Cyanide-Bridged Heterobimetallic Complexes of the Group 6 Metal Carbonyls and Copper(I). X-ray Structures of $(CO)_5MCNCu(PPh_3)_3$ (M = Cr, W) Derivatives

Donald J. Darensbourg,* Jeffrey C. Yoder, Matthew W. Holtcamp,
Kevin K. Klausmeyer, and Joseph H. Reibenspies

Department of Chemistry, Texas A&M University, College Station, Texas 77843

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The cyanide-bridged compounds $(CO)_5MCNCu(PPh_3)_3$ where M = W in **1**, and M = Cr in **2** have been prepared by the reaction of $NaM(CO)_5CN$ with $Cu(CH_3CN)_4BF_4$ and PPh_3, and their solid-state structures have been determined crystallographically. In **1**, the CN bond length was 1.15(2) Å, and the bridge was slightly bent with angles of W−C(6)−N(1) = 175.9(14)° and Cu−N(1)−C(6) = 176(2)°. Crystal data for **1**: monoclinic, space group $P2_1/n$, $a = 20.376(4)$ Å, $b = 12.436(3)$ Å, $c = 22.423(5)$ Å, $\beta = 97.28(3)°$, $Z = 4$, $R = 7.90\%$. The chromium analog, complex **2**, was isomorphous with **1**. In addition, the isocyanide-bridged complex $(CO)_5WNCCu(PPh_3)_3$ (**3**) was prepared by the reaction of CuCN with PPh_3 and $W(CO)_5(THF)$ at −78 °C. The structure of this compound was determined by infrared and ^{13}C NMR measurements. The isocyanide-bridged **3** was found to undergo thermal rearrangement to yield the cyanide-bridged **1**. In the ^{13}C NMR spectrum of **1** at room temperature, the CN peak is very broad (fwhh = 47 Hz) and can be found at 147.8 ppm. Dynamic ^{13}C NMR measurements on **1** revealed that this complex undergoes an equilibrium reaction in THF-d_8 solution. Two possibilities are presented which are consistent with the observations. One is a contact ion pair/solvent-separated ion pair exchange reaction which involves breakage of the Cu−N bond and insertion of a solvent molecule. The second is dissociation/recoordination of a triphenylphosphine ligand from Cu(I). Differentiation between the two is impossible on the basis of the available data. In the slow-exchange limit, the ^{13}CN peak of **1** is found at 149.0 ppm, shows ^{183}W satellites ($J_{WC} = 96$ Hz), and has a line width of 12 Hz. In the ^{13}C NMR spectrum of **3** at room temperature, the CN peak is sharp (fwhh = 0.75 Hz) and can be found at 160.7 ppm. Dynamic ^{13}C NMR measurements on **3** revealed no ion pair exchange as high as 40 °C. The ^{13}C NMR spectrum of $Cu^{13}CN(PPh_3)_3$ was also recorded at room temperature, and the CN peak can be found at 152.3 ppm with a line width of 15 Hz.

Introduction

Cyanide has been ubiquitous as a bridging ligand since the beginnings of coordination chemistry. At the end of the nineteenth century, Hofmann developed a series of cyanide-bridged cadmium and nickel compounds[1] which could include solvent molecules in a guest−host type relationship. This area of research has remained active into the 1990s with the synthesis of polymeric cadmium cyanide clathrates by Iwamoto.[2] Recently, cyanide-bridged, dinuclear transition metal compounds have seen application in the areas of electron delocalization and charge transfer.[3] Additionally, Holm et al. have prepared several dinuclear cyanide-bridged assemblies which mimic the active site of cyanide-inhibited cytochrome *c* oxidase.[4] There are, however, very few studies in the literature dealing with linkage isomerization of the cyanide bridge.[5−8]

Vahrenkamp has provided an excellent example of such behavior in a chromium−iron system.[5] Using $Cr(CO)_5CN^-$ as a cyanide-donating "ligand", the μ-CN complex is formed, but using Cp(dppe)FeCN as cyanide donor, the so-called μ-NC complex is obtained. There is no thermal rearrangement of the cyanide bridge observed at temperatures as high as 150 °C (at which both complexes decompose).

The pentacarbonyl cyanide fragment is of great synthetic and spectroscopic utility due to the fact that the carbonyl infrared stretching frequencies are extremely sensitive probes of the electronic structure of the complex. With this in mind, the synthesis of the cyanide-bridged complexes $(CO)_5M(CN)Cu(PPh_3)_3$ (where M = W in **1** and M = Cr in **2**) was carried out. In addition, the synthesis of the isocyanide-bridged complex $(CO)_5W(NC)Cu(PPh_3)_3$ (**3**) was carried out at −78 °C with the reaction being monitored by ^{13}C NMR. Reported here are the synthetic schemes used, X-ray crystal structures for **1** and **2**, the results of infrared studies on all compounds, and variable-temperature ^{13}C NMR studies on complexes **1** and **3**.

Experimental Section

Methods and Materials. Sodium bis(trimethylsilyl)amide (1 M solution in THF), cuprous cyanide, and triphenylphosphine were obtained from Aldrich and used without further purification. Tungsten and chromium hexacarbonyls were obtained from Strem and used without further purification. Cuprous [^{13}C]cyanide was obtained from Cambridge Isotope Labs and used as received. Copper acetonitrile

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(1) (a) Hofmann, K. A.; Küspert, F. *Z. Anorg. Allg. Chem.* **1897**, *15*, 204. (b) Hofmann, K. A.; Höchtlen, F. *Chem. Ber.* **1903**, *36*, 1149. (c) Hofmann, K. A.; Arnoldi, H. *Chem. Ber.* **1906**, *39*, 339.

(2) (a) Yuge, H.; Iwamoto, T. *J. Chem. Soc., Dalton Trans.* **1993**, 2842 and references therein. (b) Park, K.-M; Iwamoto, T. *J. Chem. Soc., Dalton Trans.* **1993**, 1876.

(3) (a) Zhou, M.; Pfennig, B. W.; Steiger, J.; Van Engen, D.; Bocarsly, A. B. *Inorg. Chem.* **1990**, *29*, 2456. (b) Agnus, Y.; Gisselbrecht, R. L.; Metz, B. *J. Am. Chem. Soc.* **1989**, *111*, 1494. (c) Burewicz, A.; Haim, A. *Inorg. Chem.* **1988**, *27*, 1611. (d) Christofides, A.; Connelly, N. G.; Lawson, H. J.; Loyns, Andrew C. *J. Chem. Soc., Chem. Commun.* **1990**, 597. (e) Scandola, F.; Argazzi, R.; Bignozzi, C. A.; Chiorboli, C.; Indelli, M.T.; Rampe, N. A. *Coord. Chem. Rev.* **1993**, *125*, 283.

(4) (a) Lee, S. C.; Scott, M. J.; Kauffmann, K.; Münck, E.; Holm, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 401. (b) Scott, M. J.; Lee, S. C.; Holm, R. H. *Inorg. Chem.* **1994**, *33*, 4651. (c) Scott, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11357.

(5) Zhu, N.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2090.

(6) Alvarez, S.; Lopez, C. *Inorg. Chim. Acta* **1982**, *64*, L99.

(7) Gaswick, D.; Haim, A. *J. Inorg. Nucl. Chem.* **1978**, *40*, 437.

(8) Fronczek, F. R.; Schaefer, W. P. *Inorg. Chem.* **1974**, *13*, 727.

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tetrafluoroborate was prepared according to literature procedures.[9] Hexane, benzene, and THF were dried in sodium benzophenone stills prior to use, and rigorous Schlenk techniques were utilized for all reactions. The sodium salts of tungsten and chromium pentacarbonyl cyanides were prepared according to published literature procedures.[10] Photolysis experiments were performed using a mercury arc 450-W UV immersion lamp purchased from Ace Glass Co. Infrared spectra were recorded on a Mattson 6021 FTIR equipped with DTGS and MCT detectors operating in absorbance mode.

Synthesis of 1 and 2, $(CO)_5M(\mu\text{-}CN)Cu(PPh_3)_3$. In a typical reaction, $Na(CO)_5MCN$ (2 mmol) (M = W, Cr) was loaded into a 100 mL Schlenk flask with a magnetic stir bar and loaded into an inert-atmosphere drybox. In the drybox, $Cu(CH_3CN)_4BF_4$ (2 mmol) was added to the flask. Tetrahydrofuran (25 mL) was then added via syringe. The resulting reaction mixture was stirred for approximately 15 min until the formation of a dark brown precipitate was complete. A solution of triphenylphosphine (6 mmol) in 10 mL of THF was then transferred via cannula to the dark brown reaction flask mixture. The resulting suspension was filtered through Celite into a 100 mL Schlenk flask to give a clear, light yellow solution of $(CO)_5MCNCu(PPh_3)_3$ (**1**, M = W; **2**, M = Cr). Anal. Calcd for $(CO)_5WCNCu(PPh_3)_3{\cdot}2C_4H_8O$ ($C_{68}H_{61}NO_6P_3WCu$): C, 60.74; H, 4.57. Found: C, 60.84; H, 4.60. IR (THF): 2121 cm^{-1} (ν(CN)), 2059 cm^{-1} (A_1), 1929 cm^{-1} (E), 1904 cm^{-1} (A_1). $^{13}C\{^1H\}$ NMR (THF-d_8, 22 °C): δ 147.8 (br, *C*N), 197.67 (*C*O_{eq}), 200.26 (*C*O_{ax}). Anal. Calcd for $(CO)_5CrCNCu(PPh_3)_3{\cdot}H_2O$ ($C_{60}H_{47}NO_6P_3CrCu$): C, 66.33; H, 4.36. Found: C, 65.70; H, 4.67. IR (THF): 2117 cm^{-1} (ν(CN)), 2056 cm^{-1} (A_1), 1934 cm^{-1} (E), 1907 cm^{-1} (A_1).

Synthesis of $CuCN(PPh_3)_3$. In a typical experiment, cuprous cyanide (0.13 g, 1.4 mmol) and three equiv of triphenylphosphine (1.12 g, 4.3 mmol) were loaded into a 50 mL Schlenk flask in an inert-atmosphere drybox. Tetrahydrofuran (30 mL) was added via syringe, and the cloudy solution was stirred until all CuCN dissolved and the solution was completely clear.

Synthesis of 3, $(CO)_5W(\mu\text{-}NC)Cu(PPh_3)_3$. Tungsten hexacarbonyl (1.4 mmol) in 65 mL of THF was irradiated with UV light in a quartz photolysis vessel for 45 min yielding an orange solution. This solution of $W(CO)_5(THF)$ was transferred via cannula into an inert, 100 mL Schlenk flask and cooled to −78 °C. CuCN (1.4 mmol) and 3 equiv of PPh_3 (4.2 mmol) were placed in a 50 mL Schlenk flask in an inert-atmosphere drybox, and THF (15 mL) was added via syringe. This slurry was stirred until all CuCN had gone into solution and then was cooled to −78 °C and transferred via cannula to the flask containing $W(CO)_5(THF)$. The resulting solution was stirred at −78 °C for 2 h and then allowed to come to room temperature. After overnight stirring, the solution was a clear yellow, and partial rearrangement of the CN bridge had occurred forming **1**, as evidenced by ^{13}C NMR. However, in the solution a substantial amount of $(CO)_5W(NC)Cu(PPh_3)_3$ (**3**) remained. IR (THF, −78 °C): 2122 cm^{-1} (ν(CN)), 2059 cm^{-1} (A_1), 1929 cm^{-1} (E), 1897 cm^{-1} (A_1). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 161 (s, sharp, *C*N).

X-ray Crystallographic Study of 1 and 2. Crystal data and details of data collection are given in Table 1. A colorless plate for both **1** and **2** was mounted on a glass fiber with epoxy cement at room temperature and cooled to (193 K for **1** and 163 K for **2**) in a cold N_2 stream. Preliminary examination and data collection were performed on a Siemens R3m/V X-ray diffractometer for **1** and a Rigaku AFC5R for **2** (oriented graphite monochromator; Mo Kα $\lambda = 0.710\,73$ Å for both **1** and **2**). Cell parameters were calculated from the least-squares fitting of the setting angles for 25 reflections. ω scans for several intense reflections indicate acceptable crystal quality. Data for **1** were collected for $5.0° \le 2\theta \le 50.0°$ [$\theta{-}2\theta$ scans, $-24 \le h \le 0$, $-14 \le k \le 0$, $-26 \le l \le 26$] at 193 K. Scan width for the data collection for **1** was 2.00° with a variable scan speed from 2.00 to 15.00°/min in ω. Data for **2** were collected for $4.0° \le 2\theta \le 50.0°$ at 163 K. Scan width for the data collection for **2** was $[1.60 + 0.3 \tan(\theta)]°$ with a variable scan rate from 4.00 to 16.00°/min in ω. Three control reflections (collected every 97 reflections for **1** and 150 reflections for **2**) showed no significant trends. Background measurements by stationary-crystal and stationary-counter techniques were taken at the beginning and end of each scan for (0.25 of the total scan time for **1** and 0.50 of the total scan time for **2**). Lorentz and polarization corrections were applied to 7030 reflections for **1** and 7353 reflections for **2**. Approximately 300 reflections for **1** were lost due to severe crystal icing during the later stages of data collection. A semiempirical absorption correction was applied to **1**, and a DIFABS correction was applied to **2** (*vide infra*). A total of 9910 unique reflections for **1** and 9578 unique reflections for **2** with $F > 4.0\sigma_F$ for **1** and $F > 6.0\sigma_F$ for **2** were used in further calculations. Structures **1** and **2** were solved by direct methods [SHELXS, SHELXTL-PLUS program package, Sheldrick (1990)]. Initial refinements of **2** indicated considerable error in the data collection and absorption correction. Since the crystal quality was questionable and crystal selection was limited, it was decided to attempt to correct the absorption problems of the available data set with DIFABS.[11] The DIFABS correction contrived a reasonable data set, and isotropic refinement produced $R = 20\%$ at convergence. It was then decided to attempt the anisotropic refinement. Unfortunately the refinement proved unstable and unusual metric parameters were seen. It was decided to restrain the bond distances in the phenyl rings to idealize values and to restrain the thermal parameters to isotropic behavior. The resulting model was then compared to its isomorphic analog (see the structure of **1**) for any obvious deviations. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded [$I > 2\sigma_I$] $R(F) = 0.079$, $R_w(F^2) = 0.139$, and $S(F^2) = 1.02$ for **1** and $R(F) = 0.131$, $R_w(F^2) = 0.287$, and $S(F^2) = 1.05$ for **2** at convergence [Sheldrick, 1993]. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at $-1.2B$(adjacent carbon atom). Near the final stages of refinement for **1** and **2** an included half molecule of THF was located in an e density map, and its coordinates were added to the overall atom lists. Neutral atom scattering factors and anomalous scattering correction terms were taken from the *International Tables for X-ray Crystallography*, Vol. C.

Table 1. Crystallographic Data and Data Collection Parameters

	1	**2**
formula	$C_{62}H_{49}NO_{5.5}P_3WCu$	$C_{62}H_{49}NO_{5.5}P_3CrCu$
fw	1235.40	1103.55
space group	$P2_1/n$	$P2_1/n$
a, Å	20.376(4)	20.079(11)
b, Å	12.436(3)	12.383(7)
c, Å	22.423(5)	21.975(10)
β, deg	97.28(3)	97.86(4)
V, Å^3	5636(2)	5413(5)
Z	4	4
d(calc), g/cm^3	1.419	1.336
abs coeff, mm^{-1}	2.549	0.733
λ, Å	0.710 73	0.710 73
T, K	193(2)	163(2)
transm coeff	0.791−0.984	DIFABS
R,[a] %	7.90	13.14
R_w,[a] %	13.79	28.70

[a] $R = \sum|F_o - F_c|/\sum F_o$. $R_w = \{\sum w(F_o - F_c)/\sum w(F_o)^2\}^{1/2}$. GOF = 1.016 and 1.049 for complexes **1** and **2**, respectively.

^{13}C NMR Spectroscopy. All spectra were recorded on a Varian XL-200E FT-NMR spectrometer (50 MHz ^{13}C). A ^{13}C-labeled analogue of **1** was prepared as above using $W(^{13}CO)(CO)_5$ synthesized by stirring $W(CO)_5(THF)$ under an atmosphere of ^{13}CO for several hours. This labeled hexacarbonyl was used to prepare $NaW(CO)_5CN$ with ^{13}C label statistically distributed between CO and CN groups. The labeled complex **1*** (100 mg) was dissolved in THF-d_8 (1 mL) in a 5 mm quartz NMR tube in an inert-atmosphere drybox. Spectra were recorded every 20 °C from −80 to +20 °C using liquid N_2 as coolant. The line width at half-height of the ^{13}CN peak was recorded at each temperature.

^{13}C-labeled $Na(CO)_5WCN$ (100 mg) was added to acetone-d_6 (1 mL), and the resulting slurry was filtered into a 5 mm quartz NMR tube,

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(9) Heckel, E.; German Patent 1,230,025; *Chem. Abstr.* **1967**, *66*, 46487e.
(10) King, R. B. *Inorg. Chem.* **1967**, *6*, 25.
(11) Walker, N.; Straut, D. *Acta Crystallogr.* **1983**, *A39*, 158.

giving a clear, slightly yellow solution. Cuprous [^{13}C]cyanide tris(triphenylphosphine) was prepared from Cu^{13}CN in the same manner as the nonlabeled compound (*vide infra*). Cu^{13}CN(PPh$_3$)$_3$ (100 mg) was dissolved in CDCl$_3$ (1 mL) in a 5 mm quartz NMR tube in an inert-atmosphere drybox. Spectra for both of these compounds were recorded at room temperature, and the line width at half-height of the ^{13}CN peak was recorded.

A ^{13}C-labeled analogue of **3** was prepared as above by substituting Cu^{13}CN for CuCN. After photolysis of W(CO)$_6$ (0.085 mmol), the THF was evacuated from the light orange solution of W(CO)$_5$(THF), resulting in a brown powder. THF-d_8 (2 mL) was then added via syringe, yielding a dark brown solution, which was cooled to −78 °C. Cuprous [^{13}C]cyanide (0.085 mmol) and PPh$_3$ (0.25 mmol) were placed in a 5 mm quartz NMR tube in an inert-atmosphere drybox and cooled to −78 °C. The dark brown solution of W(CO)$_5$(THF) was transferred via cannula to the NMR tube, and spectra were recorded every 20 °C from −60 to +40 °C. The line width at half-height of the ^{13}CN peak was recorded at each temperature. After the spectrum was recorded at 40 °C, the solution was again cooled to −60 °C and a second spectrum was recorded and found to be identical to the first.

Results

Synthesis and Infrared Spectroscopy. The cyanide-bridged compounds were prepared using sodium cyanopentacarbonyl metalates as cyanide group donors (eq 1). When the group 6

$$\mathrm{Na(CO)_5MCN + Cu(CH_3CN)_4BF_4 \xrightarrow[THF]{PPh_3} (CO)_5M{-}CN{-}Cu(PPh_3)_3} \quad (1)$$

sodium cyanopentacarbonyl metalates were added to copper acetonitrile tetrafluoroborate, a rapid reaction ensued which could be followed visually by the precipitation of NaBF$_4$. The reactions proceeded rapidly to completion, and before dimerization around the copper ion could take place, a 2-fold molar excess of triphenylphosphine was added to the reaction mixture. Interestingly, the crystals which grew for both compounds contained three triphenylphosphine moieties (*vide infra*). The addition of triphenylphosphine did not result in any visible changes in the reaction mixture but was evidenced in the infrared spectra by the appearance of the triphenylphosphine bands at 1435 and 1481 cm^{-1} and by the shift to lower energy of the cyanide stretch from 2132 to 2121 cm^{-1} for **1** and from 2129 to 2117 cm^{-1} for **2**.

Infrared spectroscopy proved to be the ideal method for monitoring the progress of these reactions. The CN stretching frequency of all compounds was a gauge used to determine whether coordination had taken place. The infrared spectral patterns of cyano carbonylates have been analyzed thoroughly, and the effects on ν(CN) due to coordination by cations and Lewis acids are well-known.[12]

The ν(CN) in THF solution of Na(CO)$_5$WCN is found at 2121 cm^{-1}. THF is a fairly polar solvent (dielectric constant D = 7.4), and therefore this compound exists in the solvent-separated ion-pair form.[12] Upon reaction with Cu(CH$_3$CN)$_4$BF$_4$, the cyanide stretching band shifts to higher energy at 2132 cm^{-1}. This is indicative of coordination by a Lewis acid. Rather than pulling electron density away from the group 6 metal through the cyanide bridge, which would decrease ν(CN), a Lewis acid allows for cyanide nitrogen lone pair coordination. The electron pairs of both atoms in the C≡N moiety are antibonding with respect to the C≡N bond.[13] Hence, the C−N bond order and, accordingly, the ν(CN) frequency increase with increasing donation of these lone pairs.

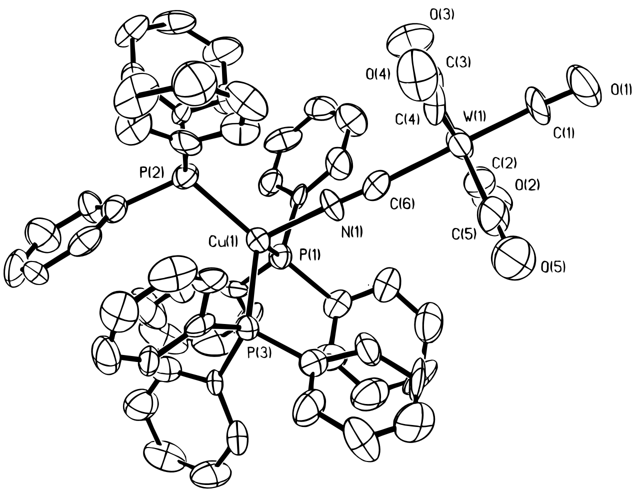

Figure 1. Thermal ellipsoid drawing of **1** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

This *in-situ*-formed intermediate exists in a strongly bonded, contact-ion-pair form. After addition of triphenylphosphine, the CN stretching frequency shifts back to lower energy at 2121 and 2117 cm^{-1} for **1** and **2**, respectively. This is indicative of a return to a more solvent-separated form of the bridged assembly. Precedence exists for this type of behavior in crystal structures of tris(triphenylphosphine)copper (I) complexes with noninteracting or very weakly interacting counterions (cf. Saturnino's (Ph$_3$P)$_3$Cu···Cl−FeCl$_3$[14] and references therein). Also, copper(I), having a completely filled 3d shell will have labile metal−L bonds with most ligands. The isocyanide coordination motif presents a relatively hard N-donor atom to the soft copper(I) ion, making this bond even more labile than most Cu−L bonds.

The linkage isomer of **1**, the so-called "isocyanide"-bridged compound, **3**, was prepared from W(CO)$_5$(THF) using CuCN(PPh$_3$)$_3$ as cyanide group donor (eq 2). This reaction was carried

$$\mathrm{(CO)_5W(THF) + CuCN(PPh_3)_3 \rightarrow (CO)_5WNCCu(PPh_3)_3} \quad (2)$$

out at −78 °C to avoid possible rearrangement processes leading to **1**. Addition of 1 equiv of preformed CuCN(PPh$_3$)$_3$ to the W(CO)$_5$(THF) compound resulted in a gradual change of the solution from light orange to light yellow. An infrared spectrum taken after 2 h at −78 °C revealed only slight changes from the IR of **1**. The cyanide stretching band is essentially unmoved at 2122 cm^{-1} and the higher frequency A$_1$ and E ν(CO) bands are unchanged. The only significant difference from the IR spectrum of **1** is that the lower frequency A$_1$ band has shifted from 1904 to 1897 cm^{-1}. This band derives most of its character from the CO *trans* to the cyanide group. When the isocyanide coordination motif is presented to tungsten, a decrease in back-bonding relative to the cyanide motif results. Thus, excess electron density on the tungsten is donated to the CO group *trans* to the cyanide, lowering its bond order and ν(CO). Similar IR behavior was noted also in Vahrenkamp's[5] linkage isomers of (CO)$_5$Cr[CN]Fe(dppe)Cp.

X-ray Crystallography. Crystals suitable for an X-ray structure analysis were obtained via slow diffusion of hexane into a concentrated tetrahydrofuran solution of the dinuclear complex at −20 °C for both **1** and **2**. Figure 1 shows a thermal ellipsoid drawing of complex **1**, and Figure 2 shows a thermal

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[12] Darensbourg, M. Y.; Barros, H. L. C. *Inorg. Chem.* **1979**, *18*, 3286.

[13] Purcell, K. F. *J. Am. Chem. Soc.* **1967**, *89*, 247, 1639.

[14] Saturnino, D. J.; Arif, A. M. *Inorg. Chem.*, **1993**, *32*, 4157.

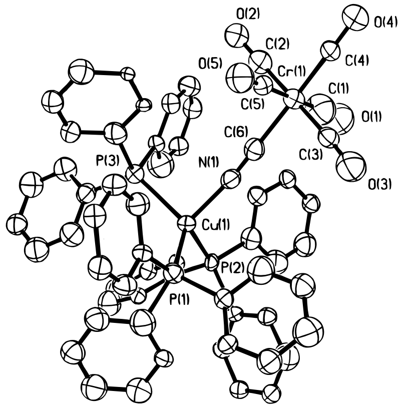

Figure 2. Thermal ellipsoid drawing of **2** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**[a]

N(1)−C(6)	1.15(2)	Cu(1)−N(1)	1.998(12)
Cu(1)−P(1)	2.349(6)	Cu(1)−P(2)	2.326(5)
Cu(1)−P(3)	2.341(5)	W(1)−C(6)	2.18(2)
W(1)−C(1)	2.01(2)	W(1)−C(2)	2.00(3)
W(1)−C(3)	2.03(2)	W(1)−C(4)	1.96(3)
W(1)−C(5)	2.05(2)		

C(6)−N(1)−Cu(1)	176(2)	N(1)−C(6)−W(1)	175.9(14)
P(1)−Cu(1)−N(1)	96.2(4)	P(2)−Cu(1)−N(1)	109.6(4)
P(3)−Cu(1)−N(1)	108.7(4)	P(1)−Cu(1)−P(2)	119.2(2)
P(1)−Cu(1)−P(3)	112.1(2)	P(2)−Cu(1)−P(3)	109.6(4)
C(1)−W(1)−C(6)	179.2(8)	C(2)−W(1)−C(6)	90.3(7)
C(3)−W(1)−C(6)	90.1(6)	C(4)−W(1)−C(6)	87.5(8)
C(5)−W(1)−C(6)	89.6(6)		

[a] Estimated standard deviations are given in parentheses.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **2**[a]

N(1)−C(6)	1.19(2)	Cu(1)−N(1)	1.99(2)
Cu(1)−P(1)	2.319(6)	Cu(1)−P(2)	2.329(6)
Cu(1)−P(3)	2.328(6)	Cr(1)−C(6)	1.97(2)
Cr(1)−C(1)	1.78(3)	Cr(1)−C(2)	1.81(2)
Cr(1)−C(3)	1.83(2)	Cr(1)−C(4)	1.80(2)
Cr(1)−C(5)	1.76(2)		

C(6)−N(1)−Cu(1)	173(2)	N(1)−C(6)−Cr(1)	178(2)
P(1)−Cu(1)−N(1)	110.5(5)	P(2)−Cu(1)−N(1)	108.2(5)
P(3)−Cu(1)−N(1)	95.8(5)	P(1)−Cu(1)−P(2)	108.9(2)
P(1)−Cu(1)−P(3)	119.2(2)	P(2)−Cu(1)−P(3)	113.1(2)
C(1)−Cr(1)−C(6)	90.8(10)	C(2)−Cr(1)−C(6)	92.3(9)
C(3)−Cr(1)−C(6)	87.7(8)	C(4)−Cr(1)−C(6)	179.0(8)
C(5)−Cr(1)−C(6)	89.1(8)		

[a] Estimated standard deviations are given in parentheses.

ellipsoid drawing of **2**. Selected bond distances and angles are provided for **1** in Table 2 and for **2** in Table 3. Because of the poorer quality of the data obtained on complex **2**, discussion of metric data will focus on complex **1**. Nevertheless, complex **2** is isomorphous with **1** and displays no exceptional bond distances or angles.

The fact that the copper ions in **1** and **2** are four-coordinate was surprising since only 2 equiv of phosphine was present in the solutions from which these molecules crystallized. Indeed, tris(triphenylphosphine) complexes of copper(I) are rare. However, the extra stability afforded by tetrahedral coordination can evidently outweigh steric interactions among the phosphine phenyl rings.[15] The three triphenylphosphine ligands and the cyanide moiety coordinate to the copper(I) ion in a slightly distorted tetrahedral geometry in both **1** and **2**. The nearly equivalent Cu−P bond lengths (average 2.339[5] Å for **1** and 2.325[6] Å for **2**) are as expected for complexes containing three triphenylphosphine ligands. In both **1** and **2**, the group 6 metal ion is complexed in an almost ideal octahedron. The large standard deviations in the M−C bond lengths and M−C−O angles preclude any detailed discussion beyond this.

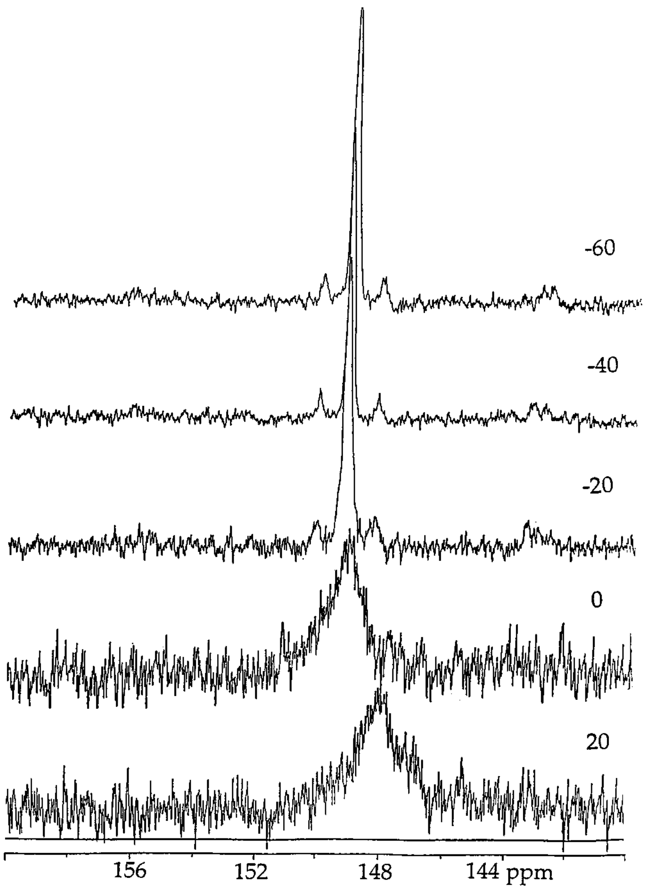

Figure 3. 50 MHz dynamic ^{13}C NMR spectra of **1** obtained from a solution of the complex in THF-d_8. Numbers indicate temperatures (°C) at which spectra were obtained.

The W−C(6) distance in **1** is 2.18(2) Å, whereas, the N(1)−C(6) bond length is 1.15(2) Å. The latter value is identical to that of free, gaseous HCN ($C\equiv N$ = 1.156 Å) and is in the range of most other gaseous cyanides.[16] The infrared CN stretching frequency of free HCN is 2089 cm^{-1}, while the ν(CN) of **1** appears at 2121 cm^{-1}. This difference is indicative of the fact that, in **1**, both the carbon and nitrogen lone pairs of the cyanide moiety are complexed. Both of these electron pairs are antibonding with respect to the $C\equiv N$ bond and thus, when complexed, will increase the frequency of the CN stretching band. The cyanide bridge in **1** is very slightly bent with angles of W−C(6)−N(1) = 175.9(14)° and Cu−N(1)−C(6) = 176(2)°, whereas, the corresponding values in the **2** are 178(2) and 173(2)°, respectively. These slight deviations from linearity are not statistically compelling because of the significant errors associated with them.

^{13}C NMR Experiments. ^{13}C{^{1}H} NMR spectra of **1** were recorded every 20 °C from −80 to +20 °C. Figure 3 is a stack plot of the NMR spectra obtained at each temperature. Table 4 contains a listing of the ^{13}CN peak line widths at each temperature as well as the W−C coupling constants and peak positions. The line width decreased between −80 and −40 °C and reached a minimum of 11 Hz at −40 °C. Tungsten satellites

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(15) For an example of a greatly hindered tris(triphenylphosphine) complex see: Darensbourg, D. J.; Holtcamp, M. W.; Khandelwal, B.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1995**, *34*, 2389.

(16) Britton, D. *Perspect. Struct. Chem.* **1967**, *1*, 109.

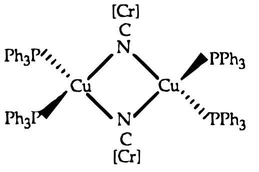
Table 4. Variable-Temperature ^{13}C NMR Data for the ^{13}CN Peak of **1**

temp, °C	^{13}CN peak position, ppm	J_{W-C}, Hz	line width at half-height, Hz
−80	149.0	96	13
−60	149.0	94	12
−40	149.1	96	11
−20	149.1	94	15
0	148.9	*a*	43
20	147.8	*a*	47

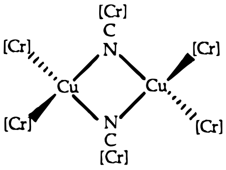
[a] ^{183}W satellites were not resolved at this temperature.

are evident in the spectra from −80 to −20 °C with $J_{W-CN} \approx$ 96 Hz at every temperature. Above −20 °C, the ^{13}CN peak broadened rapidly and no ^{183}W satellites were resolved. This temperature-dependent behavior is reproducible over time with the same sample. There is also a small peak evident at ca. 143.5 ppm which is possibly due to trace quantities of $(CO)_5WCNCu(PPh_3)_2$.

The isocyanide-bridged complex, **3**, was prepared from ^{13}C-labeled CuCN in an NMR tube at −78 °C, and spectra were recorded every 20 °C from −60 to +40 °C. Two peaks are evident in the CN region of the spectrum. One, at 152 ppm, is possibly due to the presence of slight amounts of unreacted $Cu(^{13}CN)(PPh_3)_x$. Quantum yield restrictions ensure that not all $W(CO)_6$ reacts by photolysis, so it is not unusual for small amounts of $Cu^{13}CN(PPh_3)_x$ to be present in the reaction mixture. Alternatively, this peak could be due to the formation of a dimeric structure such as **4**. Fehlhammer et al. reported the formation of a complex of similar structure[17] (shown as **5**) upon the addition of 4 equiv of $Na(CO)_5CrCN$ to $CuSO_4$ in pH = 1 water. However, the formation of **4** is unlikely here since 3 equiv of PPh_3 was present in the solution. The cyanide peak of complex **3** is found in the NMR spectrum at 161 ppm. This peak is downfield from that of complex **1**, is much less broad, and, as expected, shows no ^{183}W satellites. The lack of spin−spin coupling in this peak was used to assign it positively to the cyanide carbon of complex **3**.



4



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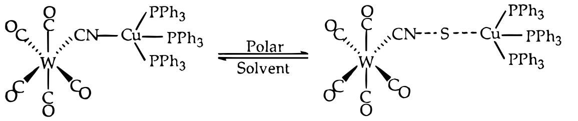
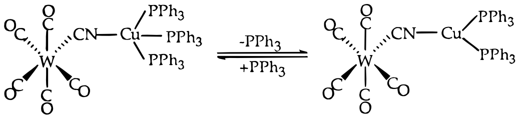
Discussion

The cyanide peak in the ^{13}C NMR spectrum of **1** was extremely broad at room temperature (fwhh = 47 Hz). Several exchange mechanisms which could account for the observed line broadening are plausible. Nuclei with $I > {}^1/_2$ possess an electric quadrupole moment which can interact with the electric field gradients on the nuclei of interest.[18] This provides an additional pathway for relaxation of the NMR nucleus and can result in line broadening. A second mechanism, the contact ion pair/solvent-separated ion pair equilibrium, is shown graphically in eq 3. Also shown in eq 3 is another conceivable mechanism, dissociation of a phosphine ligand from Cu(I), affording a three-coordinate copper center.



(3a)



(3b)

The line width of the ^{13}CN peak for **1** at room temperature is 47 Hz. The line width of the ^{13}CN peak for $Na(CO)_5WCN$, however, is only 2 Hz. Therefore, coupling to the ^{14}N ($I = 1$) quadrupole does not provide an efficient pathway for rapid relaxation of the perturbed ^{13}C nucleus. In $Cu^{13}CN(PPh_3)_3$, the line width of the ^{13}CN peak is 15 Hz. Copper quadrupolar broadening is thus somewhat efficient for this complex at room temperature. However, in **1**, the cyanide carbon is separated from the copper nucleus by an additional bond, and this will greatly decrease the amount of coupling between the ^{13}C and Cu nuclei. So, in **1**, the mechanism of quadrupolar broadening should be negligible and definitely less efficient than that in $CuCN(PPh_3)_3$.

One of the two equilibria shown in eq 3 is therefore assumed to be the dominant mechanism which gives rise to line broadening of the CN peak in the ^{13}C NMR. Infrared spectroscopy supports the ion-pair exchange interaction. As triphenylphosphine is added to the intermediate $[(CO)_5W-CN-Cu]$, the ν(CN) band shifts to lower energy. Because this shift is not due to an increase in the amount of π-back-bonding, it must indicate that one of the CN lone pairs of electrons is being held more tightly by the CN moiety. Statistically, then, the Cu−N σ-bond is weaker after addition of PPh_3 to the reaction mixture.

The ^{13}C NMR experiments, however, were ambiguous. The chemical shift of the solvent-separated complex was taken as the chemical shift for $Na(CO)_5WCN$. In THF, this complex exists in the solvent-separated ion-pair form.[12] The ^{13}C NMR spectrum was obtained in THF-d_8, and the chemical shift of the CN peak was 136.4 ppm. The chemical shift of the contact-ion-pair form of the complex was taken as the chemical shift of the cyanide carbon of **1** at −60 °C, which is 149.0 ppm.

The ^{13}C NMR experiments carried out on **1** reveal behavior which is typical for systems that undergo an intermolecular exchange reaction such as the ones shown in eq 3. As the temperature was raised from −60 °C, the line began to broaden slightly. Between −20 and 0 °C, sufficient kinetic energy was available to the system to shift the equilibria of eq 3 far enough to the right for the product to be observable on the NMR time scale. As the temperature was raised past 0 °C, these equilibria continued to shift toward product. Because there are two species present in the solution, as the equilibrium shifts to the right, a concomitant movement of the observed peak should result. At 20 °C, this begins to be apparent as the CN peak shifts upfield to 147.8 ppm.

It is unclear which equilibrium process is broadening the ^{13}CN peak in the ^{13}C NMR. It is possible that the small peak at 143.5 ppm is $(CO)_5WCNCu(PPh_3)_2$ and the line broadening is brought about by phosphine dissociation/recoordination. Alternatively, the peak at 143.5 ppm could be a small amount of unknown impurity with the line broadening brought on by Cu(I)−NC bond breakage/re-formation. The experiments performed to date are not definitive and do not allow differentiation between these two scenarios.

The variable-temperature ^{13}C NMR experiment performed on complex **3** revealed the CN peak to be at approximately 161

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(17) Fritz, M.; Rieger, D.; Bär, E.; Beck, G.; Fuchs, J.; Holzmann, G.; Fehlhammer, W. P. *Inorg. Chim. Acta* **1992**, *198*, 513.

(18) Günther, H. *NMR Spectroscopy. An Introduction*; John Wiley and Sons: Chichester, U.K., 1980; pp 9−11, 278−9.

ppm at every temperature. Because **3** contains an "isocyanide" bridge, the electronic environment around the cyanide carbon will be completely different from that in **1**. Copper(I) is a poor π-donor and thus will not back-bond to an appreciable extent. Isocyanide is a poorer π-acceptor than cyanide, and so the tungsten will also not be able to donate much electron density through π-back-bonding. The M−cyanide σ-bonds in **3** are apparently weaker than the σ-bonds in **1** due to the fact that the ν(CN) IR band of **3** is the same as that of **1**. The lack of back-bonding to the cyanide moiety in **3** is completely balanced by the weaker donation of the N and C lone pairs. Hence, the same amount of electron density is in cyanide π^*-orbitals in **3** and in **1**.

The fact that the line width of the cyanide peak is so narrow in **3** is explained by the fact that there is little or no ion-pair exchange taking place in this complex. The Cu−C bond will be relatively strong because the carbon end of the cyanide ligand is a much softer base and also is much more unstable when free. Tungsten is still able to π-donate somewhat to the isocyanide moiety so the W−N bond will also be fairly strong. The line width of the CN peak of **3** did not change from −60 to +40 °C, indicating a lack of quadrupolar coupling. This is somewhat unusual in that $Cu^{13}CN(PPh_3)_3$ does exhibit quadrupolar broadening at room temperature. Apparently, the weaker donation of the lone pairs in **3** is sufficient to effectively decouple the quadrupolar copper nucleus from the cyanide carbon.

In a tetrahydrofuran solution at room temperature, **3** undergoes rearrangement of the isocyanide bridge to form **1**. This reaction is evidently slow since no rearrangement occurred during the NMR study of **3** even up to 40 °C. The fact that **1** is the thermodynamic product of both synthetic reactions is somewhat unusual in that the hard/soft acid−base theory would predict the soft copper(I) to prefer the softer carbon end of the cyanide group. Also, the Cu−N bond in **1** is labile, which would permit facile rearrangement of the cyanide bridge. It is tungsten, therefore, that determines the bonding arrangement in this particular set of isomers. The increased π-back-bonding capability of tungsten in isomer **1** leads to a very strong W−C bond. This strong bond prevents rearrangement of **1** from taking place once formed. In this way, chance rearrangements of the cyanide bridge in complex **3** are trapped as isomer **1**, and the thermodynamic product is built up over time.

Conclusion

The syntheses of the linkage isomers of a tungsten cyanide-bridged assembly have been performed. Also completed was the synthesis of the chromium analogue of the cyanide-bridged compound. The solid-state structures of both cyanide-bridged compounds were confirmed by X-ray structure analysis, and they were found to be quite similar. The structure of the tungsten isocyanide-bridged complex was deduced by IR and ^{13}C NMR studies, and this complex was found to be thermally unstable in THF. The cyanide-bridged isomer of the tungsten system was thermodynamically preferred due to the increased ability of C-bound cyanide to accept electron density from tungsten.

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Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates and equivalent isotropic displacement parameters, anisotropic thermal parameters, and complete bond lengths and angles as well as ball-and-stick drawings for complexes **1** and **2** (18 pages). Ordering information is given on any current masthead page.

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