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THE VIBRATIONAL SPECTRA OF THE HOMOLEPTIC ISOCYANIDE COMPLEXES $[Re(CNR)_6]PF_6$, (R = Me, Ph, AND $4\text{-}MeC_6H_4$)

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Summary

Raman and infrared spectra of the complexes $[Re(CNR)_6]PF_6$ (R = Me, Ph, and $4\text{-}MeC_6H_4$) have been obtained in the solid state and in solution. Fundamental vibrations have been assigned on the basis of local O_h symmetry for the $Re(CNC)_6$ skeletons and for the PF_6^- anions. The methyl and phenyl internal modes of the methyl isocyanide and phenyl isocyanide complexes have been assigned in terms of C_{3v} and C_{2v} symmetry, respectively. The Raman-active $\nu(N{\equiv}C)$ bands of the complexes have anomalous relative intensities, the E_g bands being considerably more intense than the bands assigned to the totally symmetrical A_{1g} vibrations. Although this feature has been reported for metal carbonyls, it has not previously been mentioned for metal isocyanide complexes.

Introduction

Although the vibrational spectra of transition metal carbonyls have been explored extensively, there have been few detailed studies of the spectra of isoelectronic isocyanide complexes. Vibrational spectroscopic information on most metal isocyanide complexes has been limited to the infrared-active $\nu(N{\equiv}C)$ frequencies. However, fairly complete studies have been reported for the complexes $[M(CNMe)_4](PF_6)_2$, $[M_2(CNMe)_6](PF_6)_2$, (M = Pd and Pt), and $[Pd_3(CNMe)_8](PF_6)_2$ [1], for $[Co(CNR)_5]ClO_4$, (R = Me, Et, or Ph), $[Co(CNPh)_5](ClO_4)_2$ and $[Co_2(CNR)_{10}](ClO_4)_4$, (R = Me or Et) [2], for $[Mn(CNR)_6]I$, (R = Me, Ph, or $4\text{-}ClC_6H_4$) [3,4], and for $[Fe(CNMe)_6]Cl_2 \cdot 3H_2O$ [4]. Even among this small group of complexes some conflicting results have been published. For example, in

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two independent studies of $[Co_2(CNMe)_{10}](ClO_4)_4$ [2,5] there is agreement on the assignment of the metal–metal stretching frequency but striking disagreement on the assignment of bands associated with ν(NC), ν(CoC) and δ(CoCN) modes. Some of the proposed assignments in the two studies of the vibrational spectrum of $[Mn(CNMe)_6]I$ also differ [3,4].

In view of the limited amount of data currently available and the importance of isocyanide complexes in transition metal chemistry, we have initiated a study of the vibrational spectra of a selection of homoleptic transition metal isocyanide complexes and report here on the species $[Re(CNR)_6]PF_6$ (R = Me, Ph, and $4\text{-}MeC_6H_4$). These complexes are now much more readily available in good yield as a result of a recent study [6] of the reductive cleavage of the dinuclear quadruply bonded complexes $Re_2(O_2CR)_4Cl_2$ by isocyanides. Most attention has been focussed on the vibrational spectra of the methyl and phenyl isocyanide complexes because of the well-founded assignments of the vibrational spectra of these two free isocyanides [7–9].

Experimental

Preparation of $[Re(CNMe)_6]PF_6$. Methyl isocyanide (2.0 cm^3, 35.6 mmol) was added to a stirred suspension of $Re_2(O_2CMe)_4Cl_2$ (0.41 g, 0.60 mmol) in methanol (15 cm^3). The mixture was refluxed for 4 h, reduced to dryness under a stream of nitrogen gas, and treated with a solution of KPF_6 (0.30 g, 1.60 mmol) in acetone (15 cm^3). This mixture was stirred for 0.5 h and filtered. The solid remaining (mostly KCl) was washed with additional acetone (30 cm^3) and the acetone washings and filtrate combined and again reduced to dryness. The residue was washed with petroleum ether (50 cm^3), followed by diethyl ether (50 cm^3). The solid remaining was dissolved in acetone (100 cm^3) and precipitated with water. This solid was filtered off and recrystallized from hot acetone (50 cm^3). Slow evaporation of the acetone solution over a period of one week left large colourless crystals of $[Re(CNMe)_6]PF_6$. Yield: 0.26 g, 38%. Found: C, 25.0; H, 3.69. $C_{12}H_{18}F_6N_6PRe$: C, 25.0; H, 3.14%. The aryl isocyanide complexes were prepared by a procedure to be published [10].

Spectroscopic measurements. Infrared spectra of Nujol and hexachlorobutadiene mulls held between caesium iodide plates were recorded between 4000 and 200 cm^{-1} using Perkin–Elmer 599B and Beckman IR-12 spectrophotometers. Calibration was achieved by reference to the spectrum of polystyrene. Some solution studies were carried out using dichloromethane solutions in a cell with potassium bromide windows. Low-frequency (500–50 cm^{-1}) spectra of Nujol mulls dispersed in polyethylene were recorded using a Digilab FTS-20B Fourier transform spectrophotometer.

Raman spectra of solid samples and dichloromethane or acetonitrile solutions held in sealed Pyrex capillary tubes were obtained at ambient temperature using the red 632.8 nm line from a Spectra Physics 125 He–Ne laser and the green 514.5 nm line from a Lexel 81 argon ion laser as excitation sources. The scattered radiation was passed through a Spex 1401 double monochromator before detection by an E.M.I. 9658 photomultiplier cooled to −15°C. Photon counting was employed. The relative intensities quoted have not been corrected for monochromator-photomultiplier response. Depolarization ratios were obtained from consecutive scans of peaks with the plane of the polarized light parallel and perpendicular, respectively, to the axis of an analyser. The bands frequencies quoted, apart perhaps for a few weak or broad peaks, are accurate to at least ±2 cm^{-1}. Calibration was achieved using indene or alternatively using argon lines present when the interference filter was removed.

Results and discussion

No structure determinations have been reported on $[Re(CNR)_6]^+$ cations, so as a first approximation it is proposed that the $[Re(CNC)_6]$ skeleton can be regarded as possessing local O_h symmetry. We believe this to be a reasonable approach for the

TABLE 1

NORMAL MODES OF VIBRATION OF A $[Re(CNC)_6]$ SKELETON OF O_h SYMMETRY

Approximate description	A_{1g} R(pol)	E_g R	T_{1g} Inactive	T_{2g} R	T_{1u} IR	T_{2u} Inactive
N≡C stretch	1	1			1	
Re–C stretch	1	1			1	
C–N stretch	1	1			1	
ReCN deformation			1	1	1	1
CReC deformation				1	1	1
C–N≡C deformation			1	1	1	1
Γ_{vib}	3	3	2	3	6	3

TABLE 2

VIBRATIONAL FREQUENCIES OF THE $[Re(CNC)_6]$ MOIETIES OF $[Re(CNR)_6]^+$ (cm^{-1})[a,b]

Assignment	Activity	R = Me	R = Ph	R = 4-MeC_6H_4
ν(N≡C) A_{1g}	R	2209(13) (2214,34,pol, ρ = 0.02)	2182(18) (2188,26,pol, ρ = 0.08)	2178(21) (2186,36,pol, ρ = 0.02)
ν(N≡C) E_g	R	2136(100) (2141,100,dp, ρ = 0.74)	2095(100) (2107,100,dp, ρ = 0.75)	2099(52) (2106,82,dp, ρ = 0.74)
ν(N≡C) T_{1u}	IR	2125vs, 1937w (2128vs, 1945vw,br)	2080vs, 2020sh (2082vs, 2018vvw)	2086vs, 2036sh
ν(Re–C) A_{1g}	R	358(14)	273(2)	276(2)
ν(Re–C) E_g	R	235(7)	250(2)	
ν(Re–C) T_{1u}	IR	293m	217m	210ms
ν(C–N) A_{1g}	R	977(12) (979,3,pol)	[c]	[c]
ν(C–N) E_g	R	957sh	[c]	[c]
ν(C–N) T_{1u}	IR	950m, 909w	[c]	[c]
δ(ReCN) T_{2g}	R	464(5)	551(6) (552,20,dp, ρ = 0.72)	(550,1,dp)
δ(ReCN) T_{1u}	IR	544vs	544ms (548s)	542ms
δ(CReC) T_{2g}	R	129(15)		131(1)
δ(CReC) T_{1u}	IR	100sh		

[a] The intensities of the Raman bands are quoted relative to a strongest band for the whole complex of 100 units. Results are mainly from solid state spectra, but solution results, (CH_2Cl_2 except for solution Raman of R = Me which was run in MeCN), are given in parentheses. Solution results are presented in the order: frequency, relative intensity, polarization measurement. [b] For δ(CNC) assignments see text and Tables 4 and 5. [c] For ν(C–N) of R = Ph and 4-MeC_6H_4 complexes see text and Table 5.

TABLE 3

FREQUENCIES OF THE PF_6^- VIBRATIONS OF $[Re(CNR)_6]PF_6$ (cm^{-1})[a]

Assignment	Activity	R = Me solid	R = Ph solid	R = Ph CH_2Cl_2 soln	R = 4-MeC_6H_4 solid
ν_1 A_{1g}	R	738(7)[b]	739vw	741vw	740(4)
ν_2 E_g	R	563vw	564[c]	566[c]	565(2)[d]
ν_3 T_{1u}	IR	880sh, 855sh, 836vs	875m, 842vs 835sh, 823sh	842vs	879m, 844vs, 816sh, 811s
ν_4 T_{1u}	IR	558s	556ms	560sh	555s
ν_5 T_{2g}	R	473w	479vw	475vw	452(2)[d]

[a] The intensities of the Raman bands are quoted relative to a strongest band for the whole complex of 100 units. [b] Polarized band ($\rho = 0.10$) at 740 cm^{-1} in MeCN solution. [c] Coincident with an X-sensitive in-plane ring deformation mode. [d] In CH_2Cl_2 solution ν_2 and ν_5 are observed at 560 and 450 cm^{-1}, respectively.

following reasons: (1) the vibrational spectrum of the isoelectronic $[Re(CO)_6]^+$ cation has been fully assigned [11] in terms of O_h symmetry without the benefit of a structure determination, and (2) many homoleptic metal isocyanide complexes are known to contain essentially linear MCNC moieties. This feature is maintained irrespective of overall geometry, for example, in tetrahedral $[Cu(CNMe)_4]^+$ [12], square pyramidal $[Co(CNPh)_5]^+$ [13], trigonal bipyramidal $[Co(CNMe)_5]^+$ [14], octahedral $[Fe(CNMe)_6]^{2+}$ [15] and seven-coordinate $[Mo(CNMe)_7]^{2+}$ [16].

As already stated, the vibrational spectra of $[Re(CNR)_6]PF_6$ (R = Me and Ph) will be considered in greatest detail. Using the concept of isolated group vibrations, the spectra will be treated as arising from a combination of the vibrations of a $[Re(CNC)_6]$ skeleton of O_h symmetry, a PF_6^- anion also of O_h symmetry, together with either methyl groups of C_{3v} local symmetry or planar phenyl groups of C_{2v} local symmetry. The distribution of the normal modes of vibration of the $[Re(CNC)_6]$

TABLE 4

OTHER VIBRATIONAL BANDS OF $[Re(CNMe)_6]PF_6$ (cm^{-1})[a]

Assignment	Infrared		Raman	
	ν	Int.	ν	Int.
CH_3 asym. str. E			2992	3
CH_3 sym. str. A_1	2950	mw	2941	32
	2935	sh		
$2 \times CH_3$ asym. bend	2880	w	2875	2
	2472	w		
CH_3 asym. bend E	1452	mw		
	1420	sh		
CH_3 sym. bend A_1	1413	s	1413[b]	30
	1305	vw,br		
	1168	vw,sh		
CH_3 rock E	1155	vw		
	775	vw		
	494	w		
δ(CNC) T_{1u}	183	m		

[a] Solid state spectra; assignments according to the symmetry species of C_{3v} point group for CH_3 groups (except δ(CNC)). [b] 1411 cm^{-1} polarized band in MeCN solution.

TABLE 5

OTHER VIBRATIONAL BANDS OF $[Re(CNPh)_6]PF_6$ (cm^{-1})

Assignment [a]	Infrared				Raman			
	Solid		Solution		Solid		Solution	
	ν	Int	ν	Int	ν	Int	ν	Int
ν_{23} CH str. B_2	3108	vw						
ν_1 CH str. A_1					3080	sh		
ν_2 CH str. A_1	3062	vvw			3065	2	3071	4(ρ 0.04)
ν_{24} CH str. B_2							3054	2(ρ 0.74)
ν_3 CH str. A_1	3035	sh			3038	1		
$\nu_6 + \nu_{26}$	2926	vw						
	2402	vw			2401	1		
$\nu_{10} + \nu_{28}$					2288	w		
ν_5 CC str. A_1	1592	s	1593	s	1589	45	1592	95(ρ 0.49)
ν_{25} CC str. B_2	1583	m						
ν_6 CC str. A_1	1486	ms	1484	ms	1485	10	1486	18(ρ 0.38)
ν_{26} CC str. B_2	1454	w	1452	w	1454	1		
ν_{27} CC str. B_2	1310	vw,br						
ν_{28} CH in-plane def. B_2	1287	vw			1283	1		
					1232	sh	1236	4
ν_7 CN str. X-sensitive A_1	1205	vw,br			1205	20	1206	80(ρ 0.24)
ν_8 CH in-plane def. A_1	1173	mw			1167	15	1166	60(ρ 0.22)
ν_{29} CH in-plane def. B_2	1163	mw			1162	sh		
ν_{30} CH in-plane def. B_2	1071	m	1070	m				
ν_9 CH in-plane def. A_1	1025	w	1022	w	1020	sh		
ν_{10} Ring breathing A_1	1000	w	1000	w	998	7	999	35(ρ 0.11)
ν_{16} CH out-of-plane def. B_1	993	w						
ν_{13} CH out-of-plane def. A_2	960	vw			958	vw		
ν_{17} CH out-of-plane def. B_1	916	mw	910	mw	917	vw		
ν_{14} CH out-of-plane def. A_2					815	w	815	2
ν_{11} in-plane ring def. X-sensitive A_1	790	ms	788	mw	800	1	802	3(ρ 0.45)
ν_{18} CH out-of-plane def. B_1	756	s			753	w	755	3(ρ 0.75)
ν_{19} out-of-plane ring def. B_1	684	s	680	m				
ν_{31} in-plane ring def. B_2	620	vw			617	w	618	2(ρ 0.75)
ν_{12} in-plane ring def. X-sensitive A_1					564	2	566	12(ρ 0.07)
ν_{20} out-of-plane ring def. X-sensitive B_1	522	s	520	s	519	vw		
	514	sh					509	1
	491	w						
ν_{32} in-plane CN def. B_2	482	mw						
ν_{15} out-of-plane ring def. A_2	425	vw						
ν_{33} in-plane CNC def. X-sensitive B_2	328	vw			330	1		
ν_{21} out-of-plane CN def. B_1	277	w						
ν_{22} out-of-plane CNC def. X-sensitive B_1					183	3	185	5

[a] Assignments according to the symmetry species of C_{2v} point group for the phenyl groups. The numbering system relates directly to that used for free PhNC (ref. 9).

moiety according to the symmetry species of the O_h point group is given in Table 1. In Table 2, the infrared and Raman bands associated with the $[Re(CNC)_6]$ units of $[Re(CNR)_6]^+$ (R = Me, Ph and 4-MeC_6H_4) are listed.

The infrared and Raman bands assigned to PF_6^- fundamentals are listed separately in Table 3. Three Raman-active vibrations, $\nu_1(A_{1g}$, polarized), $\nu_2(E_g)$, and $\nu_5(T_{2g})$, and two infrared-active vibrations, $\nu_3(T_{1u})$ and $\nu_4(T_{1u})$, are predicted. The T_{2u} deformation (ν_6) is formally inactive [17]. All other bands observed for

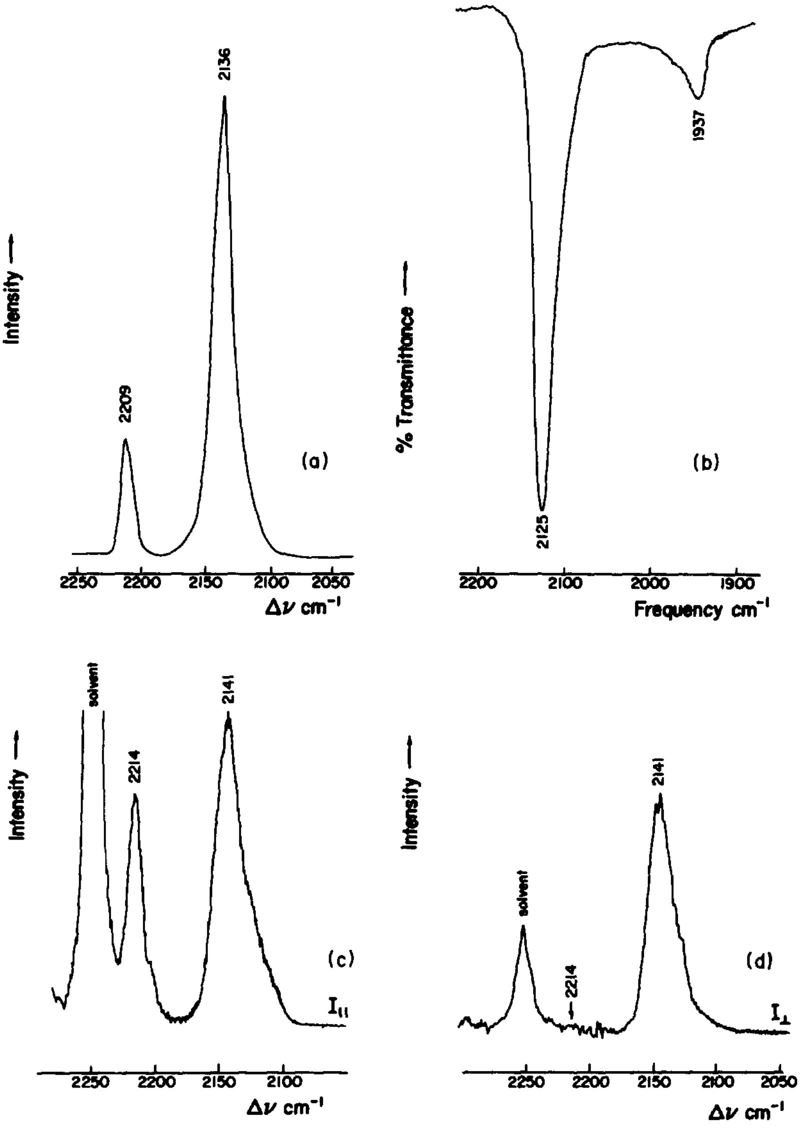

Fig. 1. Spectra of $[Re(CNMe)_6]PF_6$ in the region 2300-1900 cm^{-1}: (a) solid state Raman spectrum; (b) Nujol mull IR spectrum; (c) Raman spectrum of CH_3CN solution with parallel polarization; (d) Raman spectrum of CH_3CN solution with perpendicular polarization.

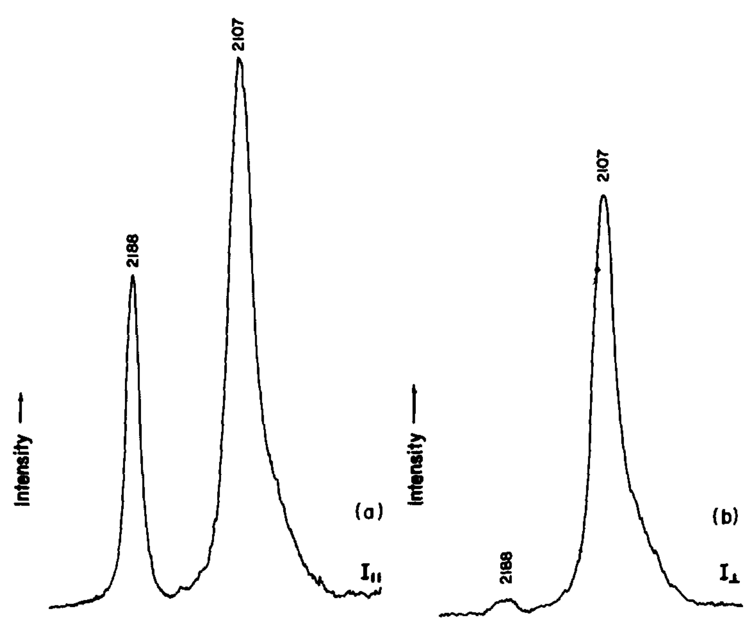

Fig. 2. Raman spectrum of CH_2Cl_2 solution of $[Re(CNPh)_6]PF_6$ in the region 2200-2000 cm^{-1}: (a) with parallel polarization; (b) with perpendicular polarization.

$[Re(CNMe)_6]PF_6$ are listed, together with proposed assignments, in Table 4, similar results for $[Re(CNPh)_6]PF_6$ being presented in Table 5. Vibrational bands of $[Re(CNC_6H_4\text{-}4\text{-}Me)_6]PF_6$ arising from motions within the aryl groups will not be discussed in any detail.

The ν(N≡C) region (2300–1900 cm^{-1}). The ν(NC) bands (Fig. 1 and 2) are, as expected, among the most intense in both the infrared and Raman spectra and present no assignment difficulties. Polarization measurements (Fig. 1c, 1d, 2a, 2b) slow clearly that the highest frequency Raman band is the A_{1g} mode and the lower frequency band the E_g mode. For each of the complexes, the infrared-active T_{1u} fundamental appears at a slightly lower frequency than the E_g and is split in a somewhat inconsistent manner. Thus, $[Re(CNMe)_6]PF_6$ displays a very strong T_{1u} band at 2125 cm^{-1} with a weak component as low as 1937 cm^{-1} (Fig. 1b), whereas, $[Re(CNPh)_6]PF_6$ and $[Re(CNC_6H_4\text{-}4\text{-}Me)_6]PF_6$ both exhibit a very strong T_{1u} band at ca. 2080 cm^{-1} with a shoulder only 50–60 cm^{-1} lower in frequency. This splitting cannot be ascribed to a solid state effect because it is also apparent in the solution spectra. It has also been observed for other $[M(CNPh)_6]$ (M = Cr, Mo, or W) [18] and $[Mn(CNR)_6]^+$ [3] species and might be related to a lowering in symmetry through the non-linearity of some of the M–C≡N–C units.

Although the ν(N≡C) frequencies vary with the nature of the organic group, ν(N≡C) of the free isocyanide always falls between the A_{1g} and E_g frequencies of the complexes. The ν(N≡C) frequencies of the phenyl and *p*-tolyl complexes are, not surprisingly, very similar. However, the ν(N≡C) frequencies of the methyl isocyanide complex are some 25–40 cm^{-1} higher than those of the aryl isocyanide complexes.

This no doubt reflects the difference in the π-acceptor ability of the alkyl versus aryl isocyanides.

In the Raman spectrum of each complex, the A_{1g} band is considerably less intense than the E_g band. Thus the generalization that totally symmetric vibrations are the most intense in the Raman spectra is not found for the $[Re(CNR)_6]^+$ cations. This anomalous feature has been previously noted for neutral metal hexacarbonyls and for $[Re(CO)_6]^+$ [11], but we believe that this is the first time that it has been reported for metal isocyanide complexes. The intensity ratios $I_\nu(A_{1g})/I_\nu(E_g)$ recorded for metal carbonyls vary from 0.08 for $[V(CO)_6]^-$ in acetonitrile to 0.15 for $M(CO)_6$ (M = Cr, Mo or W) in dichloromethane, and 0.44 for $[Re(CO)_6]^+$ in acetonitrile. The intensity ratios for the isocyanide complexes, obtained by measuring peak areas are, for example, 0.13 and 0.34 for $[Re(CNMe)_6]^+$ in the solid state (Fig. 1a) and in acetonitrile solution (Fig. 1c) respectively, and 0.18 and 0.26 for $[Re(CNPh)_6]^+$ in the solid state and in dichloromethane solution (Fig. 2a), respectively. It has been suggested [19] for metal carbonyls that these anomalous intensity ratios can be related to the feature that when the CO bonds stretch the polarizability changes along and perpendicular to the CO bond axis are of opposite sign. Commonly, for example in metal hexahalogeno-species, longitudinal and transverse bond polarizability tensor elements are believed to be of the same sign leading to intense bands corresponding to totally symmetric vibrations. Since organic isocyanides are potentially capable of synergic σ- and π-bonding comparable to carbon monoxide, similar bond polarizability changes are likely leading to the anomalous band intensities for both groups of compounds.

The ν(ReC) and δ(ReCN) region (600–200 cm^{-1}). Apart from the ν_2, ν_4 and ν_5 fundamentals of PF_6^- (Table 3), the only bands appearing in this region for $[Re(CNMe)_6]PF_6$ must be assigned to δ(ReCN) and ν(ReC) vibrations. The spectra of the aryl isocyanide complexes will contain additional aryl vibrational bands. Proposed assignments for δ(ReCN) and ν(ReC) bands are given in Table 2. In line with the assignments proposed for $[Mn(CNR)_6]^+$ (R = Me, Ph or 4-ClC$_6$H$_4$) [3,4] and $[Co(CNR)_5]^+$ (R = Me, Et or Ph) [2] and by analogy with δ(MCO) and ν(MC) band assignments of metal carbonyls, bands of higher frequency, which are usually strong in the infrared but weak in the Raman, are assigned to δ(ReCN) vibrations. Conversely, bands of lower frequency, which are weak in the infrared but somewhat stronger in the Raman, are assigned to ν(MC) vibrations. However, such an approach should be viewed with caution because for some complexes the stretching and deformation regions overlap. For example, the δ(NiCO) and ν(NiC) bands of $Ni(CO)_4$ all fall in the region 460–300 cm^{-1} [20] and the δ(AgCN) and ν(AgC) bands of $[Ag(CNMe)_4]ClO_4$ are closely grouped between 300–350 cm^{-1} and are, at best, of only moderate intensity [21]. Nonetheless, the simplistic division between deformation and stretching regions seems to hold quite well for octahedral metal carbonyls and isocyanides.

The selection rules for O_h symmetry (Table 1) predict four δ(ReCN) deformations, two inactive, one infrared-active (T_{1u}) and one Raman-active (T_{2g}). For $[Re(CNMe)_6]PF_6$ we propose that the very strong infrared band at 544 cm^{-1} can be assigned to the T_{1u} fundamental and the weak Raman band at 464 cm^{-1} to the T_{2g} fundamental. These positions and intensities are similar to those of the δ(ReCO) bands of $[Re(CO)_6]^+$ (584 and 486 cm^{-1}, respectively) [11]. However, the δ(ReCN) frequencies are markedly sensitive to the nature of the organic group of the isocyanide. The assignments of Table 2 show that although the intense infrared T_{1u} δ(ReCN) band varies little in frequency, the weaker, depolarized, Raman-active T_{2g} δ(ReCN) band shows an increase of some 85 cm^{-1} when R = Ph or 4-MeC$_6$H$_4$ relative to the R = Me species. We suspect that this shift can be interpreted as an increase in the conjugation of the N≡C group with the aryl ring, lowering the N–C bond order but increasing the Re–C bond order.

The ν(ReC) assignments are less assured. Three such fundamentals are predicted, A_{1g} and E_g which are Raman-active and T_{1u} which is infrared-active. Ideally, they are capable of unique assignment by polarization measurements, but because of the weakness of the Raman bands in the 400–200 cm^{-1} region and the presence of strong solvent bands (380 cm^{-1}, MeCN and 284 cm^{-1}, CH$_2$Cl$_2$), we have been unable to obtain useful polarization information. For [Re(CNR)$_6$]PF$_6$ (R = Me and Ph) we place the A_{1g} band at higher frequency than the E_g band, as found for [Re(CO)$_6$]$^+$ [11]. For the *p*-tolyl complex only one weak Raman-active band could be assigned to a ν(ReC) fundamental. The infrared spectra are less problematical. Only one medium to strong band is observed for each complex and this is thereby assigned to the T_{1u} fundamental. This band is some 70 cm^{-1} higher in frequency for the methyl complex than for the aryl complexes, a feature noted previously for the [Mn(CNR)$_6$]$^+$ (R = Me, Ph or 4-ClC$_6$H$_4$) cations [3].

The δ(CReC) region (below 200 cm^{-1}). Only [Re(CNMe)$_6$]PF$_6$ gave good quality infrared and Raman spectra in this region, and the bands observed at 129 and 100 cm^{-1} in the Raman and infrared spectra respectively are assigned as the T_{2g} and T_{1u} δ(CReC) fundamentals (see Tables 1 and 2). The infrared spectrum also contains a medium intensity band at 183 cm^{-1}. In line with the assignment of a strong band at 185 cm^{-1} in the infrared spectrum of [Mn(CNMe)$_6$]I [3], this band is attributed to the δ(Me–N–C) bend, much shifted from its free ligand frequency of 288 cm^{-1} [7].

The C–N stretching and bending frequencies of the R–NC bonds. The selection rules for O_h symmetry (Table 1) predict three uniquely assignable ν(CN) stretches, (IR, T_{1u}; R, A_{1g} (pol.) + E_g). The ν(CN) fundamental of free methyl isocyanide is found at 928 cm^{-1} [7] and for [Re(CNMe)$_6$]PF$_6$ a medium intensity band at 950 cm^{-1} with a weak component at 909 cm^{-1} in the infrared spectrum is assigned to the T_{1u} ν(CN) mode. A band at 977 cm^{-1} (979 cm^{-1}, polarized, in solution) and a shoulder at 957 cm^{-1} in the Raman spectrum are assigned to the A_{1g} and E_g fundamentals, respectively. The assignment of the T_{1u} δ(Me–N–C) bend to an infrared band at 183 cm^{-1} has already been mentioned.

The complexes [Re(CNR)$_6$]PF$_6$ (R = Ph or 4-MeC$_6$H$_4$) represent more difficult cases. For the phenyl complex we initially need to consider the frequency of the so-called X-sensitive ν(C–NC) band (ν_7) of free phenyl isocyanide [9] (labelled as band 19 of PhNC in [8] and as vibration *q* in the Whiffen notation [22] of mono-substituted benzenes, C$_6$H$_5$–X). For free PhNC, this band is found at 1188 cm^{-1} in the infrared and as a polarized band at 1183 cm^{-1} in the Raman (A_1 using C_{2v} point group symmetry) and is very strong in both spectra [9]. In [Re(CNPh)$_6$]PF$_6$ a band at 1205 cm^{-1} (weak in the infrared, strong and polarized in the Raman spectrum) is assigned to this X-sensitive ν_7 fundamental. This shift to higher frequency can again be related to the increased conjugation of the isocyano group with the phenyl ring on coordination of the ligand to the metal. A further, very strong infrared and polarized Raman band found nearby (1167 and 1160 cm^{-1}, respectively) in free PhNC [9] shifts only to 1173 cm^{-1} in the infrared and to 1166

cm^{-1} (polarized) in the Raman spectrum of $[Re(CNPh)_6]PF_6$. This band is therefore assigned to the X-insensitive mode ν_8 [9] (band 20 of ref. 8 or vibration *a* in the Whiffen notation [22]), an in-plane C–H deformation of A_1 symmetry, rather than to a ν(C–NC) stretch.

There are also two bending modes of the C_6H_5–NC ligand; ν_{32} is an in-plane bend of B_2 symmetry and ν_{21}, an out-of-plane bend of B_1 symmetry. In the infrared spectrum of the free ligand, ν_{32} is found at 478 cm^{-1} but ν_{21} has not positively been identified although it may be coincident with either of the X-sensitive bands ν_{33} or ν_{22} found at 325 and 162 cm^{-1}, respectively. We suggest that ν_{32} for $[Re(CNPh)_6]PF_6$ can be correlated with an infrared band at 482 cm^{-1} and ν_{21} with a weak infrared band at 277 cm^{-1}.

Using similar arguments based on assignments for *para*-disubstituted benzenes, the very strong, polarized, Raman band at 1211 cm^{-1} and the medium-weak infrared band at 1214 cm^{-1} are assigned to the A_1 X-sensitive ν(C–NC) stretch of $[Re(CNC_6H_4\text{-}4\text{-}Me)_6]PF_6$. An infrared band at 496 cm^{-1} and a depolarized Raman band at 493 cm^{-1} can be assigned to the C–NC in-plane bend, ν_{32}, of the *p*-tolyl isocyanide ligands in the complex.

The methyl vibrations of $[Re(CNMe)_6]PF_6$. Assuming isolated methyl groups of C_{3v} symmetry, one CH_3 symmetric stretch and one CH_3 symmetric bend, both of A_1 symmetry, and one CH_3 asymmetric stretch, one CH_3 asymmetric bend and one CH_3 rock, each of *E* symmetry, are predicted. All will be both infrared- and Raman active. The assignments proposed are given in Table 4 and follow those of the free ligand [7]. The A_1 modes are, as expected, very prominent in the Raman spectrum, whereas the CH_3 rock and asymmetric bending modes of *E* symmetry are only detected in the infrared spectrum. The CH_3 rock was not observed in the Raman spectrum of the free ligand [7].

The phenyl ring vibrations of $[Re(CNPh)_6]PF_6$. Assuming that the planarity of PhNC is maintained in the complex, its vibrations can be treated using C_{2v} point group symmetry. Thirty fundamentals ($11\ A_1 + 3\ A_2 + 6\ B_1 + 10\ B_2$) are predicted for the C_6H_5–N part of each ligand, all being Raman-active and all except the A_2 modes being infrared-active. Our proposed assignments are given in Table 5, the designations used relating directly to those given to the free ligand in ref. 9. The fundamentals ν_7, ν_8, ν_{21} and ν_{32} have already been discussed. The totally symmetric A_1 modes are very prominent in the Raman spectrum and easily assigned by depolarization ratios of between 0.04 and 0.49. Other Raman bands with depolarization ratios close to 0.75 are clearly associated with B_1 or B_2 modes, but several fundamentals of these symmetry classes are only observed in the infrared spectrum. The three A_2 fundamentals, ν_{13}–ν_{15}, are of extremely weak intensity and although not formally infrared-active, two are observed in the infrared spectrum, a feature previously noted for free PhNC and other mono-substituted benzenes.

The proposed assignments of Table 5 take account of the feature that 24 of the 30 normal modes of a mono-substituted benzene C_6H_5–X have reasonably constant frequencies irrespective of the nature of X [22]. The five ν(CC) bands (ν_5 and ν_6, A_1; ν_{25}, ν_{26} and ν_{27}, B_2) fall into this category, all appearing in the infrared spectrum, but only three in the Raman spectrum. The two intense A_1 fundamentals are easily assigned by depolarization measurements, although the ρ values are well above zero, as found for the free ligand [9]. The five ν(CH) bands (ν_1, ν_2 and ν_3, A_1; ν_{23} and ν_{24}, B_2) are also X-insensitive, but are rather arbitrarily assigned as a result of their very weak intensity in the infrared spectrum. Our assignments follow those given for the free ligand [9]. There are also five CH in-plane deformations. Four are insensitive to the nature of X (ν_8, ν_9, ν_{29} and ν_{30}) and are assigned to bands between 1173 and 1025 cm^{-1}, ν_{30} not being observed in the Raman spectrum. The remaining fundamental of this type, ν_{28}, is usually found as a weak infrared and Raman band in mono-substituted benzenes between 1250 and 1350 cm^{-1}, hence the band at 1287 cm^{-1} in the complex is so assigned. The final in-plane deformation, ν_{33}, is a C–NC bend and is one of the six X-sensitive modes. It shifts, for example, from 209 cm^{-1} in triphenylphosphine to 381 cm^{-1} in phenyl cyanide. We suggest that the very weak infrared band at 328 cm^{-1} (330 cm^{-1} in the Raman) can be attributed to ν_{33} of the complex.

Of the four in-plane ring deformations (ν_{10}, ν_{11} and ν_{12}, A_1; ν_{31}, B_2), the ν_{10} mode is usually described as the ring breathing vibration. This X-insensitive mode can be correlated with an intense, polarized, Raman band (weak in the infrared) at 999 cm^{-1}. The ν_{11} mode is X-sensitive, being coupled with the already discussed ν_7. A band at 761 cm^{-1} in free PhNC is assigned to ν_{11}, and since the only polarized Raman band of the complex between 999 and 566 cm^{-1} is found at 802 cm^{-1}, this must similarly be assigned to ν_{11}. The ν_{12} mode is also X-sensitive, the only polarized Raman band of the free ligand between 300 and 530 cm^{-1}, at 469 cm^{-1}, being assigned to this fundamental [9]. Analogously, the only polarized Raman band of the complex below 800 cm^{-1} is found at 566 cm^{-1} and so is assigned to ν_{12}. Finally, since ν_{31} is X-insensitive and found at 613 cm^{-1} for PhNC and 618 cm^{-1} for PPh_3, it is logical to assign the depolarized Raman band at 618 cm^{-1} for the complex to this fundamental.

Turning to the nine out-of-plane vibrations, five are CH bends, three are ring deformations and one is best described as a C–NC deformation. Of the five out-of-plane CH bends, the two A_2 fundamentals, ν_{13} and ν_{14} have already been discussed. The remaining three, ν_{16}–ν_{18}, are B_1 fundamentals and X-insensitive and pose no assignment problems, their frequencies being within 4 cm^{-1} of their positions in free PhNC [9]. Of the three out-of-plane ring deformations, ν_{15} (A_2) has already been considered. The band at 684 cm^{-1} in the infrared spectrum of the complex and 680 cm^{-1} in the infrared spectrum of the free ligand is assigned to ν_{19} (B_1). The other B_1 fundamental, ν_{20}, is X-sensitive, bands at 512 cm^{-1} for PhNC, 420 cm^{-1} for $PhNO_2$ and 548 cm^{-1} for PhCN being assigned to this mode. In the complex, the strong infrared and very weak Raman band at 520 cm^{-1} is assigned to ν_{20}.

The remaining band of the thirty fundamentals of the C_6H_5–N moiety, ν_{22}, is the X-sensitive out-of-plane C–NC deformation of B_1 symmetry. A depolarized Raman band at 162 cm^{-1} has been assigned as ν_{22} for free PhNC. The only Raman band in this region for the complex, apart from bands assigned to ν(ReC) vibrations, is found at 185 cm^{-1} and so is assigned to this fundamental.

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