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Effect of intramolecular π - π and CH- π interactions between ligands on structure, electrochemical and spectroscopic properties of *fac*-[Re(bpy)(CO)₃(PR₃)]⁺ (bpy = 2,2'-bipyridine; PR₃ = trialkyl or triarylphosphines)[†]

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Intramolecular π - π and CH- π interactions between the bpy and PR₃ ligands of *fac*-[Re(bpy)(CO)₃(PR₃)]⁺ affect their structure, and electrochemical and spectroscopic properties. Intramolecular CH- π interaction was observed between the alkyl groups on the phosphine ligand (R = "Bu, Et) and the bpy ligand, and intramolecular π - π and CH- π interactions were both observed between the aryl group(s) on the phosphorus ligand (R = *p*-MeOPh, *p*-MePh, Ph, *p*-FPh, OPh) and the bpy ligand, while no such interactions were found in the trialkylphosphite complexes (R = O'Pr, OEt, OMe). The intramolecular interactions distort the pyridine rings of the bpy ligand as long as 3.7×10^{-2} Å in crystals. Molecular orbital calculations of the bpy ligand suggest that this distortion decreases the energy gap between its π and π^* orbitals. An absorption band attributed to the π - π^* (bpy) transition of the distorted rhenium complexes, measured in a KBr pellet, was red-shifted by 1–5 nm compared to the complexes without the distorted bpy ligand. Even in solution, similar red shifts of the π - π^* (bpy) absorption were observed. The redox potential $E_{1/2}$ (bpy/bpy⁺) of the complexes with the trialkylphosphine and triarylphosphine ligand are shifted positively by 110–120 mV and 60–80 mV respectively, compared with those derived from the electron-attracting property of the phosphorus ligand. In contrast with these properties, three ν_{co} IR bands, which are sensitive to the electron density on the central rhenium because of π -back bonding, were shifted to higher energy, and a Re(1/II)-based oxidation wave was observed at a more positive potential according to the electron-attracting property of the phosphorus ligand.

Introduction

 π - π and CH- π interactions are important noncovalent forces that contribute to self-assembly and molecular recognition processes in various chemical and biological systems.¹⁻⁸ In coordination chemistry, these weak interactions are important in determining the conformations,9-12 the selectivities of the reactions,¹³⁻¹⁵ and the crystal structures¹⁶⁻¹⁹ of metal complexes. For example, *cis-trans* isomerization,⁹ the enantioselective Diels–Alder reaction,^{13–15} and photochemical ligand substitution reaction²⁰ of metal complexes are all successfully controlled using the interligand π - π and/or CH- π interactions. It has recently been reported that the photophysical properties of transition metal complexes are affected by intramolecular π - π and CH-π interactions.²¹⁻²⁷ For instance, Barigelletti et al. suggested that the excited-state lifetime of a ruthenium(II) polypyridine complex is prolonged by intramolecular π - π interaction between a terpyridine ligand and a phenyl group bonded to another ligand.²¹ Such interligand interactions might be used to control various properties of metal complexes. However, no systematic studies of the effects of these interactions on electrochemical and photophysical properties of metal complexes have yet been performed.

† Electronic supplementary information (ESI) available: Colour version of Fig. 5. ORTEP drawings of 2^+-4^+ , 7^+ , and 9^+ , list of $v_{\rm CO}$ frequencies for 1^+-10^+ measured in acetonitrile solution and complete ¹H-NMR data, and plot of $E_p^{\rm ox}-E_{1/2}^{\rm red}$ versus the MLCT absorption maximum measured in an MeCN solution at room temperature. See http://www.rsc.org/suppdata/dt/b4/b407947g/

The present study aims to clarify how large interligand weak interactions affect the molecular structure, redox properties, and absorption spectra of transition metal complexes in crystal and in solution. Accordingly, we synthesized the series of rhenium(I) complexes fac-[Re(bpy)(CO)₃(PR₃)]⁺ (1^+ - 10^+ in Scheme 1 and Table 1); the phosphorus ligand (PR₃) is located in the cis position relative to the 2,2'-bipyridine ligand (bpy) and the R group(s) should be closely located to the bpy ligand not only in crystal but also in solution. The complexes are classified into three types according to the substituent groups on the phosphorus ligand: R = alkyl groups which are expected to make intramolecular CH $-\pi$ interaction with the bpy ligand; or R = phenyl and its derivatives which are expected to make intramolecular π - π interaction with the bpy ligand; or R = alkoxy and phenoxy groups with the alkyl and phenyl groups located further from the bpy ligand because of the presence of the oxygen atom, and the interligand "weak" interactions might be weaker.



The photochemical, photophysical, and electrochemical properties of fac-[Re(bpy)(CO)₃(L)]⁺ have been widely studied as a result of their excellent emitting abilities²⁸⁻³⁰ and photochemical and electrochemical catalyses.³¹⁻³⁴ However, to our

Table 1 Phosphorus ligands of the fac-[Re(bpy)(CO)₃(PR₃)]⁺ and their properties

			Cone angle/°	
	R	χ^{a}	Tolman's value ^b	Stahl's value ^c
1+	"Bu	5.25	132	
2+	Et	6.30	132	137
3+	p-MeOPh	10.5	145	
4+	<i>p</i> -MePh	11.5	145	
5 ⁺	Ph	13.2	145	
6+	p-FPh	15.7	145	
7+	Ô'Pr	19.0	130	
8+	OEt	21.6	109	134
9+	OMe	24.1	107	128
10^{+}	OPh	30.2	128	

 $^a\chi$ Represents the net electron-attracting ability of a phosphorus compound. 42a b From ref. 42b c From ref. 49

knowledge, there have been only a few reports concerning interligand weak interactions in rhenium complexes,^{24,35} and detailed understanding is still lacking.

Experimental

Physical methods

IR spectra were recorded with a JEOL JIR-6500 FTIR spectrophotometer at 1 cm⁻¹ resolution. UV/vis spectra were recorded using an Hitachi-330 spectrophotometer (±0.2 nm wavelength accuracy; ± 0.1 nm reproducibility). Pellets for solidstate UV/vis absorption measurement were prepared from a mixture of 1 mg of a complex and 100 mg of KBr and were dried in vacuo at 100 °C for one day prior to use. Air was used as reference for this measurement, and the counter anion was the same as is used in X-ray crystallography. Emission spectra were recorded at 25 °C with a JASCO FP-6600 spectrofluorometer with correction for the detector sensitivity determined using correction data supplied by JASCO. Proton-NMR spectra were measured in an acetone- d_6 solution at a sample concentration of 20 mM using a Bruker AC300P (300 MHz) system. Residual protons of acetone- d_6 were used as an internal standard for the measurements. Cyclic voltammograms of the complexes were measured in acetonitrile solution containing tetra-nbutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte using an ALS/CHI CHI620 electrochemical analyzer with a glassy-carbon disk working electrode (3 mm diameter), an Ag/AgNO₃ (0.1 M) reference electrode, and a Pt counter electrode. The supporting electrolyte was dried in vacuo at 100 °C for one day prior to use.

Materials

Reagents and solvents were purchased from Kanto Chemical Co., Junsei Chemical Co., Tokyo Kasei Co., Wako Pure Chemical Industries and Aldrich Chemical Company, and were used without further purification unless otherwise noted. Acetonitrile was dried three times over P_2O_5 and then distilled from CaH₂ prior to use. Acetone was distilled from Molecular Sieves 4A. Tetra-*n*-butylammonium tetrafluoroborate was triply recrystallized from ethyl acetate/benzene.

Synthetic procedures

The PF_6^- salts of *fac*-[Re(bpy)(CO)₃(PR₃)]⁺, where R = "Bu (1⁺), Et (2⁺), Ph (5⁺), O'Pr (7⁺), OEt (8⁺), OMe (9⁺), and OPh (10⁺) were synthesized according to the previously reported methods.^{36,37}

fac-[Re(bpy)(CO)₃{P(*p*-MeOPh)₃}]+PF₆⁻ (3+PF₆⁻). An acetone solution containing 64 mg (0.14 mmol) fac-Re(bpy)(CO)₃Cl and 40 mg (0.16 mmol) silver trifluoromethanesulfonate

(Ag⁺CF₃SO₃⁻) was refluxed under a nitrogen atmosphere for 5 h in darkness. After removal of precipitated AgCl by filtration, 257 mg (0.73 mmol) tris(4-methoxyphenyl)phosphine (P(p-MeOPh)₃) was added to the filtrate. The solution was refluxed overnight under a nitrogen atmosphere in darkness and then evaporated under reduced pressure. The resulting yellow solid was recrystallized from CH2Cl2-ether to give the CF3SO3- salts of 3⁺. To 2 mL of methanolic solution of these salts was added dropwise a concentrated NH₄⁺PF₆⁻ methanolic solution. The precipitated PF_6^- salt of 3^+ was collected by filtration, washed with water, and dried in vacuo. Elemental analysis data was obtained using the $CF_3SO_3^-$ salt of 3^+ . Yield: 69% (Found: C, 45.58; H, 3.11; N, 3.02. C₃₅H₂₉N₂O₉F₃PReS requires C, 45.31; H, 3.15; N, 3.02%). ¹H-NMR (300 MHz, CD₃COCD₃): δ 8.92 (2H, dd, J = 5.5, 0.8 Hz, bpy-6,6'), 8.55 (2H, dd, J = 8.1, 1.4 Hz, bpy-3,3'), 8.29 (2H, ddd, J = 8.1, 7.6, 0.8 Hz, bpy-4,4'), 7.65 (2H, ddd, *J* = 7.6, 5.5, 1.4 Hz, bpy-5,5'), 7.2–7.1 (6H, m, Ph-*m*), 7.0-6.8 (6H, m, Ph-o), 3.82 (9H, s, CH₃O).

fac-[Re(bpy)(CO)₃{P(p-MePh)₃}]+PF₆⁻ (4+PF₆⁻), and *fac*-[Re(bpy)(CO)₃{P(p-FPh)₃}]+PF₆⁻ (6+PF₆⁻). The PF₆⁻ salts of 4⁺ and 6⁺ were synthesized in a similar manner to that of 3⁺ using tris(4-methylphenyl)phosphine (P(p-MePh)₃) and tris(4-fluorophenyl)phosphine (P(p-FPh)₃), respectively, instead of P(p-MeOPh)₃. All elemental analysis data were obtained using the CF₃SO₃⁻ salts of the complexes.

Data for **4**⁺. Yield: 78% (Found: C, 47.41; H, 3.23; N, 3.18. C₃₅H₂₉N₂O₆F₃PReS requires C, 47.78; H, 3.32; N, 3.18%). ¹H-NMR (300 MHz, CD₃COCD₃): δ 8.89 (2H, dd, J = 5.6, 0.7 Hz, bpy-6,6'), 8.53 (2H, dd, J = 8.1, 1.4 Hz, bpy-3,3'), 8.27 (2H, ddd, J = 8.1, 7.6, 0.7 Hz, bpy-4,4'), 7.62 (2H, ddd, J = 7.6, 5.6, 1.4 Hz, bpy-5,5'), 7.25–7.05 (12H, m, Ph-*o*, *m*), 2.33 (9H, s, CH₃–Ph).

Data for **6**⁺. Yield: 46% (Found: C, 42.70; H, 2.21; N, 3.05. $C_{33}H_{29}N_2O_9F_3PReS$ requires C, 43.10; H, 2.26; N, 3.14%). ¹H-NMR (300 MHz, CD₃COCD₃): δ 8.95 (2H, dd, J = 5.5, 0.7 Hz, bpy-6,6'), 8.60 (2H, dd, J = 7.1, 0.8 Hz, bpy-3,3'), 8.31 (2H, td, J = 7.1, 0.7 Hz, bpy-4,4'), 7.68 (2H, ddd, J = 7.1, 5.5, 0.8 Hz, bpy-5,5'), 7.40–7.25 (6H, m, Ph-*m*), 7.25–7.15 (6H, m, Ph-*o*).

Crystal structure determination

The single crystals of the PF_6^- salts of 1^+ , 2^+ , 5^+ , 7^+ , 8^+ , and 10⁺, and the CF₃SO₃⁻ salts of 3^+ , 4^+ , and 9^+ , were obtained by slow diffusion of diethyl ether into a dichloromethane solution containing the complex. No single crystal of 6^+ adequate for X-ray crystallography could be obtained. All diffraction data were collected at room temperature on a Mac Science MXC18K four-circle diffractometer using graphite-monochromated Mo-Ka ($\lambda = 0.71073$ Å) radiation. The unit cell dimensions were determined from 22 reflections in the ranges measured. Diffraction intensity data were collected using a 2θ - θ scan over all the 2θ range. Three standard reflections were measured at intervals of 100 reflections. The intensity data were corrected for Lorentz and polarization effects. All crystal structures were determined by the direct method using the Sir92 program, 38a and the structures were refined versus F^2 by full-matrix least-square procedures using the SHELXL-97 program.38b Atomic and anomalous scattering factors were taken from the literature.39a No secondary extinction corrections were applied. Absorption correction was applied for 2^+ and 7^+ using the ψ scan method. All crystals have only a single crystallographically distinct rhenium cation in the asymmetric unit. In the least-square refinements, all atoms other than hydrogen were refined with anisotropic displacement parameters; all hydrogen atoms were assigned by calculation at ideal positions, and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens). Table 2 gives crystal parameters and details of data collection and refinement.

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Table 2Crystallographic data for 1^+-5^+ and 7^+-10^+

		$1 + PF_{6} -$	$2^{+} P F_{6}^{-}$	$3^+ \mathrm{CF}_3 \mathrm{SO}_3^-$	$4^{+}CF_{3}SO_{3}^{-}$	$5^+ \mathrm{PF}_6^-$	$7^+ \mathrm{PF_6}^-$	$8^+ \mathbf{PF_6}^-$	$9^{+}CF_{3}SO_{3}^{-}$	$10^{+}PF_{6}^{-}$
	Formula	$\mathrm{C}_{25}\mathrm{H}_{35}\mathrm{N}_2$	$\mathrm{C}_{19}\mathrm{H}_{23}\mathrm{N}_2$	$\mathrm{C}_{35}\mathrm{H}_{29}\mathrm{N}_2$	$\mathrm{C}_{35}\mathrm{H}_{29}\mathrm{N}_2$	$\mathrm{C}_{31}\mathrm{H}_{25}\mathrm{N}_2$	$\mathbf{C}_{22}\mathbf{H}_{29}\mathbf{N}_2$	$\mathrm{C}_{19}\mathrm{H}_{23}\mathrm{N}_2$	$\mathbf{C}_{17}\mathbf{H}_{17}\mathbf{N}_2$	$C_{31}H_{23}N_2$
		$O_3F_6P_2Re$	$O_3F_6P_2Re$	O_9F_3PSRe	O_6F_3PSRe	$O_3F_6P_2Re$	$O_6F_6P_2Re$	$O_6F_6P_2Re$	O_9F_3PSRe	$O_6F_6P_2Re$
	Formula weight	773.69	689.53	927.83	879.83	835.65	779.61	737.53	699.56	881.65
	Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
	Space group	$P2_1/n$	$Pna2_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$	P-1	P-1	Cc	P-1
	a/Å	12.605(4)	16.185(3)	20.965(2)	21.205(2)	13.129(3)	8.793(3)	9.931(3)	13.574(2)	10.880(3)
	$b/\text{\AA}$	23.792(6)	14.044(2)	11.083(1)	11.028(1)	22.200(7)	11.660(10)	11.158(2)	12.052(2)	10.972(4)
	$c/\text{\AA}$	11.351(4)	10.644(2)	16.156(2)	15.438(2)	10.614(2)	16.127(6)	12.489(4)	14.391(2)	15.286(5)
	$a/^{\circ}$	90	90	90	90	60	99.49(6)	93.04(2)	90	71.11(2)
	$\beta/^{\circ}$	115.75(3)	90	110.11(1)	106.22(1)	99.39(1)	102.22(3)	97.23(2)	94.79(1)	76.66(3)
	y /°	60	90	90	<u> </u>	60	106.75(5)	104.04(2)	60	77.73(3)
	V/Λ^3	3066.1(16)	2419.4(7)	3525.1(6)	3466.5(6)	3052.1(13)	1501.7(15)	1326.9(6)	2346.1(6)	1661.0(9)
	Z	4	4	4	4	4	5	7	4	5
	$\mu(Mo-K\alpha)/mm^{-1}$	4.132	5.224	3.625	3.675	4.159	4.227	4.778	5.411	3.833
	T/K	298	298	298	298	298	298	298	298	298
	No. of data	8657	3702	10290	10109	7009	6891	8609	3552	7613
	No. of params	355	301	472	445	404	357	328	310	433
	$R1[I > 2\sigma(I)]^{a}$	0.0592	0.0454	0.0405	0.0674	0.0629	0.0773	0.0562	0.0482	0.0551
	$wR2[I > 2\sigma(I)]^{b}$	0.1365	0.0954	0.0822	0.1775	0.1517	0.1979	0.1592	0.1215	0.1361
	GOF^e on F^2	1.069	1.123	1.134	1.035	1.132	1.079	1.176	1.238	1.086
$R1 = \Sigma(.$	$ F_{\circ} - F_{\circ})/\Sigma F_{\circ} , ^{b}wR2$:	$= [\Sigma [w(F_{a}^{2}-F_{a}^{2})^{2}]_{b}$	$\sum [w(F_{s}^{2})^{2}]^{1/2}$, e GOF	$= \Sigma w(F_{\alpha}^2 - F_{\alpha} $	${}^{2 }^{2}/(m-n)^{1/2}$	where $m = \text{number}$	t of reflections and	$1 n = \text{number of } p_i$	arameters.	
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Molecular orbital calculation

Our MOPAC (parameters: PM3) calculation was performed with a CAChe working system³⁹ on an Apple Power Macintosh G3 computer. Coordinates of the bpy ligands obtained by the X-ray crystallographic analyses were used in calculating the orbitals of a 2,2'-bipyridine molecule.

Results

Infrared spectra

All complexes have three intense IR bands in the $v_{\rm CO}$ region which are similar in intensity. This is typical of the facial form of tricarbonyl rhenium bipyridine complexes with $C_{\rm s}$ symmetry.^{40,41} Fig. 1 illustrates the linear relationship between the $v_{\rm CO}$ frequencies and Tolman's χ value,⁴² which indicates the electron-attracting ability of the phosphorus ligand. It clearly shows that a stronger electron-attracting PR₃ ligand reduces the electron densities of the d π orbitals of the central rhenium, which in turn causes weaker π -back donation from the central rhenium to the carbonyl ligands.



Fig. 1 Plots of v_{co} frequencies *versus* the χ value of the phosphorus ligand.

Proton-NMR

All complexes showed four ¹H-NMR signals, due to the bpy protons in an acetone- d_6 solution, between 25 °C to -90 °C. This indicates that the two pyridine rings of the bpy ligand are equivalent on the NMR time scale. The chemical shifts for the bpy protons in the complexes measured at 25 °C are summarized in Table 3.

Redox potentials

The cyclic voltammogram of 4^+ measured in an acetonitrile solution is shown in Fig. 2 as an example. In the cathodic scan, one reversible and one irreversible wave were observed

Table 3 $\,$ ^1H-NMR Chemical shifts for bpy-protons in 1+–10+ measured in acetone- d_6 at 25 $^\circ C^a$

	$\delta/{ m ppm}$			
	$H_{3,3'}$	$H_{4,4^{\prime}}$	H _{5,5'}	$H_{6,6^{\prime}}$
1+	8.89	8.50	7.95	9.35
2+	8.86	8.47	7.93	9.33
3+	8.55	8.29	7.65	8.92
4+	8.53	8.27	7.62	8.89
5 ⁺	8.60	8.26	7.61	8.89
6+	8.60	8.31	7.68	8.95
7+	8.85	8.45	7.93	9.23
8 ⁺	8.83	8.45	7.90	9.22
9+	8.83	8.45	7.89	9.23
10^{+}	8.76	8.40	7.77	9.01

^{*a*} All complexes were PF_6^- salts.



Fig. 2 Cyclic voltammograms of 4^+ (0.5 mM) measured in a MeCN solution containing *n*-Bu₄NBF₄ (0.1 M) using a glassy carbon working electrode, a Pt counter electrode, and a Ag/AgNO₃ (0.1 M) reference electrode. The scan rate was 200 mV s⁻¹.

at -1.57 V and -2.01 V, respectively. In the anodic scan, one irreversible wave was observed at 1.5 V. Similar voltammograms were observed for the other complexes. The redox potentials are summarized in Table 4.⁴³ The reversible redox wave is attributable to reduction of the bpy ligand (bpy/bpy^{•-}), and the irreversible waves to rhenium-based reduction (Re¹/Re¹¹) respectively, based on similarity to analogous rhenium complexes.^{30,31c,44-47}

 Table 4
 Electrochemical data for 1⁺-10^{+a}

	$E_{1/2}^{\rm red b}$	$E_{ m p}^{ m red}/{ m V}^c$	$E_{\rm p}^{\rm ox}/{ m V}^d$
	V vs. Ag/AgNO ₃		
1+	-1.55 (63)	-2.11	1.49
2^+	-1.54(69)	-2.11	1.51
3+	-1.57(67)	-2.03	1.50
4+	-1.57(64)	-2.01	1.50
5 ⁺	-1.56(68)	-1.98	1.55
6+	-1.53(70)	-1.92	1.58
7+	-1.59(63)	-2.09	1.57
8 ⁺	-1.59(63)	-2.10	1.56
9+	-1.56 (64)	-2.04	1.60
10+	-1.54 (60)	-1.94	_e

^{*a*} All complexes were PF₆⁻ salts (0.5 mM). Cyclic voltammograms of 1⁺– 10⁺ were taken in MeCN solutions containing *n*-Bu₄NBF₄ (0.1 M) as a supporting electrolyte at a 200 mV s⁻¹ scan rate using a glassy carbon working electrode, a Pt counter electrode, and a Ag/AgNO₃ (0.1 M) reference electrode.⁴³ ^{*b*} Redox potential for the reversible process, that was measured by a scan reversed after the first reduction peak. Values in parentheses are the peak-to-peak separation in mV. Experimental errors were \pm 0.01V. ^{*c*} Peak potential for irreversible reduction. ^{*a*} Peak potential for irreversible oxidation. ^{*c*} We were unable to determine E_p^{ox} for 10⁺ because we observed a catalytic wave upon oxidation of 10⁺.

 Table 5
 Photophysical data for 1⁺-10⁺ in MeCN solution and in a KBr pellet^a

UV/vis absorption and emission spectra

Fig. 3 shows the UV/vis absorption spectra of 4^+ in an acetonitrile solution, a dichloromethane solution, and a KBr pellet. The intense and relatively sharp absorption band around 320 nm, which was almost identical in all media, is attributed to the π - π * transition localized on the bpy ligand. A broad absorption band was also observed around 350 nm in acetonitrile solution, which shifted by 20 nm to longer wavelength in dichloromethane. This is typical of metal-to-bpy charge-transfer (MLCT) absorption of rhenium bipyridine complexes.^{30,44-46,48}



Fig. 3 UV/vis absorption spectra (— line in MeCN; --- line in CH_2Cl_2 ; ... in KBr) of 4⁺ measured at room temperature.

The complex 4^+ emits strongly at room temperature. The emission was unstructured and a broad band, with a maximum at 540 nm, and was efficiently quenched by O₂. We have reported previously that *fac*-[Re(bpy)(CO)₃(PR₃)]⁺ type complexes including 8^+ emit from their lowest ³MLCT excited state.³⁷ Since the emission properties of 4^+ are very similar to these, the emissive state of 4^+ should also be ³MLCT. The other complexes showed similar UV/vis absorption and emission spectra, and the data are summarized in Table 5.

Fig. 4a plots the maximum of the π - $\pi^*(bpy)$ absorption wavelength, measured in a KBr pellet against the χ value. Although no clear correlation is observed, the complexes divide into two groups: one contains the trialkyl- and triarylphosphine complexes (1⁺-6⁺), and the other contains the trialkyl- and triphenylphosphite complexes (7⁺-10⁺) for which the π - $\pi^*(bpy)$ absorption maxima were observed at 319–322 and 317–318 nm, respectively. The π - $\pi^*(bpy)$ absorption of 6⁺ and 7⁺ were different by 2 nm, for example, but their phosphorus ligands have similar χ values. Since ligand-centered absorption is affected little by the electronic properties of the other ligands, the "redshifted" π - $\pi^*(bpy)$ absorption for 1⁺-6⁺, which have the trialkylor triarylphosphine ligand, implies the existence of a direct interaction between the PR₃ and bpy ligands. Interestingly, a similar

	Absorption λ_{\max} (ε)	$/nm (M^{-1} cm^{-1})$			
	MLCT in MeCN	π – π *(bpy) in MeCN	π – π *(bpy) in KBr	$E_{\rm em}/\rm{nm}^{b}$	
1+	354 (3500)	317.7 (1.1)	319	561 ^{<i>d</i>}	
2^{+}	352 (4200)	317.6 (1.4)	319	561 ^d	
3+	346 (3400)	319.1 (1.2)	319 ^c	547	
4+	343 (3500)	320.3 (1.3)	322 ^c	544	
5 ⁺	341 (3100)	319.4 (1.0)	321	540^{d}	
6+	340 (3600)	319.0 (1.4)	320	537	
7^+	330 sh	315.7 (1.6)	318	543 ^d	
8+	330 sh	315.3 (1.2)	317	542 ^{<i>d</i>}	
9+	325 sh	315.5 (1.5)	318 ^c	543 ^d	
10^{+}	320 sh	317.0 (1.5)	318	522	

^{*a*} All complexes were PF_6^- salts unless otherwise stated. ^{*b*} Emission maximum in an acetonitrile solution at room temperature. ^{*c*} CF₃SO₃⁻ Salts were used. ^{*d*} From reference 37.



Fig. 4 Plots of the π - π *(bpy) absorption maximum of the rhenium complex *versus* the χ value, (a) in a KBr pellet (b) in a MeCN solution.

behavior was observed for the π - π *(bpy) absorption measured in acetonitrile solution (Fig. 4b). The average differences were 1.8 nm between 1⁺, 2⁺ and 7⁺-10⁺ and 3.6 nm between 3⁺-6⁺ and 7⁺-10⁺ (the reproducibility of the spectrometer was \pm 0.1 nm and these differences of the absorption maxima are large enough to be distinguished).

A good linear relation is observed between the MLCT absorption maximum observed in acetonitrile solution and $E_p^{\text{ox}} - E_{1/2}^{\text{red}}$ (see Fig. 6S in ESI†). This is expected since MLCT transition energy should depend on both the energy levels of the $d\pi$ orbital of the central rhenium and on those of the π^* orbital of the by ligand.

Crystal structure

X-Ray crystallographic analyses were performed successfully for all complexes except for 6^+ , for which no adequate single crystal could be obtained. All complexes have facial structures in agreement with their spectroscopic data. Fig. 5 shows ORTEP drawings of $\mathbf{1}^+ PF_6^-$, $\mathbf{5}^+ PF_6^-$, $\mathbf{8}^+ PF_6^-$, and $\mathbf{10}^+ PF_6^-$ as examples, and selected bond distances and angles are listed in Table 6. The Re–P bond distances vary with PR_3 ligand, such that Re–P =2.49-2.50 Å for 1⁺ and 2⁺, 2.50-2.52 Å for 3⁺-5⁺, and 2.41-2.44 Å for 7^+ –10⁺. The strength of the Re–P π -back bonding is mainly responsible for these differences, and the cone angles of the PR_3 ligands (Table 1)^{42b,49} possibly contribute a weak effect, including the shorter Re–P length in 1^+ and 2^+ than in 3^+ – 5^+ . The Re-N bond lengths are similar for all the complexes except for 2^+ . The bond distances of Re–C(3) in 7^+ – 10^+ are slightly longer than in 1^+-5^+ probably because the stronger π -back donation to the phosphorus ligand in the trans position to the carbonyl ligand weakens the Re–C(3) bond.

Intramolecular interactions between the bpy and PR₃ ligands

The ORTEP drawing of $1^+PF_6^-$ is shown in Fig. 5a, in which atoms interacting with each other are shown in light grey and are connected by dotted lines. This shows the intramolecular CH- π interaction between the hydrogen atoms in the two *n*-butyl groups of the tri-*n*-butylphosphine ligand and the bpy ligand: the *n*-butyl groups are closely located along the N(1)–C(4) and

	$1^+\mathrm{PF_6}^-$	$2^+\mathbf{PF}_6^-$	$3^+ \mathrm{CF}_3 \mathrm{SO}_3^-$	$4^{+} CF_{3} SO_{3}^{-}$	$5^+\mathrm{PF_6}^-$	$7^+\mathrm{PF_6}^-$	$8^+\mathbf{PF}_6^{-}$	$9^{+}\mathrm{CF}_{3}\mathrm{SO}_{3}^{-}$	$10^{+} PF_{6}^{-}$
Re-P(1)	2.487(3)	2.498(4)	2.516(1)	2.502(2)	2.508(3)	2.437(4)	2.426(2)	2.429(3)	2.407(2)
Re-N(1)	2.194(8)	2.258(12)	2.174(4)	2.180(7)	2.191(10)	2.182(7)	2.173(7)	2.159(9)	2.150(7)
Re-N(2)	2.178(9)	2.245(11)	2.176(4)	2.165(5)	2.169(9)	2.190(10)	2.206(7)	2.174(10)	2.171(7)
Re-C(1)	1.947(11)	1.913(13)	1.923(6)	1.935(6)	1.939(15)	1.941(18)	1.932(12)	1.966(13)	1.926(12
Re-C(2)	1.920(12)	1.833(17)	1.904(6)	1.883(8)	1.939(17)	1.909(15)	1.936(11)	1.906(13)	1.883(9)
Re-C(3)	1.942(12)	1.936(14)	1.950(6)	1.962(7)	1.915(12)	1.994(16)	1.965(9)	1.971(14)	1.963(9)
P(1)-Re-N(1)	87.9(2)	88.4(3)	89.27(12)	90.38(18)	90.5(2)	86.1(2)	87.96(18)	86.6(3)	96.67(19)
P(1)-Re-N(2)	88.8(2)	86.6(3)	88.58(12)	91.35(17)	90.9(3)	86.4(2)	85.16(18)	86.7(3)	88.13(19)
P(1)-Re-C(1)	87.5(3)	91.2(6)	89.88(16)	86.4(2)	89.4(4)	91.9(5)	89.6(4)	91.7(5)	92.3(3)
P(1)-Re-C(2)	91.5(4)	90.8(6)	90.46(16)	90.2(2)	88.7(4)	91.4(5)	91.6(4)	91.5(4)	86.7(3)
P(1)-Re-C(3)	174 0(4)	175 4(8)	176 72(16)	173 10	176 0(3)	177 8(6)	170 1(3)	177 4(4)	175 0(3)



Fig. 5 ORTEP drawings (50% probability thermal ellipsoids) of (a) $1^+PF_6^-$, (b) $5^+PF_6^-$, (c) $8^+PF_6^-$, and (d) $10^+PF_6^-$. Atoms interacting with each other are shown in light grey and are connected by dotted lines. Counter anions were omitted for clarity. For treatment of the hydrogens, see the Experimental section.

Table 7 Interatomic contacts (Å) between the PR_3 and bpy ligands in $1^+\text{-}5^+$ and $7^+\text{-}10^+$

	Distances/Å
1+	C(4)-H(15A) 2.89, C(13)-H(19A) 2.69
2^{+}	C(4)–H(15A) 2.46
3+	N(1)-C(14) 3.259(7), $N(1)-C(19)$ 3.153(7), $C(4)-C(19)$ 3.270(8)
	C(6)-C(18) 3.517(9), $C(8)-C(14)$ 3.352(7), $C(9)-C(15)$ 3.473(8).
	C(13)–H(25) 2.62
4+	N(1)-C(14) 3.271(9), $C(4)-C(19)$ 3.208(13), $N(2)-C(25)$
	3.193(9) C(13)–C(25) 3.242(10), N(2)–H(25) 2.71, C(9)–H(25)
	2.65 C(10)–H(25) 2.89
5 +	N(1)-C(14) 3.268(15), C(4)-C(19) 3.178(21), N(2)-C(25)
	3.218(16), C(13)–C(25) 3.216(18), C(9)–H(25) 2.77
7+	_
8+	
9+	C(4)–H(14A) 2.94
10+	C(8)-C(15) 3.320(14), C(9)-C(15) 3.384(14)

N(2)–C(13) bonds of the bpy ligand. Table 7 summarizes the interatomic contacts between the PR₃ and bpy ligands. Similar intramolecular CH– π interactions were observed in the crystal of **2**⁺PF₆⁻.

Fig. 5b shows the ORTEP drawing of $5^+PF_6^-$. In this case, intramolecular $\pi - \pi$ interaction was observed between one of the three phenyl groups on the triphenylphosphine ligand and the bpy ligand. The distance between the centers of the π stacked rings is 3.62 Å, and the angle between the rings is 19.4°. These are typical distances (3.3-3.8 Å) and angles (< 40°) for π -stacked aromatic rings.⁵¹ The short distances between the atoms of the two rings are 3.218(16) Å for N(2)– C(25) and 3.208(13) Å for C(4)–C(19), which are shorter by 0.10 and 0.33 Å respectively than the sums of the corresponding van der Waals radii⁵⁰ as shown in Table 7. Intramolecular CH- π interaction was also observed between one of the other phenyl groups on the triphenylphosphine ligand and the bpy ligand; C(9)–H(25) bond length is 2.77 Å and the angle between the rings is 44.8°. Similar interactions were also observed in the crystals of $3^{+}CF_{3}SO_{3}^{-}$ and $4^{+}CF_{3}SO_{3}^{-}$. The distances between the centroids of the pyridine ring and the aryl group are 3.65 Å and 3.70 Å, and the corresponding angles between the rings are 14.0° and 22.7°. Although CH– π interaction was also observed in 3^+ and 4^+ (Table 7), the relative configurations of the phenyl ring and the pyridine ring are rather different with plane-plane angles of 84.6° and 40.2° respectively.

Fig. 5c shows the ORTEP drawing of $\mathbf{8}^+ PF_6^-$. No intramolecular $\pi - \pi$ or CH $-\pi$ interactions were observed in $\mathbf{7}^+$ and $\mathbf{8}^+$ between the alkoxy groups on the trialkylphosphite ligand and the bpy ligand. In the case of $\mathbf{9}^+$, the distance between H(14A) on the trimethylphosphite ligand and C(4) on the bpy ligand (2.942 Å) is close to the sum of the van der Waals radii of the aromatic carbon and hydrogen atoms.⁵⁰

The ORTEP drawing of 10^{+} PF₆⁻ (Fig. 5d) shows that a phenyl group of the triphenylphosphite ligand is located close to the bpy ligand, with a centroid–centroid distance of 3.71 Å. However, the closest distance between the atoms in the two rings is 3.320(14) Å for C(8)–C(15), about 0.1 Å longer than in $3^{+}-5^{+}$. This phenyl group is interposed by the bpy ligand in the same complex and a phenyl ring of the triphenylphosphite ligand in a closeneighboring complex as shown in Fig. 6. The packing effect should enforce the short distance among these rings. In fact the P(1)–Re–N(1) angle (96.7°) in 10^{+} was significantly wider than in the other complexes with no packing effect (86.1°–90.5°). No intramolecular CH– π interaction was observed in the crystal of 10^{+} .

Distortion of the pyridine rings

Fig. 7 illustrates two pyridine rings in the bpy ligand of the complexes viewed in the lateral direction along with the respective C(5)-C(6)-C(7) and C(10)-C(11)-C(12) planes; the



Fig. 6 Packing diagram of 10^+ PF₆⁻. One phenyl group in the triphenylphosphite ligand is interposed between the bpy ligand in the same complex and the phenyl ring in the close neighboring complex as shown by dotted lines.



Fig. 7 Lateral view of the pyridine rings of the bpy ligand in 1^+-5^+ and 7^+-10^+ , which are doubly extended in a direction perpendicular to the π -planes. The pyridine rings are viewed in the direction along the $C_5-C_6-C_7$ and $C_{10}-C_{11}-C_{12}$ planes, respectively.

direction perpendicular to the π -plane is magnified twofold. Interestingly, the pyridine rings in 1^+-5^+ in which intramolecular π - π and/or CH- π interactions were observed between the bpy and PR₃ ligands are considerably distorted, whereas those in 7⁺- 9^+ with no such interaction, and 10^+ in which P(OPh)₃ interacts weakly with the bpy ligand are almost flat. In particular, the N(1), N(2), C(4), C(8), C(9), and C(13) atoms which directly interact with the PR₃ ligands in 1^+-5^+ are strongly distorted; their deviations from the best least-squares planes of the pyridine rings are up to 3.7×10^{-2} Å, whereas those in 7⁺-10⁺ are less than 1.6×10^{-2} Å (Table 8). The distortions observed in 1^+ – 5^+ were 2-3 times larger than their standard deviations while those observed in 7^+-10^+ were approximately within their standard deviations. Furthermore, the value of $\Sigma(d^2/\sigma^2)$ (where σ is the standard deviation of each atom), which represents the probability with which each pyridine ring takes a non-plane structure, are 21.0–56.5 for 1^+ – 5^+ and 8.1–11.8 for 7^+ – 10^+ . The intermolecular packing effect does not seem to be the reason for the distortion of the pyridine rings, however, because the $\Sigma(d^2/\sigma^2)$ values are not affected by the presence or absence of the intermolecular interaction. Typically, in $\mathbf{4}^+$ with a relatively large distortion of the pyridine rings, no intermolecular interaction

Table 8 Deviations ($\times 10^{-3}$ Å) of the atoms in the pyridine rings of the bpy ligand from their best least-squares planes⁶

		,		÷.					
	1+	2 ⁺	3+	4 ⁺	5+	7+	8 ⁺	9 ⁺	10 ⁺
N(1)	-17.0(6.8)	1.6(10.2)	5.1(3.7)	21.5(5.8)	12.2(8.2)	3.2(7.0)	5.4(5.7)	-3.4(9.9)	11.7(6.1)
C(4)	1.2(8.0)	-4.8(12.0)	-1.7(4.5)	-16.5(7.2)	-2.1(9.0)	1.1(7.4)	-2.6(7.2)	-4.1(10.0)	-10.2(7.7)
C(5)	20.0(9.0)	15.0(14.9)	-3.2(5.4)	4.8(8.8)	2.2(10.9)	-8.3(7.4)	-5.0(7.9)	3.4(13.3)	-0.7(9.5)
C(6)	-25.9(9.3)	-21.9(14.5)	4.6(5.5)	1.6(9.8)	-11.3(12.0)	11.3(6.8)	9.8(7.6)	11.5(10.9)	10.1(10.1)
C(7)	10.5(8.6)	18.7(14.1)	-1.2(4.8)	3.5(8.8)	20.1(10.8)	-7.3(6.1)	-6.8(6.5)	4.6(11.2)	-8.2(8.5)
C(8)	11.2(7.2)	-8.6(12.7)	-3.7(4.0)	-15.0(6.6)	-21.1(9.6)	0.1(6.2)	-0.7(5.6)	-11.9(12.5)	-2.7(6.5)
N(2)	-30.0(7.5)	5.6(9.7)	-25.2(3.7)	15.3(5.4)	-25.9(8.2)	-3.4(6.6)	7.9(5.5)	16.5(8.2)	-1.8(6.3)
C(9)	27.4(8.2)	-26.9(10.3)	15.0(4.4)	-15.6(5.8)	-11.4(9.8)	0.7(7.6)	-2.0(5.6)	-11.7(9.1)	-4.2(6.8)
C(10)	-6.5(9.2)	20.7(12.1)	4.7(5.3)	2.4(6.8)	37.1(10.8)	7.3(8.7)	-2.0(7.0)	-5.9(9.2)	6.3(8.5)
C(11)	-11.0(10.1)	4.9(15.6)	-14.6(5.7)	10.8(7.7)	-25.6(11.1)	-12.9(9.4)	0.1(7.9)	-9.6(10.6)	-2.6(9.4)
C(12)	7.8(9.9)	-25.9(15.3)	4.6(5.2)	-10.7(7.1)	-11.5(9.7)	10.5(9.1)	5.7(7.6)	14.6(10.9)	-3.3(8.4)
C(13)	12.2(8.7)	21.5(11.4)	15.5(4.3)	-2.3(6.0)	37.2(8.2)	-2.3(7.3)	-9.6(6.5)	-3.8(10.0)	5.5(7.2)

^{*a*} Standard deviations are shown in parentheses. Positive values imply deviations from the best least-squares planes toward the C(3)O(3) ligand, and negative values imply deviations toward the PR₃ ligand. Deviations larger than 1.2×10^{-2} (Å) are shown in bold. Atoms close to the PR₃ ligands are written in Italic. ^{*b*} d_{ave} denotes the average deviation for all the atoms.

was observed between the carbon atoms on the bpy ligand and the counter anions or other complexes. On the other hand, the pyridine rings in $\mathbf{8}^+$ were not distorted even though one PF_6^- counter anion was located close to the π -plane of the bpy ligand. Disorder also does not seem to be the reason for the distortion because we defined the distortion as a function of standard deviation, which is generally proportional to thermal ellipsoids. These results suggest that the intramolecular π - π and CH- π interactions between the bpy and PR₃ ligands cause the distortion of the pyridine rings of the bpy ligand.

The dihedral angle between the two pyridine rings of the bpy ligand also seems to be affected by the intramolecular π - π and CH- π interactions. The observed dihedral angles are 5.5° for 1⁺, 5.8° for 2⁺, 8.1° for 3⁺, 4.6° for 4⁺, 7.9° for 5⁺, 3.8° for 7⁺, 0.2° for 8⁺, 3.8° for 9⁺, and 8.2° for 10⁺. The larger dihedral angles for 3⁺-5⁺ are at least partially due to the intramolecular π - π interaction, since the pyridine rings engaged in intramolecular π - π ligand. In contrast, the phenyl group in 10⁺ pushed down the pyridine ring. As discussed above, this phenyl group was interposed between the pyridine ring of the same complex and a phenyl group of another complex. These results suggest that the intramolecular interaction in 10⁺ is different from the π - π interaction in 3⁺-5⁺. The alkyl groups of the trialkylphosphine ligand pushed down the pyridine rings in 1⁺ and 2⁺.

Discussion

Solid state properties

The rhenium complexes synthesized in this study can be classified into three groups on the basis of their X-ray crystallographic data: 1^+ and 2^+ display CH– π interaction between the trialkyl substituent on the phosphorus ligand and the bpy ligand; 3^+ – 5^+ (probably 6^+ is included in this group) have π – π and CH– π interactions between the aryl substituent on the phosphorus ligand and the bpy ligand; 7^+ – 10^+ have no or only very weak interaction between the phosphorus and bpy ligands.

The through-space interaction between the aryl or alkyl group(s) on the phosphorus ligand and the bpy ligand causes distortion of the pyridine rings of the bpy ligand, as shown in Fig. 7. Deviations of the atoms from the best least-squares plane of the pyridine ring are as long as 3.7×10^{-2} Å for 1^+-5^+ with the interligand interactions but less than 1.6×10^{-2} Å for 7^+-10^+ with weak or no interaction. Decrease of the electron density in the bonding π orbital on the bpy ligand as a result of the CH– π interaction should be largely responsible for the distortion of the pyridine rings on 1^+ and 2^+ . With the π - π interaction, partial charge transfer from the π -electrons on the aryl group to the antibonding π^* orbital on the pyridine ring may be a driving

force because of the lower electron density on the pyridine rings, causing the distortion of the pyridine rings. This will be discussed in more detail below.

The UV/vis absorption spectra of the rhenium complexes measured in KBr pellets seem to be affected by the intramolecular interaction. The bpy-localized (π - π *(bpy)) absorption were 319-322 nm for 1^+-6^+ with intramolecular interaction, but 317–318 nm for 7^+ –10⁺ without the interaction (Fig. 4a). The differences between the two groups were relatively small (1 nm-5 nm) but are large enough to be distinguished in view of the reproducibility of the spectrometer, namely ± 0.1 nm. It is noteworthy that the π - π *(bpy) absorption maximum of Re(bpy)(CO)₃Cl measured in KBr is 318 nm that is almost identical to those of 7^+ – 10^+ even though the electronic properties of Cl⁻ are very different from the phosphorus ligands. In fact, through-bond electronic perturbation on the bpy ligand by the phosphorus ligand via the central rhenium ion, which is quantitatively indicated by the χ value of the phosphorus ligand, does not affect the π - π *(bpy) absorption (see Fig. 4).⁵²

Two possible causes of the difference in $\pi - \pi^*$ (bpy) absorption are suggested by the structural data of 1^+-5^+ and 7^+-10^+ ; one is the non-planarity of the pyridine ring in 1^+-5^+ , and the other is the dihedral angle between two pyridine rings in 1^+ - 5^+ . To estimate the effects of these structural distortions of the bpy ligand, we made molecular orbital calculations using the MOPAC PM3 method. Fig. 8 is plot of the calculated HOMO-LUMO energy-gap ΔE_{calc} vs. (a) average deviation of the atoms in the bpy ligand from their best least-squares plane (d_{ave}) obtained by X-ray crystallography, and (b) the dihedral angle between the pyridine rings, respectively. The distortion from planarity of the pyridine ring itself has a significant effect on ΔE_{calc} ; an increase in d_{ave} induces higher ΔE_{calc} , of which the maximum difference reached 409 meV. The effect of the dihedral angle between the pyridine rings on ΔE_{calc} is much smaller between 0° and 8° ,⁵³ which is the maximum angle observed for the complexes 3^+ and 10^+ ; the increase of ΔE_{calc} is less than 10 meV. We therefore conclude that the dihedral angle between the pyridine rings has a negligible effect in these cases.

Fig. 9 shows the relation between ΔE_{calc} and the $\pi - \pi^*(bpy)$ energies derived from the absorption maxima of the rhenium complexes. They are reasonably correlated except for 2^+ , suggesting that the non-planarity of the pyridine ring in 1^+-5^+ is one of the reasons for the difference in $\pi - \pi^*(bpy)$ absorption from $7^+-10^{+.54}$ Electronic perturbations of the CH- π and π - π interactions are further causes of this difference, probably causing the deviation in Fig. 9. The difference in electronic perturbation between the CH- π and $\pi - \pi$ interactions will be discussed in a later section.

Two important questions now arise, (1) are the intramolecular CH $-\pi$ and $\pi-\pi$ interactions maintained in fluid solution? If so,



Fig. 8 Plots of the calculated HOMO–LUMO energy-gap (ΔE_{calc}) vs. (a) average deviation of the atoms in the bpy ligand from the best least-squares plane of the pyridine rings (d_{ave}), and (b) dihedral angle between two pyridine rings in 2,2'-bipyridine.



Fig. 9 Plot of calculated HOMO–LUMO energy-gap (ΔE_{calc}) vs. the π - π *(bpy) energy obtained from the UV/vis absorption spectrum of the rhenium complex in a KBr pellet.

(2) how do these "weak" interactions affect the properties of the complexes in solution?

Electrochemical and spectroscopic properties in solution

Fig. 10a shows the relation between the oxidation potential $(E_p^{\circ \alpha})$ and the χ value of the PR₃ ligand in which the complex with higher χ value has more positive $E_p^{\circ \alpha}$. In spite of the irreversibility, the peak potentials are expected to reflect the electron density on the central rhenium. This relation clearly shows that the electron densities of the $d\pi$ orbitals of the central rhenium decrease with a stronger electron-attracting phosphorus ligand. This is consistent with the observed infrared spectra of the complexes (see Results section).

Plots of the reduction potentials $(E_{1/2}^{\text{red}})$ versus the χ value fall onto three lines having distinct slopes and intercepts (Fig. 10b), *i.e.*, for the trialkylphosphine complexes (1⁺ and 2⁺), for the triarylphosphine complexes (3⁺-6⁺), and for the trialkyl- and triphenylphosphite complexes (7⁺-10⁺). If $E_{1/2}^{\text{red}}$ depended only



Fig. 10 Plots of (a) E_{p}^{ox} versus χ , (b) $E_{1/2}^{\text{red}}$ versus χ , and (c) $E_{1/2}^{\text{red}}$ versus E_{calc} .

on the electron density on the central rhenium ion, that is, the phosphorus ligand affects the electron accepting ability of the bpy ligand only through the P-Re-N(bpy) bond, then only a single relation, similar to Fig. 10a, would be observed between $E_{1/2}^{\text{red}}$ and χ . But there is a difference in $E_{1/2}^{\text{red}}$ of 60 mV between 6^+ and 7^+ , even though these have similar χ values. The differences in the observed $E_{1/2}^{\text{red}}$ from the values obtained by extrapolation of the linear $E_{1/2}^{\text{red}}$ vs. χ relation for the complexes with the trialkyl- and triphenylphosphite ligand (7^+-10^+) are 110–120 mV for the trialkylphosphine complexes $(1^+ \text{ and } 2^+)$, and 60–80 mV for the triarylphosphine complexes (3^+-6^+) ; in the same series of complexes, the $E_{1/2}^{red}$ were "normally" dependent on the χ values (Fig. 10b). This result implies that there is a perturbation on the electron affinity of the bpy ligand by the PR₃ ligand even in solution, beyond the P-Re-N(bpy) through-bond interaction, *i.e.*, the through-space π - π and CH- π interactions similar to those in the crystals.

The π - π^* (bpy) absorption maxima of the complexes measured in acetonitrile solution correlate well with those measured in a KBr pellet, which were affected by the intramolecular π - π and CH- π interactions as described above (Fig. 11). This also supports that similar intramolecular interactions between the ligands are dynamically maintained in solution as in crystal.

Proton-NMR spectra of the complexes measured in acetonitrile solution show that the PR_3 ligand can rotate around the Re–P bond on the time scale of the NMR measurements, at least above -90 °C, since only four kinds of bpy-protons were observed for all of the complexes. The finer detail of their chemical shifts in Table 3 provides some information on the relative conformation between the ligands, however, Vos



Fig. 11 Correlation between the π - π *(bpy) absorption maxima of the complexes measured in an MeCN solution and those measured in a KBr pellet.

and co-workers55 have reported that, in proton-NMR spectra of some ruthenium(II) bpy complexes with π - π interaction between the bpy ligands and a phenyl ring bonded to another ligand, aromatic proton resonances are upfield-shifted because of shielding effects of the ring currents. A similar shielding effect of the aryl group(s) on the triarylphosphine ligand is apparent on the bpy-protons in 3^+-6^+ ($\Delta\delta = -0.14$ to -0.34 ppm compared with 7⁺-9⁺), but is much weaker in 10⁺ ($\Delta \delta$ = -0.05 to -0.22 ppm compared with 7^+-9^+). This indicates that conformations in which the bpy ligand and the aryl group(s) on the triarylphosphine ligand are located close to each other in parallel fashion are more favorable in 3^+-6^+ than in 10^+ , suggesting that the intramolecular interactions are dynamically maintained in solution. One of two phenoxy groups over the bpy ligand can bend away from the bpy ligand as a result of the flexibility of the P-O-C bonds of the triphenylphosphite ligand in 10^+ , as in the crystal structure (see Fig. 5d). Since the redox character and the π - π *(bpy) absorption of 10⁺ in solution are similar to the group of the complexes with the trialkylphosphite ligand 7^+-9^+ , as shown in Figs. 10b and 4b, the weak $\pi-\pi$ interaction observed in the crystal of $10^+ PF_6^-$ probably becomes weaker in solution or disappears entirely. This π - π interaction in the crystal of 10⁺ is supported by the packing effect with another complex (see Results section), which is lost in solution.

The chemical shifts of $H_{6,6'}$ in 1^+ and 2^+ with the trialkylphosphine ligand were observed in magnetic fields lower by ~0.13 ppm than in 7^+-9^+ . This strongly suggests that the CH– π interaction between the alkyl group(s) and the bpy ligand is also maintained in solution and affects the electron density of $H_{6,6'}$ which is bound to the closest bpy-carbon to the alkyl groups in the phosphine ligand. The CH– π interaction generally has a charge-transfer character from π orbital of aromatic ring to σ^* orbital of C–H bond,¹ and the electron density on the bpy ligand should fall.

On the other hand, the π - π interaction may have a charge transfer character from the aryl group on the phosphine ligand to the bpy ligand because of lower charge density on the bpy ligand. In addition, perturbations between the π orbitals and between the π^* orbitals of the aryl group and the bpy ligand probably give effects on the energy levels of the π and π^* orbitals of the bpy ligand. This difference in the charge-transfer character between the CH- π and π - π interactions explains the difference in the bpy-based redox potentials between 1⁺-2⁺ and 3⁺-6⁺; the observed redox potentials of 1⁺-2⁺ were about 60 mV more positive than those of 3⁺-6⁺.

Conclusions

In crystals of the salts with *fac*-[Re(bpy)(CO)₃(PR₃)]⁺ (R = alkyl and aryl groups), intramolecular π - π and/or CH- π interactions exist between the bpy and PR₃ ligands attached to the central rhenium in *cis* positions relative to each other. These interactions distort the pyridine rings in the bpy ligand and cause a red-shift

in the π - π^* (bpy) absorption in the crystal. MOPAC calculations indicate that the distortion of the pyridine rings decrease its LUMO energy and increase the HOMO energy. Spectral data and electrochemical results for the complexes suggest that the intramolecular interactions are maintained even in solution. As a result of the π - π and CH- π interactions, the bpy-based reduction potentials of the complexes are shifted positively by 60–120 mV. Similar red-shifts in the π - π^* (bpy) absorption due to these interactions were also observed in solution. In contrast, the Re(I/II)-based oxidation potentials and the v_{co} bands of the complexes are predominantly controlled by the electronic properties of the phosphorus ligands; these "weak" interactions do not strongly affect the electron densities of the central rhenium.

CCDC reference numbers 239864–239872 for 1^+ – 5^+ and 7^+ – 10^+ .

See http://www.rsc.org/suppdata/dt/b4/b407947g/ for crystallographic data in CIF or other electronic format.

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References

- 1 M. Nishio, M. Hirota and Y. Umezawa, *The CH/\pi Interaction: Evidence, Nature, and Consequences,* Wiley-VCH, Weinheim, 1998.
- 2 J.-M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, Wiley-VCH, Weinheim, 1995.
- 3 J.-M. Lehn, Angew. Chem., Int. Ed. Engl., 1990, 29, 1304–1319.
- 4 G. R. Desiraju, Angew. Chem., Int. Ed. Engl., 1995, 34, 2311-2327.
- 5 P. R. Ashton, J. Huff, S. Menzer, I. W. Parsons, J. A. Preece, J. F. Stoddart, M. S. Tolley, A. J. P. White and D. J. Williams, *Eur. J. Chem.*, 1996, 2, 31–44.
- 6 D. Philp and J. F. Stoddart, Angew. Chem., Int. Ed. Engl., 1996, 35, 1155–1196.
- 7 C. A. Hunter, K. R. Lawson, J. Perkins and C. J. Urch, J. Chem. Soc., Perkin Trans. 2, 2001, 651–669.
- 8 E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 2003, **42**, 1210–1250.
- 9 L. Hirsivaara, M. Haukka and J. Pursiainen, *Eur. J. Inorg. Chem.*, 2001, 2255–2262.
- 10 (a) K. Yamanari, T. Nozaki, A. Fuyuhiro and S. Kaizaki, Chem. Lett., 1996, 35–36; (b) K. Yamanari, T. Nozaki, A. Fuyuhiro, Y. Kushi and S. Kaizaki, J. Chem. Soc., Dalton Trans., 1996, 2851–2856.
- 11 M. Mizutani, S. Tomosue, H. Kinoshita, K. Jitsukawa, H. Masuda and H. Einaga, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 981–988.
- 12 O. Yamauchi and A. Odani, J. Am. Chem. Soc., 1985, 107, 5938–5945.
- 13 R. W. Quan, Z. Li and E. N. Jacobsen, J. Am. Chem. Soc., 1996, 118, 8156–8157.
- 14 (a) S. Otto, G. Boccaletti and J. B. F. N. Engberts, J. Am. Chem. Soc., 1998, **120**, 4238–4239; (b) S. Otto and J. B. F. N. Engberts, J. Am. Chem. Soc., 1999, **121**, 6798–6806.
- 15 M. Yamakawa, I. Yamada and R. Noyori, Angew. Chem., Int. Ed. Engl., 2001, 40, 2818–2821.
- 16 D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, 98, 1375–1405.
- 17 D. Gut, A. Rudi, J. Kopilov, I. Goldberg and M. Kol, J. Am. Chem. Soc., 2002, 124, 5449–5456.
- 18 H. Suezawa, T. Yoshida, Y. Umezawa, S. Tsuboyama and M. Nishio, *Eur. J. Inorg. Chem.*, 2002, 3148–3155.
- 19 G. A. Bogdanovic, A. Spasojevic-de Bire and S. D. Zaric, *Eur. J. Inorg. Chem.*, 2002, 1599–1602.
- 20 F. Wu, E. Riesgo, A. Pavalova, R. A. Kipp, R. H. Schmehl and R. P. Thummel, *Inorg. Chem.*, 1999, **38**, 5620–5628.
- 21 (a) F. Barigelletti, B. Ventura, J.-P. Collin, R. Kayhanian, P. Gavina and J.-P. Sauvage, *Eur. J. Inorg. Chem.*, 2000, 113–119; (b) J.-P. Collin, R. Kayhanian, J.-P. Sauvage, G. Calogero, F. Barigelletti, A. De Cian and J. Fisher, *J. Chem. Soc., Chem Commun.*, 1997, 775–776.

- 23 E. C. Riesgo, Y.-Z. Hu, F. Bouvier, R. P. Thummel, D. V. Scaltrito and G. J. Meyer, *Inorg. Chem.*, 2001, 40, 3413–3422.
- 24 (a) G. A. Reitz, W. J. Dressick, J. N. Demas and B. A. DeGraff, J. Am. Chem. Soc., 1986, 108, 5344–5345; (b) G. A. Reitz, J. N. Demas, B. A. DeGraff and E. M. Stephens, J. Am. Chem. Soc., 1988, 110, 5051– 5059; (c) L. Sacksteder, M. Lee, J. N. Demas and B. A. DeGraff, J. Am. Chem. Soc., 1993, 115, 8230–8238.
- 25 (a) K.-H. Wong, K.-K. Cheung, M. C.-W. Chan and C.-M. Che, Organometallics, 1998, **17**, 3505–3511; (b) S.-W. Lai, T.-C. Cheung, M. C. W. Chan, K.-K. Cheung, S.-M. Peng and C.-M. Che, *Inorg. Chem.*, 2000, **39**, 255–262; (c) W. Lu, M. C. W. Chan, K.-K. Cheung and C.-M. Che, Organometallics, 2001, **20**, 2477–2486.
- 26 M. T. Miller, P. K. Gantzel and T. B. Karpishin, *Inorg. Chem.*, 1998, 37, 2285–2290.
- 27 L. B. Picraux, B. T. Weldon and J. K. McCusker, *Inorg. Chem.*, 2003, 42, 273–282.
- 28 (a) D. J. Stufkens, Comments Inorg. Chem., 1992, 13, 359–385; (b) D. J. Stufkens and A. Vlcek, Jr., Coord. Chem. Rev., 1998, 177, 127–179.
- 29 K. Kalyanasundaram, J. Chem. Soc., Faraday Trans. 2, 1986, 82, 2401–2415.
- 30 L. A. Worl, R. Duesing, P. Chen, L. Della Ciana and T. J. Meyer, J. Chem. Soc., Dalton Trans., 1991, 849–858.
- 31 (a) H. Hori, F. P. A. Johnson, K. Koike, O. Ishitani and T. Ibusuki, J. Photochem. Photobiol., A: Chem., 1996, 96, 171–174; (b) K. Koike, H. Hori, M. Ishizuka, J. R. Westwell, K. Takeuchi, T. Ibusuki, K. Enjouji, H. Konno, K. Sakamoto and O. Ishitani, Organometallics, 1997, 16, 5724–5729; (c) H. Hori, F. P. A. Johnson, K. Koike, K. Takeuchi, T. Ibusuki and O. Ishitani, J. Chem. Soc., Dalton Trans., 1997, 1019–1023; (d) H. Hori, J. Ishihara, K. Koike, K. Takeuchi, T. Ibusuki and O. Ishitani, J. Photochem. Photobiol., A: Chem., 1999, 120, 119–124.
- 32 (a) J. Hawecker, J.-M. Lehn and R. Ziessel, J. Chem. Soc., Chem Commun., 1987, 536–538; (b) J. Hawecker, J.-M. Lehn and R. Ziessel, J. Chem. Soc., Chem Commun., 1984, 328–330; (c) J. Hawecker, J.-M. Lehn and R. Ziessel, Helv. Chim. Acta, 1986, 69, 1990–2012.
 33 (a) C. Kutal, M. A. Weber, G. Ferraudi and D. Geiger,
- 33 (a) C. Kutal, M. A. Weber, G. Ferraudi and D. Geiger, Organometallics, 1985, 4, 2161–2166; (b) C. Kutal, A. J. Corbin and G. Ferraudi, Organometallics, 1987, 6, 553–557.
- 34 B. P. Sullivan, C. M. Bolinger, D. Conrad, W. J. Vining and T. J. Meyer, J. Chem. Soc., Chem Commun., 1985, 1414–1416.
- 35 V. W.-W. Yam, K. M.-C. Wong and K.-K. Chueng, Organometallics, 1997, 16, 1729–1734.
- 36 H. Hori, K. Koike, M. Ishizuka, K. Takeuchi, T. Ibusuki and O. Ishitani, J. Organomet. Chem., 1997, 530, 169–176.

- 37 K. Koike, N. Okoshi, H. Hori, K. Takeuchi, O. Ishitani, H. Tsubaki, I. P. Clark, M. W. George, F. P. A. Johnson and J. J. Turner, *J. Am. Chem. Soc.*, 2002, **124**, 11448–11455.
- 38 (a) A. C. G. Altomare, C. Ciacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, J. Appl. Crystallogr, 1994, 27, 435; (b) G. M. Sheldrick, SHELXL97, University of Göttingen, Germany, 1997.
- 39 (a) CAChe, version 4.1.1, Oxford Molecular Ltd; (b) International Tables for X-ray Crystallography, ed. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.
- 40 P. J. Giordano and M. S. Wrighton, J. Am. Chem. Soc., 1979, 101, 2888–2897.
- 41 D. M. Dattelbaun, K. M. Omberg, J. R. Schoonover, R. L. Martin and T. J. Meyer, *Inorg. Chem.*, 2002, **41**, 6071–6079.
- 42 (a) T. Bartik, T. Himmler, H. G. Schulte and K. Seevogel, J. Organomet. Chem., 1984, 272, 29–41; (b) C. A. Tolman, Chem. Rev., 1977, 77, 313–348.
- 43 The data reported here differs slightly from the values reported previously (ref. 36). We believe that repeated experiments with improved accuracy of the apparatus improve the accuracy of the data.
- 44 G. Tapolsky, R. Duesing and T. J. Meyer, *Inorg. Chem.*, 1990, **29**, 2285–2297.
- 45 L. Sacksteder, A. P. Zipp, E. A. Brown, J. Streich, J. N. Demas and B. A. DeGraff, *Inorg. Chem.*, 1990, **29**, 4335–4340.
- 46 R. Lin, Y. Fu, C. P. Brock and T. F. Guarr, *Inorg. Chem.*, 1992, **31**, 4346–4353.
- 47 W.-M. Xue, M. C.-W. Chan, Z.-M. Su, K.-K. Cheung, S.-T. Liu and C.-M. Che, *Organometallics*, 1998, **17**, 1622–1630.
- 48 M. S. Wrighton and D. L. Morse, J. Am. Chem. Soc., 1974, 96, 998–1003.
- 49 L. Stahl and R. D. Ernst, J. Am. Chem. Soc., 1987, 109, 5673–5680.
- 50 A. Bondi, J. Phys. Chem., 1964, 68, 441.
- 51 C. Janiak, J. Chem. Soc., Dalton Trans., 2000, 3885-3896.
- 52 The good linear relation between these three v_{co} bands of the complexes and the *c* values (see Fig. 1) strongly suggests that the electron density of the central rhenium is "normally" affected by the phosphorus ligand, *i.e.*, *via* the Re–P bond. See Results section.
- 53 In this calculation, only the dihedral angle was changed while the two pyridine rings were assumed to be planar.
- 54 Comparison of the absolute values between both axes has no meaning, because ΔE_{calc} was calculated for a non-coordinated "free" bpy molecule but the coordination of the bpy ligand obtained by X-ray crystallography was used.
- 55 J. A. Bolger, G. Ferguson, J. P. James, C. Long, P. McArdle and J. G. Vos, J. Chem. Soc., Dalton Trans., 1993, 1577–1583.