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Photoproduced linkage isomers of pentacarbonyl-(4-cyanopyridine)tungsten(0)

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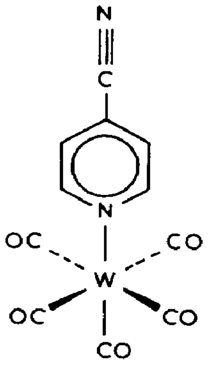
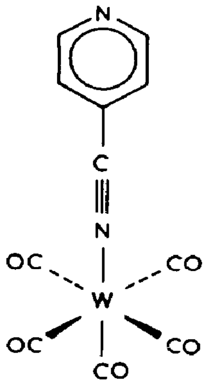
Abstract

Reaction of 4-cyanopyridine (4-CNpy) with photogenerated $W(CO)_5(THF)$ (THF = tetrahydrofuran) leads to two products both identified to be of the formula $W(CO)_5(4\text{-CNpy})$. These forms are attributed to be pyridine- and cyano-linkage isomers of $W(CO)_5(4\text{-CNpy})$ and they have been characterized by infrared and UV-visible spectroscopy. The cyano-bound isomer complex is thermally unstable in solution and converts to the pyridine-bound species by a first-order kinetic process. A kinetic analysis reveals that this thermal reaction takes place via an intramolecular mechanism.

Introduction

The subject of linkage isomerization has had a long, and often highly controversial, history in coordination chemistry. Numerous examples of linkage isomers are now recognized and this field continues to grow [1]. Recently, while investigating





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the photochemistry of $M(CO)_5L$ (M = Cr, Mo, W; L = substituted pyridine) complexes [2] we have noted that $W(CO)_5$(4-CNpy) (4-CNpy = 4-cyanopyridine) apparently exists in two forms. Here we describe the isolation and characterization of these photoproduced linkage isomers of $W(CO)_5$(4-CNpy).

The observation of both isomers provides insight into the manner by which the 4-CNpy ligand scavenges the photoproduced $W(CO)_5$(THF) (THF = tetrahydrofuran) complex.

Experimental

Materials. Tungsten hexacarbonyl was obtained from Strem Chemical Co. and used without further purification. The 4-cyanopyridine ligand was purchased from Aldrich Chemical Co. and sublimed prior to use. Tetrahydrofuran was distilled from $LiAlH_4$ and stored under argon. All other solvents used were spectroscopic grade. Neutral alumina (80–200 mesh) used in chromatography was obtained from Fisher Chemical Co. TLC analysis was carried out on pre-coated sheets of silica gel (2–25 μm particle size, 60 Å mean pore diameter) on polyester containing a 254-nm fluorescence indicator.

Synthesis. The $W(CO)_5$(4-CNpy) isomers were prepared by reacting prior photoproduced $W(CO)_5$(THF) with 4-CNpy ligand. A deoxygenated solution of $W(CO)_6$ (3 mmol) in THF (300 ml) was irradiated with a 200 W medium pressure mercury arc lamp until a deep yellow color was obtained (~ 30 min). The solution was purged with purified nitrogen [3] throughout photolysis to preclude oxidation of the metal complex. Following irradiation 4-CNpy (3 mmol) was added to the reaction vessel in the dark and the THF was removed by flash rotary evaporation below 283 K. The product is a mixture of both linkage isomers and these were separated by column chromatography on a 10 × 3 cm neutral alumina column. Elution with benzene first removes unreacted $W(CO)_6$ and subsequent elution removes the orange isomer and then the yellow isomer. The complexes were further purified by vacuum sublimation to remove any remaining unreacted starting materials. Elemental analyses were carried out by Desert Analytics of Tucson, Arizona.

Equipment. Infrared spectra were recorded on Perkin–Elmer 283B and FTIR Nicolet 20SXC spectrometers; the reported maxima are believed accurate to ± 2 cm^{-1}. UV-visible absorption spectra were recorded on a Hewlett–Packard 8450A spectrometer which incorporates a microprocessor-controlled diode array detector. The fast detector facilitated the acquisition of spectra within 5 s of complex dissolution. Reported absorption maxima are accurate to ± 2 nm. Sample solutions were filtered through a 0.22 μM Millipore filter prior to taking measurements; the solution temperature was controlled to ± 0.1 K.

Results and discussion

Isomer complexes of $W(CO)_5$(4-CNpy) were formed on reacting 4-CNpy ligand with the photochemically generated $W(CO)_5$(THF) complex in deoxygenated THF (see eqs. 1 and 2) [2,4]. TLC analysis clearly identifies two forms of $W(CO)_5$(4-CNpy), both of which

$$W(CO)_6 \xrightarrow[THF]{h\nu} W(CO)_5(THF) + CO \quad (1)$$

$$W(CO)_5(THF) \xrightarrow[4\text{-CNpy}]{\Delta} W(CO)_5(4\text{-CNpy}) + THF \quad (2)$$

appear yellow in hydrocarbon solvents. The complex isomers were readily separated on a neutral alumina column to yield products which were subsequently isolated as yellow and orange solid compounds; the compounds are moderately stable in the solid form but the yellow complex undergoes slow thermal decomposition in solution (vide infra). Melting points, elemental analyses and infrared data recorded from these materials are shown in Table 1. UV-visible spectra observed from both these $W(CO)_5(4\text{-}CNpy)$ isomer complexes in benzene are depicted in Fig. 1.

The physical data of Table 1 confirms that two stable linkage isomers have been produced. Elemental analysis values of both complexes are in accordance with the formula $W(CO)_5(4\text{-}CNpy)$ and infrared carbonyl stretching frequencies, $\nu(CO)$, are consistent with a C_{4v} local symmetry of the carbonyl ligands in each of these molecules [5]. The normally infrared inactive B_1 mode is weakly observed in the spectra of both species, indicating that in each complex there is some perturbation of the CO groups from ideal C_{4v} symmetry. The infrared results do, however, illustrate differences in the cyano group stretching vibrations, $\nu(CN)$, for these isomers. The orange complex exhibits a $\nu(CN)$ band at 2242 cm^{-1} which is relatively unmoved from that of the free ligand; this species is associated with the previously known pyridine-bound compound [2,6]. On the other hand, the yellow complex exhibits $\nu(CN)$ bands at 2245 and 2260 cm^{-1}, and this species is attributed to the cyano-bound isomer. Identical splitting of this IR band was also observed in diffuse-reflectance FTIR spectra of the solid material and in spectra of solutions that were rapidly acquired; this is apparently an intrinsic feature of the cyano-bound complex and not simply a solid state effect. The observed increase and splitting of the $\nu(CN)$ frequency for the cyano-bound complex is understood to result from an increase in the C–N stretching force constant brought about by weak coupling of the C–N and W–N vibrations [7]. Similar increases in $\nu(CN)$ have been observed on

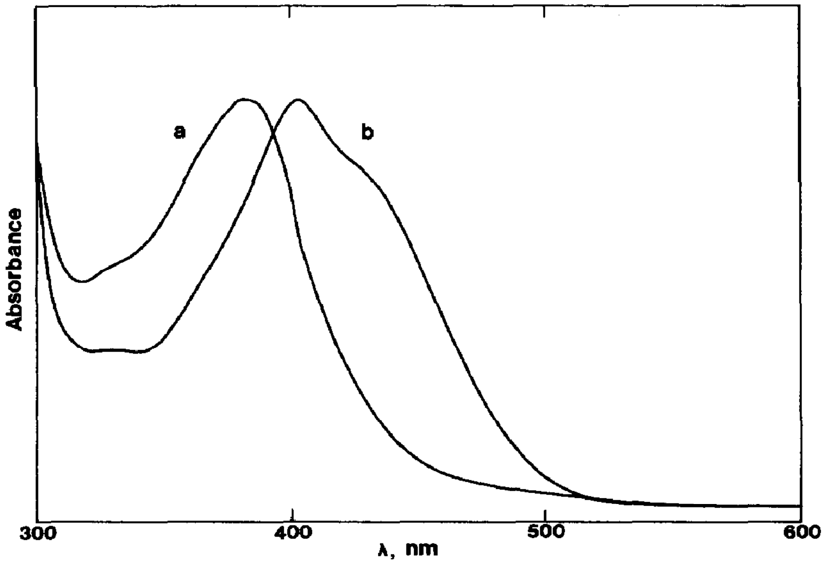


Fig. 1. UV-visible absorption spectra of (a) cyano-bound and (b) pyridine-bound $W(CO)_5(4\text{-}CNpy)$ complex isomers in benzene at 293 K. Spectra are scaled to make maximum absorbances equal.

Table 1

Colors, melting points, elemental analyses, and infrared data for the $W(CO)_5(4\text{-}CNpy)$ complex isomers and the free ligand

Compound	Color	M.p. (°C)	Elemental analysis (Found (calcd.) (%))			Infrared maxima [a]				
						ν(CN) (cm^{-1})	ν(CO) (cm^{-1})			
			C	H	N		A_1^1	B_1	E	A_1^2
Cyano-bound $W(CO)_5(4\text{-}CNpy)$	yellow	142(dec.)	30.9 (30.9)	0.8 (0.9)	6.3 (6.5)	2260, 2245	2070	1980	1920	1880
Pyridine-bound $W(CO)_5(4\text{-}CNpy)$	orange	132	30.3 (30.9)	1.0 (0.9)	6.8 (6.5)	2242	2070	1980	1922	1877
4-CNpy	white	78				2241				

[a] Infrared data recorded as Nujols mulls.

coordination of cyano groups to Lewis acids for nitriles, cyanamides, cyanogen halides and various organic cyanates [8].

Obtained UV-visible spectra (see Fig. 1) support these linkage isomer assignments. The pyridine-bound complex exhibits absorption bands at 404 and 430 nm (sh) corresponding to the ligand field (LF) ${}^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2{}^2a_1^1)$ and metal to ligand charge-transfer (MLCT) $(d\pi)W \rightarrow \pi^*$(4-CNpy) transitions, respectively, as previously noted [2,6]. However, the cyano-bound complex exhibits a single absorption band at 384 nm that is attributed to overlapping LF and MLCT bands. The MLCT band is shifted to higher energy in the latter complex because the ligand π^*-acceptor system is raised upon coordination of the cyano group to the metal center.

On standing the cyano-bound isomer complex readily decomposes in solution. Fig. 2 depicts the UV-visible absorption spectra monitored during this thermal decomposition reaction in deoxygenated benzene under dark conditions at 333 K. The observed spectral sequence indicates that the cyano-bound isomer apparently converts to the pyridine-bound isomer; this reaction appears to proceed fairly cleanly as a sharp isosbestic point was retained throughout > 75% of the conversion. In contrast, the pyridine-bound complex is much more thermally stable in 333 K solution because it suffers no significant decomposition over a 1 h period. The isomer conversion reaction was determined to be first-order, i.e., a plot of $\ln[(A_0 - A_\infty)/(A_t - A_\infty)]$ versus time is linear, with $k_{obsd} = 2.5\ (\pm 0.2) \times 10^{-4}\ s^{-1}$ at 333 K. Here A_0 is defined as the initial absorbance of the solution, A_∞ is the final absorbance, and A_t is the absorbance at various time intervals; all absorbance values being recorded at a fixed wavelength. The slope of this plot yields the observed first-order rate constant, k_{obsd}.

First-order kinetic plots were determined as a function of 4-CNpy ligand concentration, but there was no measurable effect in k_{obsd} over the 0.001–0.1 *M*

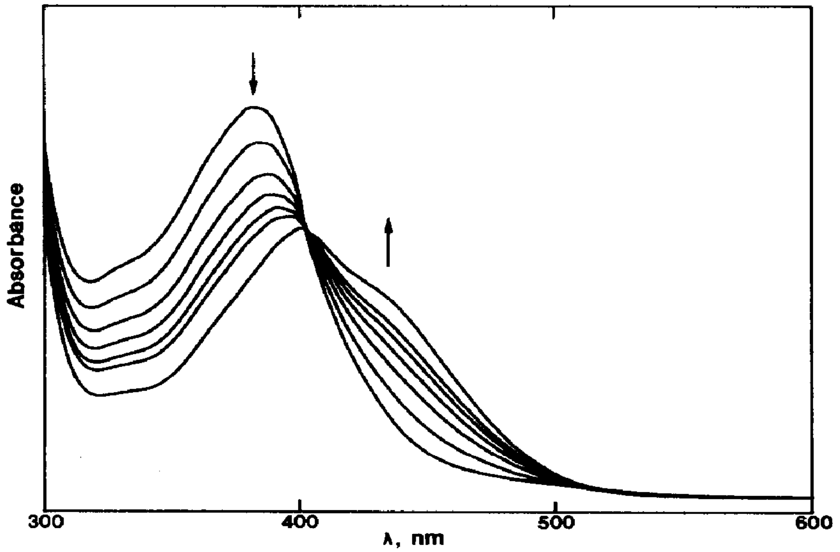
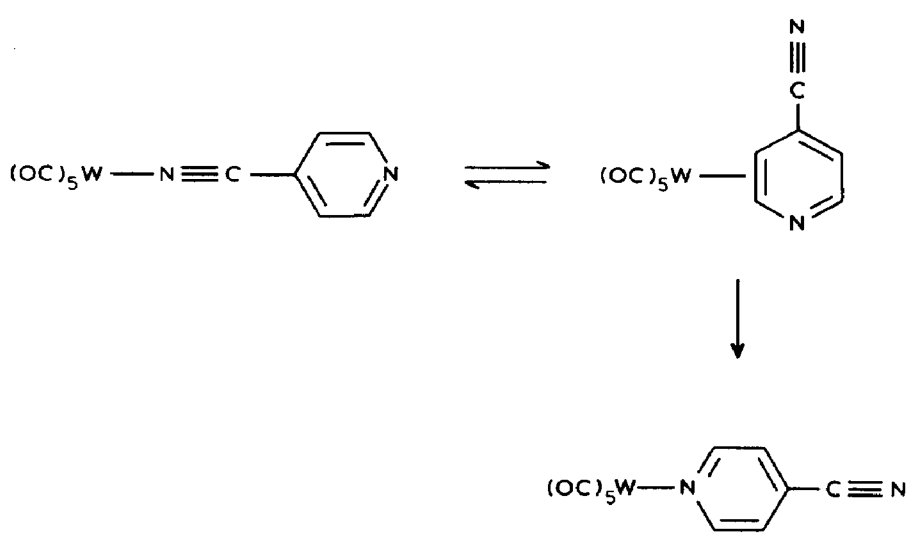


Fig. 2. UV-visible absorption spectra observed from a solution of the cyano-bound $W(CO)_5$(4-CNpy) complex in deoxygenated benzene at 333 K. Spectra are recorded at 0, 20, 40, 60, 80, 100 and 210 minutes following dissolution.



(3)

(4)

range. This result indicates that the mechanism of conversion of the cyano-bound to the pyridine-bound 4-CNpy isomers involves only the $W(CO)_5(4\text{-CNpy})$ molecules. Furthermore, the first-order rate constant was not affected through variations in the concentration of $W(CO)_5(4\text{-CNpy})$ indicating that this reaction proceeds entirely via an intramolecular mechanism. This observation, for instance, rules out mechanisms involving coordination of the cyano-bound $W(CO)_5(4\text{-CNpy})$ species with the opposite end (pyridine nitrogen) of a neighboring complex. Further details on the nature of the intramolecular isomerization mechanism are not revealed by these results. One may speculate, however, that this reaction proceeds via a η^2-arene intermediate (see eq. 3 and 4).

Photolysis at 366 nm of the cyano-bound $W(CO)_5(4\text{-CNpy})$ isomer in deoxygenated benzene results in similar isomer conversion behavior; this reaction is fairly efficient and it even takes place rapidly in room-temperature sunlight conditions. The solution photochemistry of this compound is entirely consistent with the LF reactivity characterized for a wide range of $W(CO)_5L$ species [9,10]. Further photolysis of the pyridine-bound isomer resulted in decomposition of the $W(CO)_5(4\text{-CNpy})$ complex; no evidence was obtained for a reverse photoisomerization process, even when the reaction was carried out in the presence of 0.1 *M* 4-CNpy free ligand. Presumably, the cyano-bound isomer is regenerated under such conditions, but it is more rapidly lost by thermal and photochemical isomerization than its formation rate. Indeed, the quantum efficiency of ligand photosubstitution for the pyridine-bound complex is known to be especially low because a MLCT state is at lowest energy [2a].

It was not possible to perform emission measurements on the cyano-bound $W(CO)_5(4\text{-CNpy})$ species because of the thermal chemistry and the high photoreactivity associated with this complex. Previously, the pyridine-bound isomer has been shown to emit in room-temperature solution from a lowest lying MLCT excited state [2a].

The identification of this unusual yellow compound illustrates that 4-CNpy coordinates with the photoproduced $W(CO)_5(THF)$ complex at two sites. The kinetic results demonstrate that the pyridine-bound isomer is the thermodynamically preferred form but also imply that the cyano-bound species is the kinetically favored one. Indeed, these observations can be rationalized on the basis of steric hindrance about these two coordination sites in the free ligand. The nitrogen atom of the cyano group in 4-CNpy is less sterically hindered than the pyridine nitrogen atom and it can be expected to scavenge the photogenerated $W(CO)_5(THF)$ complex more effectively. On the other hand, the pyridine nitrogen atom is of higher basicity and this accounts for the thermal stability and, thus, final formation of the pyridine-bound species.

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