Inorg. Chem. **1982**, *21*, 2521–2523

Table II. Octahedral Crystal Field Parameters (cm^{-1}) for V(II) and Ti(II) with Various Ligands[a]

		H_2O[b]	HF	Cl^- in molten $AlCl_3$	Cl^- in crystalline NaCl[c]
V(II)	*Dq*	1235	930	800	813
	B	690	720	560	565
Ti(II)	*Dq*		1300	750	850
	B		685	615	615

[a] Free ion values of *B*: V(II) = 766 cm^{-1}, Ti(II) = 718 cm^{-1}. [b] Reference 13. [c] Calculated from the band positions given in Table I.

These available spectra are compared in Table I with those observed in AHF in the present work. The previously reported[1] shift of absorption peaks to lower energy is observed in passing from aqueous to AHF solutions, and the AHF spectra correlate well with those in molten $AlCl_3$, where an octahedral environment was assumed, and with those in NaCl, where octahedral coordination is expected. There are some limits to the possible comparisons because, as stated above, Ti^{2+} cannot exist in water and there is no report of doping of NaCl with Cr^{2+}. An extinction coefficient of about 4.5 $mol^{-1}\ dm^3\ cm^{-1}$ for the 480-nm band of the Ti^{2+} spectrum, the most novel of the spectra reported here, is typical of the magnitude expected for a d transition metal.

Comparison of the AHF spectra with those in aqueous or chloride media indicates that these divalent cations are in an octahedral environment in AHF; and on this basis the absorption peaks in AHF may be assigned as shown in Table I. With standard crystal field theory,[14] the crystal field parameters *Dq* and *B* have been calculated for Ti(II) and V(II) and are given in Table II. Cr(II) gives only one broad band in all the media given in Table I, so it is not possible to derive any crystal field parameters. All that can be said is that the absorption maximum for Cr(II) in AHF is intermediate in energy between that in water and that in molten $AlCl_3$. This is consistent with the results for V(II) where the *Dq* value for HF lies between the values for H_2O and Cl^-. In our previous paper[1] it was suggested that HF had very similar crystal field parameters to those of F^-. Unfortunately no data are available for Cr(II), V(II), or Ti(II) ions in a fluoride environment. The electronic repulsion parameter *B* does show the trend expected for a fluorine containing ligand; i.e., with HF ligands, *B* is much closer to the free ion value than for H_2O or Cl^- ligands.

The crystal field parameters of Table II will reproduce the experimental absorption peaks within a few hundred wavenumbers in each case. This is strong support for our interpretation of the spectra in AHF as being due to octahedral coordination of Cr(II), V(II), and Ti(II) by HF. However, some consideration should be given to other interpretations of the results. If HF and F^- produce rather similar crystal fields, one or, less likely, more ligands could be F^- with the remainder HF molecules. In principle the peaks in the spectrum should be split but the peaks are already broad and small splittings would not be seen. Perhaps, much less likely still, some coordination positions may be occupied by fluorines from the anions BF_4^-, AsF_6^-, or SbF_6^-.

Stable Cr(II) and V(II) solutions can be produced in AHF solutions that are only weakly acidic, i.e., where BF_3 is the Lewis acid. However, Ti(II) is not stable in these solutions or even in those in which the much stronger Lewis acid AsF_5 is used; it appears that there is an equilibrium between Ti(II) and Ti(III) in HF–AsF_5, depending on the AsF_5 concentration. A molarity of about 3 for the stronger Lewis acid SbF_5 is needed to provide stable Ti(II) solutions. It is likely that in weakly acidic HF there will be small but significant concentrations of TiF^+. This species will have a more negative reduction potential than HF-solvated Ti^{2+} and will reduce H_2F^+ to H_2, thereby being oxidized to Ti(III).

On the other hand, as the absolute concentrations of AsF_5 and SbF_5 in AHF increase, the concentrations of the uncharged pentafluorides will increase relative to the concentrations of the fluoro anions[4] which are weaker oxidants than the pentafluorides. It is postulated that, in concentrated solutions of AsF_5 and SbF_5 in AHF, Ti(II) is oxidized to Ti(III) by the pentafluorides, as reported in the Experimental Section. The oxidation of V(II) and Cr(II) by very concentrated pentafluoride solutions is believed to be of similar origin.

It is of particular interest to note that AHF as a solvent appears able to provide stable solutions containing both unusually high oxidation states, e.g., Ni(IV) as NiF_6^{2-},[15] and unusually low oxidation states, e.g., Ti(II). This can be rationalized by recognizing that it has been demonstrated voltammetrically that the useable potential range in AHF is at least 4.5 V[16,17] between H_2 and F_2 evolution compared with an aqueous range of about 2 V for water reduction and oxidation.

Acknowledgment. We acknowledge financial support from the Australian Research Grants Committee, especially for the award of a Graduate Research Assistantship (R.W.C.).

Registry No. Cr, 7440-47-3; V, 7440-62-2; Ti, 7440-32-6; AHF, 7664-39-3.

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^{15}N Chemical Shifts and ^{13}C–^{15}N Coupling Constants of Cyanide Complexes

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The nuclear magnetic resonance (NMR) technique has been applied to the study of the structure and dynamic processes of molecules in solution.[1] Especially, the use of ^{13}C magnetic resonances has become extensive as a spectroscopic tool for the investigation of metal complexes with carbon-containing ligands. We have already reported the electronic structures of octahedral, hexacyano complexes as well as other types of cyanide complexes.[2-5] It is of interest to study the relationship between the NMR spectra and the electronic structures of cyanide complexes. The ^{13}C NMR spectra of cyanide complexes have been reported by Hirota et al.[6] and Pesek et al.[7] However, no reports have been found concerning ^{15}N resonances and C–N nuclear-spin coupling constants, J_{C-N}, for cyano complexes. The data for J_{C-N} and ^{15}N and ^{13}C resonances may be useful in interpreting the NMR spectra of cyano complexes.

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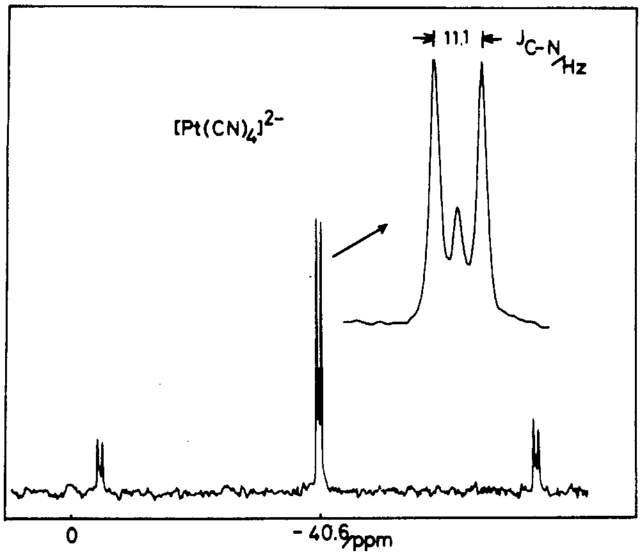

Figure 1. ^{13}C NMR spectrum of $K_2[Pt(CN)_4]$ containing isotopically enriched $^{13}C^{15}N$ in H_2O.

In this paper, we present the results of the ^{13}C and ^{15}N spectra for 13 cyano complexes.

Experimental Sections

Preparation of Compounds. All the complexes studied here are known complexes and were prepared by standard methods except for $K_4[Ru(CN)_6]$. Isotopically enriched complexes were prepared with $K^{13}C^{15}N$ (Prochem, 91.6 atom % ^{13}C and 99.9 atom % ^{15}N). Appropriate amounts of $K^{13}C^{15}N$ ($^{13}C^{15}N$:coordinated CN = 1:15) dissolved in alkaline aqueous solutions were added to aqueous solutions of $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt, Zn, Cd, and Hg) and $[M(CN)_2]^-$ (M = Ag and Au), from which isotopically enriched complexes were then isolated. So that $[Cu(CN)_4]^{3-}$ could be produced, a small quantity of $K[Cu(CN)_2]$ was treated with a stoichiometric amount of KCN containing about 20% $^{13}C^{15}N$. Stoichiometric amounts of $HgCl_2$ and KCN (20% $^{13}C^{15}N$) yield isotopically enriched $[Hg(CN)_2]$. A sample of $K_4[Fe(CN)_6]$, 9% enriched with $^{13}C^{15}N$, was prepared by adding a concentrated aqueous solution of $FeCl_2$ to a boiling aqueous solution containing KCN and $K^{13}C^{15}N$ (10:1). The product was precipitated with ethanol and purified by reprecipipation from its aqueous solution with ethanol. Isotopically enriched $K_4[Os(CN)_6]$ (9% $^{13}C^{15}N$) was prepared by dissolving K_2OsO_4 in an aqueous solution of KCN and $K^{13}C^{15}N$ (10:1). The solution was evaporated to dryness with due care to avoid fusion. The resulting colorless solid was dissolved in water, and enriched $K_4[Os(CN)_6]$ was precipitated with the addition of ethanol and purified by repricipitation from an aqueous solution with ethanol. Isotopically enriched $K_4[Ru(CN)_6]$ (16% $^{13}C^{15}N$) was prepared by a modified standard method.[8,9] A mixture of 0.05 g of ruthenium metal, 0.1 g of KNO_3, and 0.5 g of KOH was fused for 30 min in a silver crucible. The resulting black compound was dissolved in water to give a red solution. The solution was heated to boiling, treated with potassium cyanide (0.3 g of KCN and 0.06 g of $K^{13}C^{15}N$), and rapidly evaporated to dryness. The resulting colorless product was dissolved in water and precipitated with ethanol and purified by reprecipitation.

The NMR spectra showed that the compounds are of satisfactory purity for our present purpose; the chemical shifts agreed with the literature values (except for the cases described in the following section).

Table I. Coupling Constants and Chemical Shifts of ^{13}C and ^{15}N Resonances for Diamagnetic Cyano Complexes in H_2O

complex	J_{C-N}[a]	$\delta(^{13}C)$[b]	$\delta(^{15}N)$[c]
Octahedral Hexacyano Complexes			
$[Fe(CN)_6]^{4-}$	6.8	11.2	-95.9
$[Ru(CN)_6]^{4-}$	8.4	-3.8	-105.7
$[Os(CN)_6]^{4-}$	9.1	-23.5	-117.1
Square-Planar Tetracyano Complexes			
$[Ni(CN)_4]^{2-}$	9.7	-30.0	-85.9
$[Pd(CN)_4]^{2-}$	9.5	-34.5	-96.4
$[Pt(CN)_4]^{2-}$	11.1	-40.6	-105.5
Linear Dicyano Complexes			
$[Ag(CN)_2]^-$	9.2	-16.0	-100.0
$[Au(CN)_2]^-$	11.1	-12.0	-108.6
$[Hg(CN)_2]$	10.8	-19.8	-97.1
Tetrahedral Tetracyano Complexes			
$[Cu(CN)_4]^{3-}$	7.8	-4.1	-103.3
$[Zn(CN)_4]^{2-}$	8.9	-19.0	-101.4
$[Cd(CN)_4]^{2-}$	7.7	-16.5	-97.8
$[Hg(CN)_4]^{2-}$	7.2	-13.1	-98.1
Free Cyanide Ion			
CN^-	6.1	0.0	-100.4

[a] Given in Hz; ±0.2 Hz. [b] Downfield to KCN; ±0.2 ppm. [c] Downfield to $NaNO_3$; ±0.2 ppm.

NMR Spectra. All NMR spectra were obtained on a JEOL FX60 spectrometer equipped with a Fourier transform accessory. Carbon-13 spectra were obtained at 36.50 MHz with 2-μs pulses and nitrogen-15 spectra at 59.50 MHz with 8-μs pulses; external deuterium oxide (D_2O) served as a lock signal. Samples in H_2O solution were run in 10-mm tubes. Measurements were made at the probe temperature (25 °C) except for the $[HgnCN)_2]$ case where a well-defined spectrum with a narrow width was obtained at about 70 °C.[7] Potassium cyanide (^{13}C) and sodium nitrate (^{15}N) were used as external references. The chemical shift, δ, is measured downfield from the reference signals.

Results and Discussion

As an example of the ^{13}C NMR spectra, the spectrum of $[Pt(CN)_4]^{2-}$ containing $^{13}C^{15}N$ is shown in Figure 1. The main signal consists of doublet $^{13}C^{15}N$ and singlet $^{13}C^{14}N$ peaks, and two signals on both sides of the main signal arise from spin coupling (J_{Pt-C} = 1029 Hz) between ^{13}C and ^{195}Pt ($S = {}^1/_2$, 33.7%). The singlet peak is not situated at the center of the $^{13}C^{15}N$ doublet but is observed in the lower field (about 0.03 ppm). This ^{15}N-isotope shift is consistent with the ^{18}O-isotope effect on the ^{13}C signals reported by Risley and Van Etten.[10] In both ^{15}N and ^{18}O cases, the heavier isotope shifted the ^{13}C signals upfield.

The $^{13}C^{15}N$ coupling constant and the chemical shifts of ^{13}C and ^{15}N signals relative to respective references are presented in Table I. The chemical shift values are the average of doublet $^{13}C^{15}N$ peaks. When references can be made to the data reported by Pesek and Mason,[7] the ^{13}C chemical shifts show a good agreement between the present and the literature values except for the case of $[Hg(CN)_2]$, where the present result is 1.8 ppm lower than the literature value. The ^{15}N chemical shifts differ from the ^{14}N shifts reported by Bramley et al.[11] This disagreement may have arisen from the difficulty in obtaining the accurate values of ^{14}N chemical shifts because of line broadening due to the ^{14}N nuclear quadrupole moment.

The ^{15}N resonances show the following orders of increasing field for complexes of each symmetry:

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$$Fe^{2+} < Ru^{2+} < Os^{2+} \text{ for } O_h$$

$$Ni^{2+} < Pd^{2+} < Pt^{2+} \text{ for } D_{4h}$$

$$Ag^{+} < Au^{+} \text{ and } Hg^{2+} < Ag^{+} \text{ for } D_{\infty h}$$

$$Cd^{2+} < Hg^{2+} < Zn^{2+} \text{ and } Zn^{2+} < Cu^{+} \text{ for } T_d$$

The ^{15}N chemical shifts show the following trends: (i) For isoelectronic complexes of the $D_{\infty h}$ and T_d geometries, a substantial shift to lower field is observed as the metal oxidation number is increased. This trend is in contrast to that of ^{13}C chemical shifts. (ii) For the complexes of each periodic family, a shift to higher field is observed in going down the periodic table except for those of the zinc family.

The results listed in Table I show that the J_{C-N} values for all the complexes are larger than that for the free CN^- and that the J_{C-N} values for complexs of each symmetry are of the following orders:

$$Fe^{2+} < Ru^{2+} < Os^{2+} \text{ for } O_h$$

$$Pd^{2+} < Ni^{2+} < Pt^{2+} \text{ for } D_{4h}$$

$$Ag^{+} < Au^{+} \text{ and } Hg^{2+} < Au^{+} \text{ for } D_{\infty h}$$

$$Hg^{2+} < Cd^{2+} < Zn^{2+} \text{ and } Cu^{+} < Zn^{2+} \text{ for } T_d$$

As to the relationship between J_{C-N} values and ^{13}C or ^{15}N chemical shifts, J_{C-N} is in most cases found to increase with the increase in the ^{13}C and/or the ^{15}N shifts to higher field (or with decreasing δ values).

The C–N force constants of the cyanide complexes are known to be in the following orders:

$$Os^{2+} < Fe^{2+} < Ru^{2+} \text{ for } O_h \qquad Ni^{2+} < Pt^{2+} \text{ for } D_{4h}$$

$$Ag^{+} < Au^{+} \text{ and } Au^{+} < Hg^{2+} \text{ for } D_{\infty h}$$

$$Hg^{2+} < Cd^{2+} < Zn^{2+} \text{ and } Cu^{+} < Zn^{2+} \text{ for } T_d$$

A correlation between the ^{15}N shift or J_{C-N} value and the C–N force constants is observed in each family except for a few cases. This relation is also found for ^{13}C chemical shifts as noted by Pesek and Mason.[7]

However, the ^{15}N shifts and the C–N force constants show the reversed trend for the isoelectronic pairs. This reversal may be correlated with the large difference in the nitrogen charge between the complexes of the isoelectronic structures with different oxidation states.

Acknowledgment. We thank Mr. Y. Masuda and Miss M. Suzuki for their help in recording the ^{13}C and ^{15}N NMR spectra.

Registry No. $[Fe(CN)_6]^{4-}$, 13408-63-4; $[Ru(CN)_6]^{4-}$, 21029-33-4; $[Os(CN)_6]^{4-}$, 19356-45-7; $[Ni(CN)_4]^{2-}$, 45042-08-6; $[Pd(CN)_4]^{2-}$, 15004-87-2; $[Pt(CN)_4]^{2-}$, 15004-88-3; $[Ag(CN)_2]^{-}$, 15391-88-5; $[Au(CN)_2]^{-}$, 14950-87-9; $Hg(CN)_2$, 592-04-1; $[Cu(CN)_4]^{3-}$, 19441-11-3; $[Zn(CN)_4]^{2-}$, 19440-55-2; $[Cd(CN)_4]^{2-}$, 16041-14-8; $[Hg(CN)_4]^{2-}$, 19426-03-0; CN^-, 57-12-5.

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Synthesis and X-ray Structural Characterization of an Ortho-Metalated Ruthenium Complex of Acetophenone

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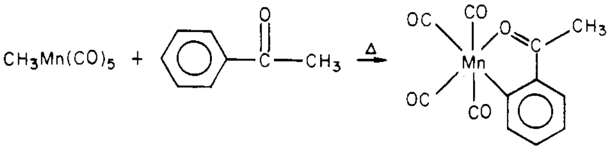
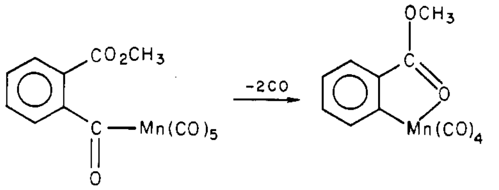
The directing effects of oxygen functional groups in the ortho metalation of aromatic rings by transition-metal complexes are now well established.[1–4] Kaesz prepared a large number of manganese compounds such as $CH_3C(\overline{O)C_6H_4}$-$\overline{Mn}(CO)_4$ by reacting $CH_3Mn(CO)_5$ with an aryl ketone (eq 1).[4] Several other compounds that contain a chelating carbonyl group, prepared via other routes, are also known.[5–10] For example, Casey prepared an ortho-metalated ester according to eq 2.[8,9]

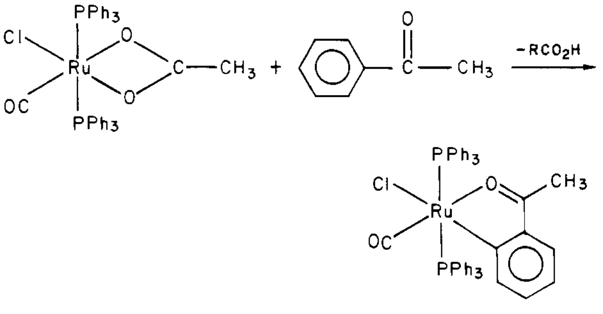


(1)



(2)

During the course of our investigation into the decarbonylation of aromatic aldehydes using Rh and Ru complexes,[11–13] we became interested in the possible existence of orthometalated aromatic aldehydes. As a model, we initially investigated the reaction of one of the catalysts with acetophenone. The reaction of $Ru[O_2C(CH_3)]Cl(CO)(PPh_3)_2$[14] with acetophenone at elevated temperatures resulted in the quantitative formation of $CH_3C(\overline{O)C_6H_4Ru}Cl(CO)(PPh_3)_2$ (**1**) according to eq 3. This new complex was characterized by ^1H and ^{31}P NMR, IR, and single-crystal X-ray diffraction. Its exchange reaction with benzoic acid has been investigated.



(3)

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Experimental Section

Reactions and Solvents. Ruthenium trichloride hydrate was obtained from Engelhard Industries. All solvents were reagent grade. Triphenylphosphine was recrystallized from ethanol. Acetophenone was

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