Studies on Transition-metal Cyano-complexes. Part 4.[1] Cyanide Hydride Complexes of Groups 6A and 8

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The new complex $K_4[MoH(CN)_7]\cdot2H_2O$ and its characterisation by ^1H, ^{13}C n.m.r. and vibrational spectra are reported. Vibrational and n.m.r. data are also presented for $[MH(CN)_5]^{3-}$ (M = Rh or Ir). Attempts to prepare other cyanide hydride species are discussed. Reactions of the above species with small molecules and unsaturated hydrocarbons are reported.

We recently reported the isolation of $K_5[W(CN)_7]\cdot H_2O$ and $K_4[WH(CN)_7]\cdot2H_2O$, the first heptacyano-complex of tungsten and the first eight-co-ordinate cyanide hydride respectively.[1] We continue our studies on cyanide hydride species and on seven- and eight-co-ordination in cyanide complexes by reporting the isolation of $K_4[MoH(CN)_7]\cdot2H_2O$, briefly described in a preliminary note.[2] We also report further studies on the pentacyanohydrido-complexes of rhodium and iridium, extending our preliminary communication on the *X*-ray crystal structure and ^{13}C n.m.r. spectrum of the anion $[RhH(CN)_5]^{3-}$.[3] Studies on some other cyanide hydride complexes have been undertaken, and reactions of these complexes described. Vibrational data for $K_4[Mo(CN)_7]\cdot2H_2O$ are compared with those of $[Mo(CNBu^t)_7][PF_6]_2$ in an attempt further to elucidate the structure of the $[Mo(CN)_7]^{4-}$ anion in the solid potassium salt.

Results and Discussion

Potassium Heptacyanohydrogenmolybdate(II), $K_4[MoH(CN)_7]\cdot2H_2O$.—Careful treatment of an ice-cold aqueous solution of $K_5[Mo(CN)_7]$ with acetic, hydrochloric, or ascorbic acid, or hydrogen sulphide, gave crystals of the dark green diamagnetic salt which gave analyses corresponding to $K_4[MoH(CN)_7]\cdot2H_2O$. The salt was also obtained in a similar manner to $K_4[WH(CN)_7]\cdot2H_2O$ by treating $K_4[Mo(CN)_8]\cdot2H_2O$ with molecular hydrogen at 400 °C, but this leads to a product contaminated with $K_5[Mo(CN)_7]$. Nevertheless, the material described as $K_3[Mo(CN)_6]$ in the literature[4] has a similar i.r. spectrum to $K_4[MoH(CN)_7]\cdot2H_2O$ and is prepared by this hydrogenation procedure; we suggest that it is in fact an impure form of the hydride. Similarly, '$K_4[Mo(CN)_6]$' has a similar i.r. spectrum to $K_5[Mo(CN)_7]$.

(*i*) *Carbon*-13 *and* ^1H *n.m.r. spectra of* $[MoH(CN)_7]^{4-}$. The ^{13}C n.m.r. spectrum[2] without proton decoupling of an aqueous solution of $[MoH(CN)_7]^{4-}$ shows a doublet at δ 162.9 and 162.7 p.p.m., $J(^{13}C-^1H)$ 11.3 Hz, which collapses to a singlet at δ 163.1 p.p.m. on proton decoupling. The ^1H n.m.r. spectrum of the same solution shows a resonance at δ 2.3 p.p.m.; a similar proton shift was observed for aqueous solutions of $[WH(CN)_7]^{4-}$.[1] On addition of strong base to the solution, the ^{13}C and ^1H n.m.r. resonances are reduced in intensity, the colour changes to yellow, and $K_5[Mo(CN)_7]$ may be precipitated by the addition of ethanol. No proton resonance was observed for a solution of $[MoH(CN)_7]^{4-}$ in ^2H_2O, suggesting that, as with the tungsten analogue, rapid exchange with ^2H_2O occurs.

The ^{13}C n.m.r. spectrum without proton decoupling of an aqueous solution of $[Mo(CN)_7]^{5-}$ (0.2 mol dm^{-3}) in CN^- (0.01 mol dm^{-3}) shows, in addition to the hydride species, a resonance at δ 167 p.p.m. due to free CN^- and a broad resonance at δ 189 p.p.m. which we attribute to $[Mo(CN)_7]^{5-}$. On addition of base to the solution, the doublet at δ 163 p.p.m. disappears and we believe that this behaviour may arise from equilibrium (1),

$$[MoH(CN)_7]^{4-} + OH^- \rightleftharpoons [Mo(CN)_7]^{5-} + H_2O \quad (1)$$

analogous to that observed for $[WH(CN)_7]^{4-}$.[1] We were unable to obtain a value for *K* for this equilibrium from the n.m.r. spectra due to traces of the paramagnetic molybdenum(III) species, $[Mo(CN)_7]^{4-}$.

(*ii*) *Vibrational spectra*. Raman and i.r. spectra (Table) of solid $K_4[MoH(CN)_7]\cdot2H_2O$ show, in addition to bands in the ν(CN) region, bands at 1 805 and 860 cm^{-1}. The band at 1 805 cm^{-1} shifts to 1 830 cm^{-1} in aqueous solution in both i.r. and Raman. We assign these bands to the Mo–H stretch and deformation respectively; on deuteriation of the complex they shift to 1 305 and 625 cm^{-1}. The profiles of the Raman spectra change little between the solid and solution, suggesting that the stereochemistry of the anion is maintained. The profiles are similar to those of $K_4[WH(CN)_7]\cdot2H_2O$[2] and *X*-ray diffraction studies have shown the compounds to be isomorphous.

By measuring the Raman spectra of a number of aqueous solutions of known initial concentrations of $[Mo(CN)_7]^{5-}$ (containing 0.60 mol dm^{-3} SO_4^{2-}) with known added amounts of HCl (from 0 to 5 mol dm^{-3}) at a constant total ionic strength of 6.0 mol dm^{-3} at 25 °C, a value of $K = (2.5 \pm 0.2) \times 10^{-3}$ dm^3 mol^{-1} for equation (1) was obtained. Areas under the peak at 2 107 cm^{-1} of $[MoH(CN)_7]^{4-}$ and that at 1 980 cm^{-1} of $[Mo(CN)_7]^{5-}$ were used to determine the concentrations of the two species. The intensity of the peak at 928 cm^{-1} (ν_1) of SO_4^{2-} was used as an internal reference for the study. Three spectra are shown in Figure 1. In (*a*) there is almost pure $[Mo(CN)_7]^{5-}$; in (*c*) almost pure $[MoH(CN)_7]^{4-}$, and in (*b*) approximately equal concentrations of both species. From this value of *K*, the pK_a of $[MoH(CN)_7]^{4-}$ is 16.6 so it is a weaker acid than $[WH(CN)_7]^{4-}$[1] (pK_a 14.4). Other comparative data for the acid strengths of second- and third-row hydride complexes are lacking but $[CoH(CN)_5]^{3-}$[5] (pK_a 20.0) is a weaker acid than $[RhH(CN)_5]^{3-}$ (pK_a 18.0).[6]

(*iii*) *Electrochemical studies*. Cyclic voltammetry of an aqueous solution of $[Mo(CN)_7]^{5-}$ in 0.1 mol dm^{-3} KCN (pH 12.0) gave a reversible oxidation at −0.97 V [*vs.* saturated calomel electrode (s.c.e.)] to $[Mo(CN)_7]^{4-}$; the latter species may be isolated from the green solution after such voltammetry. Similarly, a reversible oxidation of $[W(CN)_7]^{5-}$ was observed at −0.98 V (*vs.* s.c.e.). This indicates the presence of the new complex $[W(CN)_7]^{4-}$, and studies are in progress to isolate it.

(*iv*) *Chemical reactions of* $[MoH(CN)_7]^{4-}$. We have shown that $[WH(CN)_7]^{4-}$ will stoicheiometrically hydrogenate dienes,[1] cyclohexa-1,3-diene and cycloheptadiene giving cyclohexene and cycloheptene in 50 and 25% yields respectively. Solutions of $[MoH(CN)_7]^{4-}$ in aqueous cyanide were treated with a number of unsaturated hydrocarbons in both the

Table. Raman and i.r. spectra (cm^{-1}) of cyanide hydride complexes and related species[a]

		ν(CN)	ν(M–H)	ν(MC), δ(MCN)
$K_4[MoH(CN)_7]\cdot 2H_2O$	Raman	2 118(7), 2 106(6), 2 100(9), 2 082(7)	1 805(1)	
	Raman[b]	2 123(8)p, 2 107(10)p, 2 080(9)dp, 2 065(6)dp	1 830(1)	460(1), 440(1), 390(1)
	I.r.	2 110 (sh), 2 090vs, 2 070vs, 2 060 (sh)	1 805w[c]	510w, 460w, 390m
	I.r.[b]	2 100vs, 2 080 (sh)	1 830vw	
$K_3[RhH(CN)_5]\cdot H_2O$	Raman	2 157(3), 2 147(10), 2 136(7), 2 124(2), 2 114(3)	1 980(1)br	
	Raman[b]	2 147(10)p, 2 127(5)dp, 2 119(2)dp	1 916(2)p	
	I.r.	2 138 (sh), 2 123vs, 2 110 (sh)	1 980m,br[d] [δ(Rh–H) 781m][d]	510m, 498m, 390m
	I.r.[b]	2 105vs	1 960m	
$K_3[IrH(CN)_5]\cdot H_2O$	Raman	2 154(10), 2 130(10)	2 043(3)	
	Raman[b]	2 152(10)p, 2 125(5)dp, 2 117(2)dp	2 035(1)p	
	I.r.	2 150 (sh), 2 123 (sh), 2 110w	2 040m,br[e] [δ(Ir–H) 811m][e]	855m, 537m, 515m 452m, 403m, 395m
	I.r.[b]	2 125s, 2 110vs, 2 080m	2 040m	
$K_4[Mo(CN)_7]\cdot 2H_2O$[f]	Raman	2 115w, 2 097vs, 2 080vs, 2 060w		
	Raman[b]	2 115s,p, 2 100 (sh),p, 2 063w		
	I.r.	2 110 (sh), 2 100m, 2 064vs, 2 030 (sh)		
	I.r.[b]	2 080m, 2 040m		
$[Mo(CNBu^t)_7][PF_6]_2$	Raman	2 217.5(10), 2 192(6), 2 166(9), 2 152(9), 2 142.5(8)		
	Raman[b]	2 216(10)p, 2 179(5)dp, 2 147(7)dp		
	I.r.	2 215 (sh), 2 190 (sh), 2 140vs,br, 2 055w (sh)		
	I.r.[b]	2 140vvs		

[a] Data on solids unless otherwise indicated, relative Raman intensities are given in parentheses; p = polarised, dp = depolarised. [b] Aqueous solution. [c] ν(Mo–^{2}H) 1 305 cm^{-1}. [d] ν(Rh–^{2}H) 1 430, δ(Rh–^{2}H) 581 cm^{-1}. [e] ν(Ir–^{2}H) 1 450, δ(Ir–^{2}H) 603 cm^{-1}. [f] In $CHCl_3$ solution.

presence and absence of hydrogen. The complex reacted only with phenylacetylene (see below), with cyclohexa-1,3-diene to give cyclohexene (in 10% yield), and styrene was polymerised in high yield. Neither the molybdenum nor tungsten complex is as potent a hydrogenation catalyst as $[CoH(CN)_5]^{3-}$.

With SO_2, $[MoH(CN)_7]^{4-}$ gave $K_4[Mo(OSO_2H)(CN)_7]$ characterised by elemental analyses and vibrational spectroscopy; reactions with oxygen, nitrogen oxide (NO), and hydrogen peroxide gave $K_4[Mo(CN)_8]\cdot 2H_2O$.

Group 8 *Cyanide Hydride Complexes*, $[MH(CN)_5]^{3-}$.—The cobalt complex $[CoH(CN)_5]^{3-}$ is a well known hydrogenation and hydrocyanation catalyst; many of its reactions are reported in the literature.[7] We reported in a preliminary communication[3] that the compounds originally formulated as $K_2[RhH(CN)_4(H_2O)]$ were, in fact, $K_3[RhH(CN)_5]\cdot H_2O$. The *X*-ray single-crystal structure was determined and the Rh–C distance *trans* to the hydrido-ligand found to be 2.082(4) Å, while the four equatorial Rh–C distances averaged 2.002 Å. The Rh–H distance is 1.64(4) Å, and the NC(*cis*)–Rh–H angle is 87.5°.[3]

Unlike its rhodium analogue, there has been little mention of $K_3[IrH(CN)_5]\cdot H_2O$ in the literature[8] and no controversy as to its formulation. The i.r., electronic, and proton n.m.r. spectra were recorded[8] and from the chemical shift a charge-distribution calculation was carried out using one-electron LCAO-MO theory.[9]

We report here detailed n.m.r. data, vibrational spectra, and some reactions of these complexes.

(*i*) *N.m.r. data.* Our attempts to record a ^{13}C n.m.r. spectrum of $[CoH(CN)_5]^{3-}$ were unsuccessful; a proton n.m.r. study of ^{13}C-enriched material[10] showed only a broad resonance due to the presence of paramagnetic species.

The ^{1}H n.m.r. spectrum of $[RhH(CN)_5]^{3-}$ consists of a doublet at δ −11.4 p.p.m., $J(^{103}Rh-^1H)$ 12.5 Hz; this shift is comparable with those reported by previous workers.[11-13] The complex $[IrH(CN)_5]^{3-}$ has a singlet at δ −14.7 p.p.m. The ^{1}H-coupled ^{13}C n.m.r. spectrum of an aqueous solution of $[RhH(CN)_5]^{3-}$ is shown in Figure 2(*a*). Two sets of double doublets are observed. One set at δ 149 p.p.m. arises from the CN^- group *trans* to the hydride whilst that at δ 141 p.p.m., which is four times more intense, arises from the four *cis* cyanide ligands. These doublets of doublets collapse to doublets on proton decoupling. The coupling constants are $J(^{103}Rh-^{13}C)$ 34.5, $J(^{13}C-^1H_{trans})$ 56.6, and $J(^{13}C-H_{cis})$ 5.7 Hz, the last two being in agreement with those previously obtained from the ^{1}H n.m.r. spectrum of a ^{13}C-enriched sample.[10]

It is interesting to note that the *trans*-CN resonance occurs at a lower field than that of the *cis*, a feature which we attribute to the longer *trans* Rh–C bond resulting in deshielding of the *trans* ^{13}CN. Further studies are in progress on the effect of the *trans* influence on the ^{13}C n.m.r. resonances of $[M(CN)_5X]^{n-}$ species, (M = Mo, W, Mn, Fe, Rh, Ir, Pd, or Pt; X = H, Cl, Br, I, NO, or CO).

We have recorded the ^{15}N n.m.r. spectrum of an ^{15}N-enriched sample of $K_3[RhH(CN)_5]\cdot H_2O$ prepared from 30% enriched $KC^{15}N$. The proton-decoupled ^{15}N n.m.r. spectrum showed two resonances, the first at δ −100.2 p.p.m. (relative to aqueous $^{15}NO_3^-$) and the second, which is approximately four times more intense, at −98.5 p.p.m. The linewidth, $\nu_{\frac{1}{2}}$ 3.4 Hz, indicates broadening of the peaks due to unresolved (^{103}Rh–^{15}N) coupling. The proton-coupled spectrum showed a singlet at −99.6 p.p.m. ($\nu_{\frac{1}{2}}$ = 3.4 Hz) attributable to $C^{15}N$ *cis* to the hydride and a doublet centred at −101.3 p.p.m. attributable to $C^{15}N$ *trans* to the hydride [$J(^{15}N-^1H_{trans})$ 5.0 Hz]. The ^{103}Rh–^{15}N and $^{15}N-^1H_{cis}$ couplings were too small to be resolved but are likely to be responsible for the observed line broadening. The rhodium–nitrogen coupling over two bonds, Rh–C≡N, is then 3.4 Hz, compared to direct rhodium–nitrogen coupling in $[RhH(NH_3)_5]^{2+}$ where we find $J(^{103}Rh-^{15}N)$ = 14.3 Hz and the resonance is observed at −426.0 p.p.m. Both compounds exhibit chemical shifts in the regions typical of metal–cyano-complexes (−100 to −150 p.p.m.) and metal–ammine complexes (−350 to −470 p.p.m.).[14]

The proton-coupled ^{13}C n.m.r. spectrum of $[IrH(CN)_5]^{3-}$ is illustrated in Figure 2(*b*). The structure is much simpler than that of $[RhH(CN)_5]^{3-}$. There are two doublets, one at δ 126 p.p.m. attributable to CN^- *trans* to the hydride and one at δ 120 p.p.m., which is four times more intense, attributable to the four

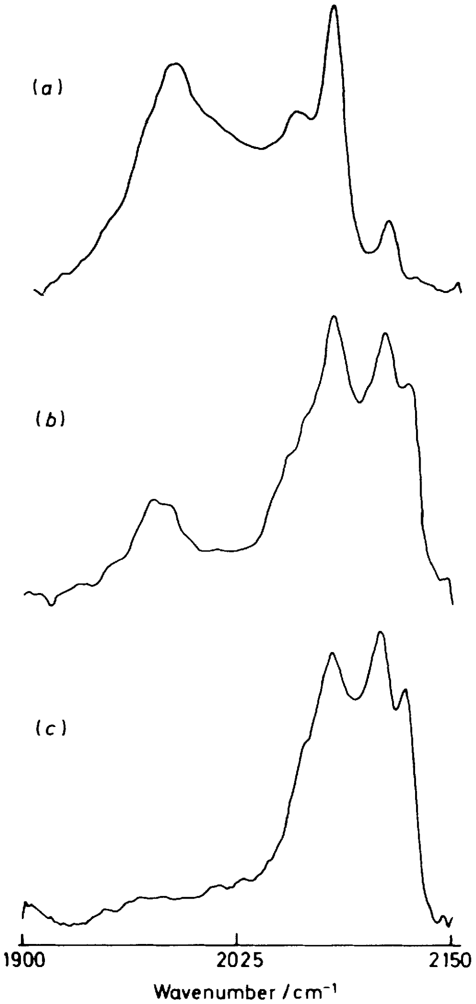

Figure 1. Raman spectra in the C≡N stretching region of $[Mo(CN)_7]^{5-}$ and $[MoH(CN)_7]^{4-}$: (*a*) total molybdenum concentration 0.05 mol dm^{-3} in 0.1 mol dm^{-3} CN^-; (*b*) as (*a*) but with 3.5 mol dm^{-3} H^+ added; (*c*) as (*a*) but with 5.0 mol dm^{-3} H^+ added

cis cyanide ligands. The coupling constants are $J(^{13}C-^{1}H_{cis})$ 5.5 and $J(^{13}C-^{1}H_{trans})$ 38.0 Hz. The *cis* coupling constant is similar to that of rhodium but the *trans* is somewhat smaller.

(*ii*) *Vibrational spectra.* Raman and i.r. data for $K_3[MH(CN)_5]\cdot H_2O$ (M = Rh or Ir) are listed in the Table. For those species with C_{4v} symmetry, three i.r.-active fundamentals ($2A_1 + E$) and four Raman-active fundamentals ($2A_1 + B_1 + E$) are expected for the ν(CN) vibrations while there will be only one i.r.- and Raman-active fundamental (A_1) for the metal–hydrogen stretch.

The solution i.r. spectrum of $[RhH(CN)_5]^{3-}$ shows only one peak at 2 105 cm^{-1}. However, for carbonyl complexes, it has been found that A_1 vibrations are higher in frequency than E modes and are either weak or unobserved;[13] this band may, therefore, be assigned as an E mode. The solution i.r. spectrum of $[IrH(CN)_5]^{3-}$, however, does show the expected three bands.

In the Raman spectra of aqueous solutions of both complexes, three of the expected four ν(CN) stretching frequencies are observed. The strongest band at 2 147 cm^{-1} (Rh) and 2 152 cm^{-1} (Ir), which is polarised, is assigned as an A_1 mode, the depolarised band at 2 127 cm^{-1} (Rh) and 2 125 cm^{-1} (Ir) as the B_1 mode, and the weak band at 2 119 cm^{-1} (Rh) and 2 117 cm^{-1} (Ir) as the E mode. Jewsbury and Maher[13] assumed that the two A_1 modes, due to CN *trans* to CN, and to CN *trans* to H, are degenerate, but this seems unlikely in view of our crystal structure determination.

It is interesting to note that the metal–hydrogen stretching frequencies increase down the Group: ν(Co–H) 1 860,[15] ν(Rh–H) 1 980, and ν(Ir–H) 2 040 cm^{-1}. This increasing M–H bond strength down the group is borne out by the lability of the hydride ligands. In $[CoH(CN)_5]^{3-}$ the hydride is readily lost, contributing to the catalytic activity of the complex; in $[RhH(CN)_5]^{3-}$ the hydride exchanges with ^2H_2O slowly over several days, whilst we find that $[Ir^2H(CN)_5]^{3-}$ may only be obtained by treating $[Ir(C_6H_8)_2Cl]$ with KCN in CH_3O^2H; no exchange is observed. Equilibrium (2) has been demonstrated[16]

$$[RhH(CN)_5]^{3-} + OH^- \rightleftharpoons [Rh(CN)_4]^{3-} + H_2O + CN^- \quad (2)$$

and the $[Rh(CN)_4]^{3-}$ anion isolated as its $[Co(en)_3]^{3+}$ (en = ethylenediamine) salt,[16] but we have found no evidence for the existence of its iridium analogue. It was not possible to study equilibrium (2) either by n.m.r. or Raman spectroscopy as the rhodium concentrations necessary to obtain good spectra would require impossibly high hydroxide concentrations.

The i.r. spectrum of 5% ^{15}N-enriched $K_3[RhH(CN)_5]\cdot H_2O$ had an extra band at 2 040 cm^{-1} in the C≡N stretching region which may correspond to the strongest band in the unenriched spectrum at 2 123 cm^{-1}.

(*iii*) *Chemical reactions of* $[MH(CN)_5]^{3-}$. The complex $[CoH(CN)_5]^{3-}$ is very reactive.[7] We find that, as expected, the reactivity decreases down the Group. Some reactions of $[RhH(CN)_5]^{3-}$ with oxygen, nitrogen oxide, and tetrafluoroethylene to give $K_4[(H_2O)(NC)_4Rh(O_2)Rh(CN)_4(H_2O)]$, $K_2[Rh(CN)_4(NO_2)(H_2O)]$, and $K_3[Rh(CN)_5(C_2F_4H)]$ respectively have been reported.[11] We find that $[RhH(CN)_5]^{3-}$ reacts with oxygen, nitrogen oxide, sulphur dioxide, and mercury(II) cyanide whilst, of these, $[IrH(CN)_5]^{3-}$ reacted only with sulphur dioxide. Reaction of $[RhH(CN)_5]^{3-}$ in aqueous solution with oxygen gave $K_4[(H_2O)(NC)_4Rh(O_2)Rh(CN)_4(H_2O)]$ as reported by Wilkinson and co-workers,[11] but we could detect no trace of a previously reported hydroperoxide.[12] Reaction with NO and SO_2 respectively yielded $K_2[Rh(CN)_4(NO_2)(H_2O)]$ and $K_2[Rh(SO_3)(CN)_3(H_2O)_2]$.

Reaction of $[CoH(CN)_5]^{3-}$ with $Hg(CN)_2$ in aqueous solution is reported to give $K_6[(NC)_5CoHgCo(CN)_5]$ *via* an intermediate species $[(NC)_5CoHg(CN)]^{3-}$.[4] We found that a similar reaction with $[RhH(CN)_5]^{3-}$ resulted in formation of $K_3[(NC)_5RhHg(CN)]\cdot H_2O$. A polarised band at 193 cm^{-1} in the Raman spectrum attributable to ν(Rh–Hg) and a doublet in the ^{199}Hg n.m.r. spectrum [$J(^{103}Rh-^{199}Hg)$ 270 Hz] indicate the presence of a rhodium–mercury bond.

Reactions were also observed with CO_2, yielding a grey solid with carbonato-bands (at 1 010, 970, 835, 770, 685, 642, and 385 cm^{-1}) in the i.r. spectrum, and with hydrogen peroxide, yielding $K_4[(H_2O)(NC)_4Rh(O_2)Rh(CN)_4(H_2O)]$ *via* an unstable peroxy-species [ν(O–O) 870, ν(CN) 2 127 cm^{-1}; % O_2^{2-} = 22.2]. Neither of these species could be reproducibly characterised; the latter may well contain H_2O_2 of crystallisation.

The reaction between $[IrH(CN)_5]^{3-}$ and SO_2 gave a product with both sulphito-bands and Ir–H bands in the i.r. and Raman spectra (see Experimental section). Microanalyses are consistent with the formulation $K_5[IrH(SO_3)_2(CN)_3]\cdot H_2O$.

Cyanide Hydrides of Other Transition Metals.—Although nickel phosphine complexes will oxidatively add HCN to yield complexes of the type $[NiH(PR_3)_3(CN)]$,[17] no cyanide hydride complex has been isolated. A species of the type $[NiH(CN)_3]^{2-}$ was proposed as an intermediate in a hydrocyanation reaction[18] but no experimental data exist. Palladium[19] and

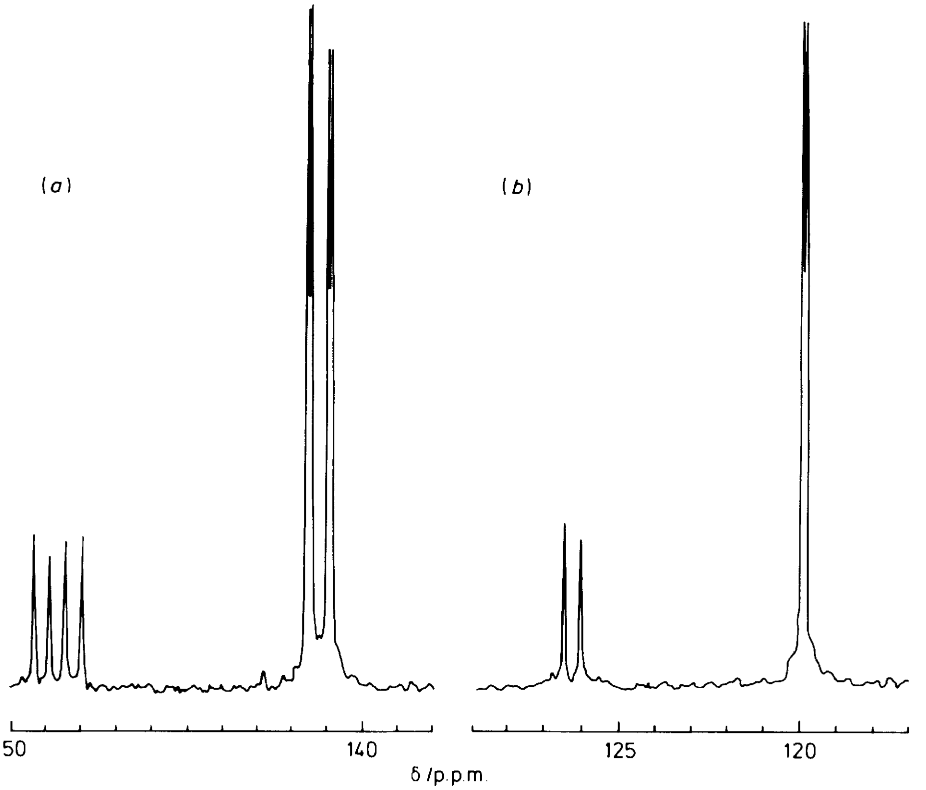

Figure 2. Carbon-13 (62.9 MHz) ^1H-coupled n.m.r. spectra (δ with respect to $Na[O_3SCH_2CH_2CH_2SiMe_3]$), with external D_2O lock, of (*a*) $[RhH(CN)_5]^{3-}$ in aqueous solution and (*b*) $[IrH(CN)_5]^{3-}$ in aqueous solution

platinum[20] species have been detected by ^1H n.m.r. spectroscopy in solution only and recently the compound $[K(18\text{-crown-6})]_2[PtH(CN)_3]$ was isolated (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane).[21]

We have been unable to isolate or detect in solution a cyanide hydride of nickel. Treatment of $[Ni(CN)_4]^{2-}$ with sodium amalgam yielded the dark red dimer $[Ni_2(CN)_6]^{4-}$. Treatment of an aqueous solution of $K_2[Pt(CN)_4]$ with sodium tetrahydroborate or sodium amalgam resulted in formation of a hydride species. In the ^1H n.m.r. spectrum a 1 : 4 : 1 triplet was observed at −8.7 p.p.m., $J(^1H-^{195}Pt)$ = 880 Hz. [Almeida and Pidcock[21] reported the ^1H resonance at −12.97 p.p.m. in 2-furyl solution, $J(^1H-^{195}Pt)$ = 738 Hz.] All attempts to record a ^{13}C n.m.r. spectrum of this solution resulted in observation of a resonance at δ 127.0 [$J(^{13}C-^{195}Pt)$ = 1 029 Hz] attributable to $[Pt(CN)_4]^{2-}$.[22] No reaction was observed between $[Pd(CN)_4]^{2-}$ and $NaBH_4$ but with sodium amalgam a ^1H resonance was observed at −10.6 p.p.m. Attempts to isolate the hydrido-species from aqueous solution invariably resulted in loss of hydrogen and precipitation of $K_2[M(CN)_4]$ (M = Pd or Pt).

Since both Group 6A (Mo or W) and 8 (Rh, Ir, Pd, or Pt) metals form cyanide hydride complexes, it seems reasonable to suppose that Group 7 metals should do so also. However we were unable to prepare a cyanide hydride complex of rhenium. Reactions of $K_5[Re(CN)_6]$ and $K_4[Re(CN)_7]$ with concentrated hydrochloric, acetic, or tetrafluoroboric acid were unsuccessful. The complex $K_5[Re(CN)_6]$ did not react with hydrogen and $K_4[Re(CN)_7]$ did not react with $NaBH_4$ or sodium amalgam.

Hydrocyanation Reactions.—The hydrocyanation of acetylenes to yield secondary saturated nitriles has been reported.[18] Phenylacetylene was catalytically converted into 2-phenylpropionitrile in 98% yield in the presence of aqueous $[Ni(CN)_4]^{2-}$, excess of cyanide, and $NaBH_4$ at 45 °C. The intermediate species postulated included $[NiH(CN)_3]^{2-}$. We duplicated these reaction conditions and followed the reaction by ^1H n.m.r. spectroscopy and gas–liquid chromatography for a number of cyano-species. The only product obtained was 2-phenylpropionitrile; ^1H n.m.r. spectroscopy of the aqueous phase showed no trace of the hydride species by the end of the reactions, *i.e.* they were not catalytic cycles. We found that $[Ni(CN)_4]^{2-}$ (75% yield of 2-phenylpropionitrile), $[RhH(CN)_5]^{3-}$ (75% yield), $[MoH(CN)_7]^{4-}$ (92% yield), and $[WH(CN)_7]^{4-}$ (94% yield) effected the transformation but $[M(CN)_4]^{2-}$ (M = Pd or Pt) and $[IrH(CN)_5]^{3-}$ did not. No reaction occurred in the absence of cyanide and/or tetrahydroborate. Addition of benzyltriethylammonium chloride as a phase-transfer catalyst had no effect on the rate of reaction.

Vibrational Spectra of $[Mo(CNBu^t)_7]^{2+}$ *and* $[Mo(CN)_7]^{4-}$.—It was suggested by Gray and co-workers[23] on the basis of e.s.r. and electronic spectral data that the anion in solid $K_4[Mo(CN)_7]\cdot 2H_2O$ was capped trigonal prismatic, a structure so far not observed in other heptacyano-complexes, and this proposal received further support from our own more extensive e.s.r. data.[1] Despite many attempts we have been unable to grow crystals of $K_4[Mo(CN)_7]\cdot 2H_2O$ suitable for *X*-ray studies. The crystal structure of $[Mo(CNBu^t)_7][PF_6]_2$ shows this to contain a capped trigonal-prismatic structure,[24] and we report here the Raman and i.r. spectra in the solid and solution states as a model for $K_4[Mo(CN)_7]\cdot 2H_2O$.

For a $[M(CN)_7]^{n-}$ or $[M(CNR)_7]^{n+}$ moiety with capped trigonal-prismatic (C_{2v}) geometry, we expect seven Raman-active modes ($3A_1 + A_2 + 2B_1 + B_2$, A_1 polarised) of which six ($3A_1 + 2B_1 + B_2$) will also be i.r. active; for a pentagonal bipyramid found in many heptacyano-complexes[1] including $NaK_3[Mo(CN)_7]$[25] there should be three Raman-active CN stretches ($2A_1' + E_1'$, A_1 polarised) and two i.r. modes ($A_2'' + E_1'$). For solid $[Mo(CNBu^t)_7][PF_6]_2$ we observe seven Raman and four i.r. bands in the CN-stretching region with three Raman–i.r. coincidences; for solid $K_4[Mo(CN)_7]\cdot 2H_2O$ there are four Raman bands and four i.r. bands again with three Raman–i.r. coincidences (Table). It therefore seems very possible that the cyano-complex does contain a similar geometry to the isocyano-one, *viz.* capped trigonal prismatic. In solution, $[Mo(CNBu^t)_7]^{2+}$ has three Raman bands (two polarised) with one broad i.r. band; if the latter envelopes the A_2'' and E_1' modes, this is consistent with pentagonal-bipyramidal symmetry; we have earlier shown that $[Mo(CN)_7]^{4-}$ has this structure in aqueous solution.[1] The ^{13}C n.m.r. spectrum[26] of $[Mo(CNBu^t)_7]^{2+}$ exhibits only one $\mathit{C}NCMe_3$ resonance at δ 164.3 p.p.m.; as with other pentagonal-bipyramidal species,[1] it is likely to be fluxional on the n.m.r. time-scale. The $CN\mathit{C}Me_3$ and $CNC\mathit{Me}_3$ resonances are at δ 57.8 and 31.0 p.p.m. respectively.

Experimental

All operations were carried out under argon unless otherwise stated. All organic solvents were dried and distilled before use. The complexes $K_5[Mo(CN)_7]\cdot H_2O$,[27] $[\{Rh(C_8H_{12})Cl\}_2]$,[28] $[Ir(C_6H_8)_2Cl]$,[29] and $[Mo(CNBu^t)_7][PF_6]_2$[30] were prepared using literature methods. Other reagents were used as supplied.

Potassium Heptacyanohydrogenmolybdate(II) *Dihydrate*, $K_4[MoH(CN)_7]\cdot 2H_2O$.—The complex $K_5[Mo(CN)_7]$ (0.72 g, 1.47 mmol) was dissolved in deoxygenated water and, with stirring and ice cooling, treated with either H_2S, L-ascorbic acid (0.1 mol dm^{-3}), acetic acid (0.1 mol dm^{-3}), or hydrochloric acid (0.1 mol dm^{-3}). The colour slowly changed from yellow to green. Addition of methanol (20 cm^3) precipitated green microcrystals which were filtered off, washed with methanol and diethyl ether, and dried *in vacuo*. The product was recrystallised from methanol–water (3:1). Yield: 0.62 g, 89.8% (Found: C, 18.7; H, 0.95; K, 32.9; N, 20.9. $C_7H_5K_4MoN_7O_2$ requires C, 17.8; H, 1.1; K, 33.2; N, 20.8%).

Potassium Heptacyano(hydrogensulphito)molybdate(IV), $K_4[Mo(OSO_2H)(CN)_7]$.—Solid $K_4[MoH(CN)_7]\cdot 2H_2O$ (0.50 g, 1.06 mmol) was dissolved in aqueous KCN solution (5 cm^3, 0.01 mol dm^{-3}) and sulphur dioxide bubbled through the solution for 30 min. Addition of ethanol precipitated the orange product which was filtered off and washed with ether. Yield: 0.44 g, 80% (Found: C, 16.2; H, 0.20; K, 30.0; N, 19.1; S, 6.20. $C_7HK_4MoN_7O_3S$ requires C, 16.3; H, 0.20; K, 30.3; N, 19.0; S, 6.20%). Infrared spectrum: 2 013vs, 1 235s,br, 1 150s,br, 1 035m,br, 965s, 600w, and 360br,m cm^{-1}.

Potassium Pentacyanohydridorhodate(III) *Monohydrate*, $K_3[RhH(CN)_5]\cdot H_2O$.—(*a*) This method is a modified version of that described by Whitesides and Maglio.[10] Potassium cyanide (2 g, 30 mmol) was added, with stirring, to methanol (80 cm^3) and the solution heated under reflux until all the solid had dissolved. Finely ground $[\{Rh(C_8H_{12})Cl\}_2]$ (0.77 g, 1.6 mmol) was slowly added to the boiling solution under nitrogen. The purple solution was heated under reflux for 15 min, cooled, and the greyish precipitate filtered off, washed with ethanol and ether. The crude product was dissolved in the minimum volume of water and reprecipitated with ethanol yielding a white product which was filtered off, washed with ether, and dried *in vacuo*. Yield: 1.0 g, 86.6% (Found: C, 16.4; H, 0.8; K, 24.3; N, 19.1. $C_5H_3K_3N_5ORh$ requires C, 16.3; H, 0.9; K, 24.6; N, 19.0%).

(*b*) This method is a modified version of that described by Wilkinson and co-workers.[11] To a solution of $[\{Rh(CO)_2Cl\}_2]$ (1.0 g, 5.3 mmol) in methanol (15 cm^3) was added a saturated aqueous solution of KCN in methanol until no more blue precipitate was obtained. To this suspension of $[\{Rh(CO)_2(CN)\}_n]$ was added a saturated solution of KCN in aqueous methanol (1:10) until evolution of carbon monoxide ceased. The white product was filtered off, washed with methanol and ether, and dried *in vacuo*. Recrystallisation from water–methanol (1:3) yielded pure product. Yield: 1.73 g, 88.7% (Found: C, 16.2; H, 0.8; K, 24.4; N, 19.1. $C_5H_3K_3N_5ORh$ requires C, 16.3; H, 0.9; K, 24.6; N, 19.0%).

Reactions of $K_3[RhH(CN)_5]\cdot H_2O$.—(*i*) *Potassium diaqua-octacyano-μ-peroxo-dirhodate*(III) *hydrate*, $K_4[(H_2O)(NC)_4Rh(O_2)Rh(CN)_4(H_2O)]\cdot H_2O$. Oxygen was bubbled through an aqueous solution of $K_3[RhH(CN)_5]\cdot H_2O$ (0.5 g) for 24 h. Addition of ethanol produced a white precipitate which was filtered off, washed with ethanol and ether, and air-dried. Yield: 70%. The same result was obtained after passing oxygen through the solution for 30 min [Found: C, 15.4; H, 0.9; K, 24.0; N, 17.5; O (peroxo), 5.6. $C_8H_4K_4N_8O_4Rh$ requires C, 15.0; H, 0.7; K, 24.5; N, 17.6; O (peroxo), 5.1%]. Infrared spectrum: 3 560s, 3 472vs [ν(O–H)], 2 123vs [ν(CN)], 1 264, 830w [ν(O–O)], 513m, 430s, 280s, and 365(sh) cm^{-1}.

(*ii*) *Potassium aquatetracyanonitrorhodate*(III), $K_2[Rh(CN)_4(NO_2)(H_2O)]$. Nitrogen oxide was passed through a solution of $K_3[RhH(CN)_5]\cdot H_2O$ (0.5 g, 1.36 mmol) in water (5 cm^3). Addition of ethanol precipitated a white solid which was filtered off and recrystallised from ethanol–water (3:1). Yield: 0.40 g, 85% (Found: C, 13.5; H, 0.4; K, 22.0; N, 20.4. $C_4H_2K_2N_5O_3Rh$ requires C, 13.8; H, 0.6; K, 22.35; N, 20.1%). Infrared spectrum: 3 450w [ν(O–H)], 2 126vs [ν(CN)], 1 400vs, 1 398vs [$\nu_{asym}(NO_2)$], 1 250vs [$\nu_{sym}(NO_2)$], and 830vs [ρ(ONO)] cm^{-1}.

(*iii*) *Potassium diaquatricyanosulphitorhodate*(III), $K_2[Rh(SO_3)(CN)_3(H_2O)_2]$. Sulphur dioxide was bubbled through a solution of $K_3[RhH(CN)_5]\cdot H_2O$ (0.5 g, 1.36 mmol) in water (5 cm^3) for 1 h. Addition of ethanol precipitated a white product (Found: C, 9.2; H, 0.7; K, 19.9; N, 11.5; S, 8.0. $C_3H_4K_2N_3O_5RhS$ requires C, 9.6; H, 1.1; K, 20.8; N, 11.2; S, 8.5%). Infrared spectrum: 2 135s, 2 127s [ν(CN)], 1 145s, 1 110vs, 1 055s, 1 050s, 975vs [ν(S–O)], 650s, 618s, 555m, 529m, 518m, 433s, 400s,br, and 355w cm^{-1}.

(*iv*) *Potassium pentacyano(cyanomercurio)rhodate*(III), $K_3[(NC)_5RhHg(CN)]\cdot H_2O$. Mercury(II) cyanide (0.1 g, 0.4 mmol) was added to an aqueous solution of $K_3[RhH(CN)_5]\cdot H_2O$ (0.28 g, 0.8 mmol) under argon. No immediate reaction was observed and the solution was stirred overnight. Addition of ethanol produced a white precipitate which was filtered off, washed with ethanol, and dried *in vacuo* (Found: C, 12.2; H, 0.1; K, 19.5; N, 13.9. $C_6H_2HgK_3N_6ORh$ requires C, 12.1; H, 0.3; K, 19.7; N, 14.1%). Infrared spectrum: 2 145w (sh), 2 135s, 2 100s [ν(CN)], 1 155, 970, 524, 510, 440, 390, and 330 cm^{-1}. Raman spectrum (in aqueous solution, relative intensities in parentheses): 2 170(6)p, 2 144(10)p, 2 124(4)dp, 2 118(3)dp [ν(CN)], and 193(4)p cm^{-1} [ν(Rh–Hg)].

Potassium Pentacyanohydridoiridate(III) *Monohydrate*, $K_3[IrH(CN)_5]\cdot H_2O$.—This method is a modification of that described by Krogmann and Binder.[8] The complex $[Ir(C_6H_8)_2Cl]$ (0.4 g, 1.0 mmol) was slowly added to a refluxing solution of KCN (0.67 g, 10 mmol) in methanol (20 cm^3). The mixture was refluxed with stirring for 2 h under nitrogen during which time the product precipitated. The mixture was cooled and the white precipitate filtered off, washed with methanol and ether, and dried *in vacuo*. The product was recrystallised from methanol–water (3:1). Yield: 0.36 g, 82% (Found: C, 13.1; H, 0.6; K, 25.1; N, 14.8. $C_5H_3IrK_3N_5O$ requires C, 13.1; H, 0.7; K, 25.5; N, 15.3%).

Potassium Tricyanohydridobis(sulphito)iridate(III) *Hydrate*,

$K_5[IrH(SO_3)_2(CN)_3]\cdot H_2O$.—The complex $K_3[IrH(CN)_5]\cdot H_2O$ (0.5 g) was dissolved in the minimum volume of water and SO_2 bubbled through the solution for 1 h. Addition of ethanol precipitated a white product which was filtered off, washed with ethanol and ether, and dried *in vacuo* (Found: C, 5.1; H, 0.5; K, 29.5; N, 6.5; S, 8.7. $C_3H_3IrK_5N_3O_7S_2$ requires C, 5.6; H, 0.5; K, 30.3; N, 6.5; S, 9.9%). Infrared spectrum: 2 150(sh), 2 125s, 2 110vs, 2 100s [ν(CN)], 2 040w [ν(Ir–H)], 1 195s, 1 175vs, 1 115m, 1 095s, 1 060m, 1 055m, 970vs [ν(S–O)], 655s, 567s, 511s, 440s, and 430m cm^{-1}.

Hydrocyanation Reactions.—In a typical reaction, $K_3[RhH(CN)_5]\cdot H_2O$ (0.3 g, 0.8 mmol) in water (4 cm^3) with KCN (0.01 g, 1.6 mmol) and $NaBH_4$ (0.008 g, 1.6 mmol) was added with vigorous stirring to 1.6 mmol of the diene/acetylene at 45 °C under N_2. After 30 min the organic layer was separated and analysed.

Raman spectra were measured on a Spex Ramalog 5 instrument (model 14018) using the exciting line at 568.2 nm obtained from a Coherent model 52 krypton ion laser. Data were collected using a GaAs photomultiplier tube coupled to a Spex Datamate computer system. Solids were taken as spinning KBr discs or in capillaries under nitrogen and solutions in a spinning cell under nitrogen.

Infrared spectra were measured on a Perkin-Elmer 683 instrument for mulls in liquid paraffin between caesium iodide plates, or aqueous solutions between calcium fluoride plates. Proton n.m.r. spectra were measured on a Perkin-Elmer R32 90 MHz instrument, ^{13}C and ^{15}N n.m.r. spectra on a Bruker WM 250 Fourier-transform spectrometer (5.9 T). Carbon-13 n.m.r. spectra were recorded at 62.9 MHz (using broad-band proton decoupling as required): digital resolution *ca.* 2 Hz per point; chemical shift reference nominally to external $Na[O_3SCH_2CH_2CH_2SiMe_3]$ in ^2H_2O.

Nitrogen-15 n.m.r. spectra were recorded at 25.4 MHz (decoupling as before). The sample showed a fairly large nuclear Overhauser effect: digital resolution 1 Hz per point, 0.3 Hz per point (not decoupled); similar resolution for line broadening; shift reference external NO_3^- of a saturated aqueous solution of NH_4NO_3. Data were multiplied by an appropriate exponential function before transformation to obtain the optimum signal-to-noise ratio. Microanalyses were performed by Mr. K. Jones of the Imperial College Microanalytical Department and Pascher (Bonn); potassium was determined gravimetrically.

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