.102
*R*1	0.070 (for 10276 reflections)
GOF [b]	3.23

[a] $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $Rw = (\Sigma\omega(|F_0| - |F_c|)^2/\Sigma\omega F_0{}^2)^{1/2}$. [b] $GOF = (\Sigma\omega(|F_0| - |F_c|)^2 /(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

CCDC-182949 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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