

Figure 5. Plot of  $\delta(\text{C}^{14}\text{NR})$  versus  $\delta(\text{N}^{13}\text{CNR})$  for 1–6.

$\delta(\text{N}^{13}\text{CNR})$  for 1–6, showing the expected inverse relationship and underscoring the differences between the two types of ligands and the greater  $\pi$  acidity of the aryl isocyanide.

While all of the data cited so far have supported the increased  $\pi$ -acceptor ability of the aryl isocyanide, the nature of the ring involvement is not reflected directly in the chemical shift measurements. It is here that a common liability of the  $^{14}\text{N}$  nucleus

may become an asset, in that its relaxation mechanism is dominated by the interaction of the large  $^{14}\text{N}$  quadrupole with the surrounding electric field gradient. Indeed, it is only because the field is relatively symmetric in these complexes that we are able to observe the  $^{14}\text{N}$  resonance at all. With little  $\pi$  interaction the cylindrical symmetry of the instantaneous field gradient about nitrogen would be expected to be effectively unperturbed, resulting in relatively long relaxation times and corresponding sharper line widths. On the other hand, if the N  $p\pi$  electron density is delocalized into the ring, the cylindrical symmetry should be perturbed, causing an increase in the instantaneous electric field gradient and a stronger coupling with the nuclear quadrupole, shorter relaxation times, and broader line widths. While factors such as variations in axial field gradients and the mobility of groups may also contribute to differences in relaxation times, the spectra in Figure 3 clearly show a substantial difference in  $^{14}\text{N}$  line widths between aliphatic and aromatic isocyanides, with greater line broadening observed as the number of isocyanide ligands is increased.

We conclude from these studies that at least in closely related metal isocyanide complexes  $^{13}\text{C}$  NMR,  $^{17}\text{O}$  NMR, and  $^{14}\text{N}$  NMR can collectively serve to provide a self-consistent picture of often subtle differences in the electronic structures of such complexes. The importance of p-orbital contributions to the field gradient at the nitrogen nucleus has been firmly established in the literature,<sup>19</sup> but other factors may also be important, and further experimental and theoretical work is clearly warranted to determine the role of  $^{14}\text{N}$  line widths in elucidating the nature of the bonding in complexes containing isocyanide ligands.

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## Synthesis, Spectroscopic Characterization, and X-ray Structural Determination of $\text{W}(\text{CO})_4(\text{PR}_3)\text{CNC}_6\text{H}_4\text{NCW}(\text{CO})_4(\text{PR}_3)$ ( $\text{R} = \text{Ph}, \text{Et}$ )

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Two bimetallic complexes containing 1,4-diisocyanobenzene as a bridging ligand have been prepared and examined by X-ray crystallography and  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR, and infrared spectroscopies.  $\text{W}(\text{CO})_4(\text{PEt}_3)\text{CNC}_6\text{H}_4\text{NCW}(\text{CO})_4(\text{PEt}_3)$  (**1**) and  $\text{W}(\text{CO})_4(\text{PPh}_3)\text{CNC}_6\text{H}_4\text{NCW}(\text{CO})_4(\text{PPh}_3)$  (**2**) both crystallized in the same space group in very similar packing environments. Crystal data: for **1**, monoclinic space group  $P2_1/n$ ,  $a = 7.780$  (2) Å,  $b = 15.930$  (3) Å,  $c = 14.137$  (6) Å,  $\beta = 99.56$  (3)°,  $Z = 2$ ,  $R = 0.040$ ; for **2**, monoclinic space group  $P2_1/n$ ,  $a = 11.641$  (2) Å,  $b = 16.970$  (2) Å,  $c = 12.463$  (2) Å,  $\beta = 101.24$  (1)°,  $Z = 2$ ,  $R = 0.047$ ; NMR chemical shifts and vibrational frequencies for  $\text{CNC}_6\text{H}_4\text{NC}$  experience significant changes upon coordination, and the presence of an organophosphine ligand in the metal coordination sphere causes the diisocyanide to experience in-plane bends of 10.8° for **1** and 4.2° for **2**. In spite of strong evidence for the M–CNR back-bonding, the C–N bond length varies only negligibly among **1**, **2**, and  $\text{CNC}_6\text{H}_4\text{NC}$ , the free ligand.

### Introduction

A vast majority of known zerovalent transition-metal complexes contain either carbon monoxide or isocyanide ligands in their coordination sphere. That there exists a plethora of such complexes

attests to the unique ability of these neutral ligands to polarize charge density away from an otherwise electron-saturated metal center. The importance of these  $\pi$ -acids is evident in the large number of crystal structures of such complexes and the routine use of M–C, C≡O, and C≡N stretching frequencies,  $^{13}\text{CO}$ ,  $\text{C}^{17}\text{O}$ , and  $\text{C}^{14}\text{N}$  chemical shifts, M–CO and M–CN charge-transfer bands, etc. as probes of both geometric and electronic

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structures of complexes containing the ligands.<sup>1</sup> Indeed, these ligands appear to sense relatively subtle changes in their electronic environments, and these changes are reflected in the spectroscopic properties of the ligands.

In spite of this, a comparison of the geometric structure of carbon monoxide before and after coordination reveals little if any change in its C–O bond length, regardless of the metal to which it is coordinated. This statement must be qualified with the obvious observation that no X-ray structure study has been performed on free carbon monoxide, but its C–O distance has been determined by microwave spectroscopy to be 1.128 Å,<sup>2</sup> and rigorous ab initio calculations indicate that the C–O distance is 1.101 Å.<sup>3</sup> M–C–O bond lengths are typically 1.100–1.155 Å,<sup>4</sup> even though force constants for the bonds are significantly lower than for the uncoordinated ligand. Unlike CO, a “permanent” gas, isocyanides generally take the form of noxious liquids at room temperature, and it would seem that a more straightforward comparison could be made between the C–N bond lengths in isocyanides before and after coordination.

Current work in our laboratories is centered around the use of bridging isocyanide ligands as charge-transfer mediators. During the course of this work we have synthesized a number of bimetallic group VI metal carbonyl isocyanide complexes containing the aromatic bridging ligand 1,4-diisocyanobenzene, a solid at room temperature for which crystal structure data are available from the literature.<sup>5</sup> <sup>13</sup>C NMR studies of these complexes indicate that the ligand is intimately involved in M–L–M  $\pi$  bonding and is capable of mediating charge polarization between two metal centers.<sup>6</sup> Limited solubility of complexes of general formula M(CO)<sub>5</sub>CNC<sub>6</sub>H<sub>4</sub>NCM'(CO)<sub>5</sub> has so far precluded the availability of single crystals. The insertion of organophosphines into the metal coordination sphere markedly increases the solubility of these new complexes, allowing for the growth of crystals suitable for structural studies. We report here the synthesis and structural and spectroscopic characterization of two of the complexes resulting from this modification.

## Experimental Section

**General Reagents and Procedures.** All reactions were performed in a dry nitrogen atmosphere by using standard Schlenk techniques; solvents were dried and deoxygenated by using standard techniques. W(CO)<sub>6</sub>, Et<sub>4</sub>NCl, PPh<sub>3</sub>, PEt<sub>3</sub>, and 1,4-diaminobenzene were purchased from Aldrich Chemical Co. and used without further purification. 1,4-Diisocyanobenzene, [W(CO)<sub>5</sub>Cl]<sup>−</sup>[Et<sub>4</sub>N]<sup>+</sup>, and [W(CO)<sub>4</sub>(PR<sub>3</sub>)<sub>3</sub>Cl]<sup>−</sup>[Et<sub>4</sub>N]<sup>+</sup> were prepared according to literature methods.<sup>11</sup> The synthesis and characterization of W(CO)<sub>5</sub>CNC<sub>6</sub>H<sub>4</sub>NCW(CO)<sub>5</sub> (**3**) have been previously reported.<sup>6</sup> Proton-decoupled <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on a Bruker WH-250 spectrometer. All samples were dissolved in CDCl<sub>3</sub>, which served as an internal reference. Chemical shifts are reported with respect to Me<sub>4</sub>Si. Infrared spectra were recorded from KBr pellets on a Nicolet MX-1 FTIR instrument.

**Synthesis of W(CO)<sub>4</sub>(PEt<sub>3</sub>)CNC<sub>6</sub>H<sub>4</sub>NCW(CO)<sub>4</sub>(PEt<sub>3</sub>) (**1**).** 1,4-Diisocyanobenzene (10.0 mmol) in 50 mL of ethanol was added to a solution of [W(CO)<sub>4</sub>(PEt<sub>3</sub>)Cl]<sup>−</sup>[Et<sub>4</sub>N]<sup>+</sup> (20.0 mmol) in 50 mL of ethanol,

**Table I.** X-ray Data Collection Parameters for **1** and **2**

compd	<b>1</b>	<b>2</b>
formula	C <sub>24</sub> H <sub>19</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> W <sub>2</sub>	C <sub>52</sub> H <sub>34</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> W <sub>2</sub>
color	yellow	yellow
M <sub>r</sub>	893.05	1244.45
space group (No.)	P2 <sub>1</sub> /n (15)	P2 <sub>1</sub> /n (15)
a, Å	7.780 (2)	11.641 (2)
b, Å	15.930 (3)	16.970 (2)
c, Å	14.137 (6)	12.463 (2)
$\alpha$ , deg	90.00 (0)	90.00 (0)
$\beta$ , deg	99.56 (3)	101.24 (1)
$\gamma$ , deg	90.00 (0)	90.00 (0)
Z	2	2
V, Å <sup>3</sup>	1731.63	2414.91
linear abs coeff, cm <sup>−1</sup>	71.8359	51.6835
temp, K	296 (5)	296 (5)
cryst size, mm <sup>3</sup>	0.2 × 0.3 × 0.3	0.2 × 0.3 × 0.5
radiation	Zr-filtered Mo K $\alpha$ ( $\lambda$ = 0.71069 Å)	Zr-filtered Mo K $\alpha$ ( $\lambda$ = 0.71069 Å)
2 $\theta$ limits, deg	4 < 2 $\theta$ < 45	4 < 2 $\theta$ < 45
scan type	$\theta$ –2 $\theta$	$\theta$ –2 $\theta$
scan speed (fixed), deg/min	2.0	2.0
bkg time/scan time	0.5	0.5
no. of unique reflns	2565	3627
no. of params	418	730
R	0.0399	0.0466
R <sub>w</sub> <sup>a</sup>	0.0452	0.0452
largest peak in final diff, e/Å <sup>3</sup>	1.92	1.45

$$^a w = (\sigma^2(|F|) + 0.009055F^2)^{-1}.$$

and the resulting solution was stirred for 12 h. Ethanol was removed in vacuo at a rate that allowed the solution to cool to ca. −20 °C during the evacuation. The product precipitated from the cold solution and was isolated by filtration of the cold solution. The final product was then rinsed with anhydrous ethanol (2 × 25 mL) and diethyl ether (25 mL) and dried under vacuum. Anal. Found (calcd): C, 35.40 (35.17); H, 3.50 (3.58); N, 3.12 (2.93). <sup>31</sup>P NMR data:  $\delta$  2.7 (relative to H<sub>3</sub>PO<sub>4</sub>), <sup>1</sup>J<sub>PW</sub> = 229 Hz.

**Synthesis of W(CO)<sub>4</sub>(PPh<sub>3</sub>)CNC<sub>6</sub>H<sub>4</sub>NCW(CO)<sub>4</sub>(PPh<sub>3</sub>) (**2**).** **2** was prepared in a manner identical with that for **1**, substituting [W(CO)<sub>4</sub>(PPh<sub>3</sub>)Cl]<sup>−</sup> for [W(CO)<sub>4</sub>(PEt<sub>3</sub>)Cl]<sup>−</sup>. Anal. Found (calcd): C, 50.13 (50.18); H, 2.79 (2.75); N, 2.47 (2.25). <sup>31</sup>P NMR data:  $\delta$  21.5 (relative to H<sub>3</sub>PO<sub>4</sub>), <sup>1</sup>J<sub>PW</sub> 238 Hz.

**X-ray Crystal Structural Determinations.** Crystals of **1** and **2** were grown from CH<sub>2</sub>Cl<sub>2</sub> at 25 °C and anchored in sealed 0.5-mm capillary tubes with epoxy. Details of the data collection are given in Table I. Data sets for both structures were collected on a Picker four-circle autodiffractometer automated for the IBM PC with PCXTAL.<sup>7</sup> Lattice constants were determined from a symmetry-constrained Monte Carlo least-squares refinement of centered angular data using software written in our laboratory. Crystal data and data collection parameters are given in Table I. Empirical absorption corrections for **2** were made by interpolation of  $\psi$ -scan intensity data using CAMEL\*JOCKEY.<sup>8</sup> The shape of the crystal for **1** was sufficiently close to a cylinder, and cylindrical absorption corrections were made. The structures were solved by using SHELXS-86<sup>9</sup> and refined by using SHELXL-76.<sup>10</sup> In **1** and **2** the tungsten atoms were located by using direct methods and all other non-hydrogen atoms were located in successive difference Fourier maps. The final positions for **1** and **2** were refined anisotropically. Hydrogen atom positions were calculated on the basis of idealized geometries for methyl and phenyl groups.

## Results

**Synthesis.** W(CO)<sub>4</sub>(PEt<sub>3</sub>)CNC<sub>6</sub>H<sub>4</sub>NCW(CO)<sub>4</sub>(PEt<sub>3</sub>) (**1**) and W(CO)<sub>4</sub>(PPh<sub>3</sub>)CNC<sub>6</sub>H<sub>4</sub>NCW(CO)<sub>4</sub>(PPh<sub>3</sub>) (**2**) were synthesized by using a modified version of a reaction scheme originally employed by Schenck<sup>11</sup> for the synthesis of monosubstituted group VI metal carbonyl derivatives. Two equivalents of a tungsten

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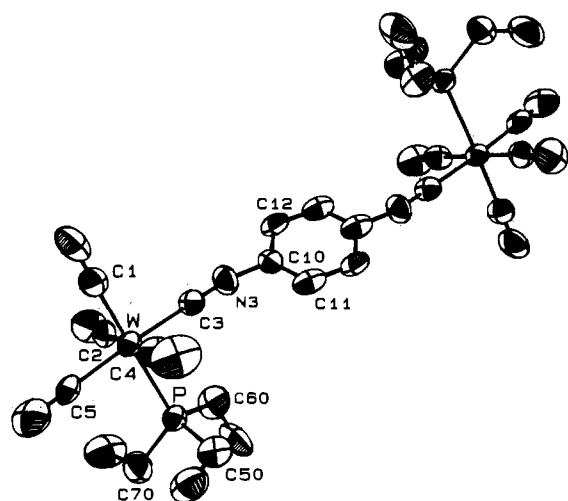
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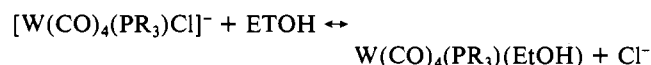
**Table II.** Fractional Atomic Coordinates and Effective Isotropic Thermal Parameters for W(CO)<sub>4</sub>(PEt<sub>3</sub>)CNPhNCW(CO)<sub>4</sub>(PEt<sub>3</sub>) (1)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>iso</sub> <sup>a</sup> Å <sup>2</sup>
W	0.07268 (6)	0.80341 (3)	0.23424 (3)	0.0474 (04)
P	0.2497 (04)	0.6790 (02)	0.1935 (02)	0.0519 (19)
C50	0.4665 (21)	0.6706 (11)	0.2648 (12)	0.0866 (110)
C51	0.4720 (21)	0.6480 (12)	0.3670 (13)	0.0935 (113)
C60	0.2989 (23)	0.6790 (11)	0.0732 (10)	0.0846 (108)
C61	0.3856 (27)	0.6042 (12)	0.0380 (13)	0.1097 (140)
C70	0.1638 (21)	0.5762 (09)	0.2074 (12)	0.0830 (105)
C71	-0.0253 (25)	0.5587 (10)	0.1439 (17)	0.1161 (143)
C1	-0.0598 (18)	0.9027 (10)	0.2640 (09)	0.0670 (89)
O1	-0.1369 (16)	0.9610 (07)	0.2806 (08)	0.0946 (79)
C2	-0.1270 (20)	0.7717 (09)	0.1256 (11)	0.0635 (89)
O2	-0.2376 (16)	0.7568 (08)	0.0674 (08)	0.0962 (84)
C4	0.2653 (20)	0.8392 (09)	0.3407 (11)	0.0671 (89)
O4	0.3704 (18)	0.8620 (08)	0.3994 (09)	0.1122 (98)
C5	-0.0284 (17)	0.7326 (09)	0.3285 (10)	0.0608 (82)
O5	-0.0823 (17)	0.6905 (07)	0.3832 (09)	0.0964 (86)
C3	0.1896 (17)	0.8752 (08)	0.1413 (09)	0.0543 (73)
N3	0.2643 (14)	0.9160 (07)	0.0928 (08)	0.0660 (69)
C10	0.3808 (16)	0.9594 (07)	0.0468 (08)	0.0490 (68)
C11	0.5574 (19)	0.9488 (09)	0.0752 (10)	0.0692 (93)
C12	0.3242 (18)	1.0117 (08)	-0.0295 (10)	0.0630 (80)

$$^a U_{iso} = \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i^* a_j^*)$$

**Figure 1.** ORTEP plot of W(CO)<sub>4</sub>(PEt<sub>3</sub>)CNPhNCW(CO)<sub>4</sub>(PEt<sub>3</sub>) (1). Thermal ellipsoids are drawn at the 50% probability level, and hydrogens have been omitted for the purpose of clarity.

carbonyl phosphine halide is dissolved in ethanol, and the following equilibrium is established:



The addition of 0.5 equiv of CNC<sub>6</sub>H<sub>4</sub>NC results in the formation of the bimetallic complexes, which can be precipitated from ethanol solution by pumping on the solution and simultaneously concentrating and cooling it.



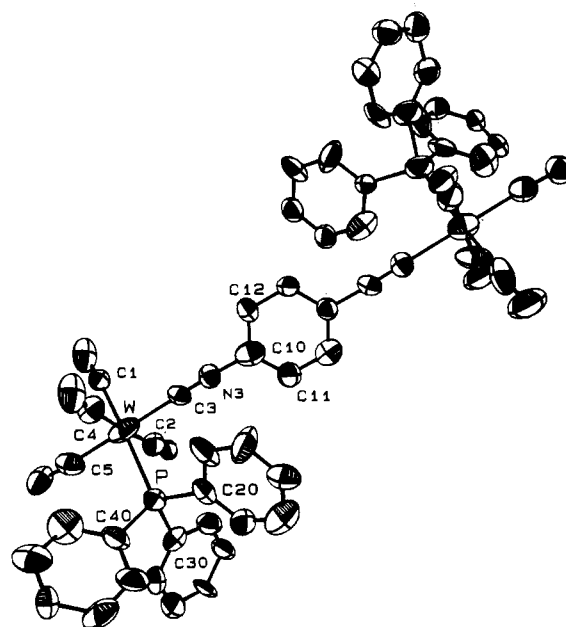
The complexes are relatively air stable and are orders of magnitude more soluble in aliphatic, aromatic, and halogenated hydrocarbons than the analogous bimetallic complexes lacking the phosphine ligand.

**Crystallography.** Crystal data and data collection parameters for X-ray crystal structural studies of **1** and **2** are listed in Table I. Fractional atomic coordinates and equivalent isotropic thermal parameters for **1** and **2** are given in Tables II and III, and ORTEP plots of **1** and **2** are illustrated in Figures 1 and 2, respectively. Selected bond lengths and angles for both molecules are reported in Tables IV and V. The C–N bond length for the free isocyanide ligand is 1.154 (3) Å,<sup>12</sup> compared to 1.168 (15) and 1.134 (12)

**Table III.** Fractional Atomic Coordinates and Effective Isotropic Thermal Parameters for W(CO)<sub>4</sub>(PPh<sub>3</sub>)CNPhNCW(CO)<sub>4</sub>(PPh<sub>3</sub>) (2)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>iso</sub> <sup>a</sup> Å <sup>2</sup>
W	0.13122 (4)	0.35038 (3)	0.65633 (4)	0.0483 (03)
P	0.03261 (24)	0.30813 (17)	0.81215 (23)	0.0449 (16)
C1	0.2026 (11)	0.3821 (08)	0.5310 (11)	0.0649 (85)
C2	0.2278 (11)	0.2489 (09)	0.6667 (09)	0.0655 (81)
C3	0.2664 (09)	0.3995 (07)	0.7713 (09)	0.0527 (71)
C4	0.0489 (11)	0.4566 (09)	0.6434 (10)	0.0631 (86)
C5	0.0041 (11)	0.3019 (07)	0.5449 (11)	0.0608 (80)
O1	0.2391 (09)	0.3999 (07)	0.4550 (08)	0.0920 (75)
O2	0.2836 (10)	0.1942 (07)	0.6658 (09)	0.1149 (89)
N3	0.3367 (08)	0.4289 (06)	0.8344 (08)	0.0646 (65)
O4	0.0062 (10)	0.5166 (07)	0.6361 (09)	0.1018 (83)
O5	-0.0645 (08)	0.2738 (06)	0.4765 (09)	0.0940 (72)
C10	0.4203 (09)	0.4658 (08)	0.9200 (10)	0.0594 (77)
C11	0.4644 (13)	0.4243 (09)	1.0118 (11)	0.0821 (97)
C12	0.4552 (14)	0.5413 (09)	0.9075 (11)	0.0837 (97)
C20	0.0865 (09)	0.3533 (07)	0.9463 (09)	0.0502 (66)
C21	0.1106 (11)	0.4334 (08)	0.9500 (11)	0.0625 (85)
C22	0.1496 (11)	0.4698 (09)	1.0522 (14)	0.0732 (91)
C23	0.1620 (12)	0.4294 (09)	1.1451 (12)	0.0796 (98)
C24	0.1348 (19)	0.3504 (11)	1.1420 (12)	0.0933 (129)
C25	0.1004 (14)	0.3131 (08)	1.0437 (10)	0.0768 (88)
C30	0.0463 (09)	0.2021 (06)	0.8431 (08)	0.0457 (66)
C31	-0.0467 (11)	0.1515 (07)	0.8267 (11)	0.0651 (76)
C32	-0.0287 (13)	0.0728 (08)	0.8518 (14)	0.0816 (106)
C33	0.0801 (15)	0.0429 (09)	0.8855 (12)	0.0786 (105)
C34	0.1742 (13)	0.0935 (09)	0.9003 (11)	0.0689 (94)
C35	0.1571 (10)	0.1724 (08)	0.8783 (09)	0.0577 (77)
C40	-0.1277 (09)	0.3268 (06)	0.7982 (09)	0.0453 (62)
C41	-0.1910 (09)	0.3567 (06)	0.7018 (09)	0.0500 (64)
C42	-0.3108 (11)	0.3711 (08)	0.6920 (11)	0.0646 (85)
C43	-0.3664 (11)	0.3545 (08)	0.7762 (12)	0.0706 (87)
C44	-0.3008 (11)	0.3248 (08)	0.8728 (11)	0.0668 (89)
C45	-0.1823 (10)	0.3099 (07)	0.8844 (10)	0.0577 (73)

$$^a U_{iso} = \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i^* a_j^*)$$

**Figure 2.** ORTEP plot of W(CO)<sub>4</sub>(PPh<sub>3</sub>)CNPhNCW(CO)<sub>4</sub>(PPh<sub>3</sub>) (2). Thermal ellipsoids are drawn at the 50% probability level, and hydrogens have been omitted for the purpose of clarity.

Å for tungsten complexes **1** and **2**. The isocyanide carbon–tungsten bond length is 2.065 (12) Å for **1** and 2.084 (11) Å for **2**. Although most terminal aryl isocyanide ligands are essentially linear, the angle described by the isocyanide carbon, isocyanide nitrogen, and quaternary carbon of the phenyl ring was found to

(12) C–N bond length reference: the value from a conventional X-ray refinement in ref 5 is 1.156 (2) Å. The value reported here is from an independent structural determination performed in our laboratories.

**Table IV.** Selected Bond Lengths and Angles for  $W(CO)_4(PEt_3)CNPhNCW(CO)_4(PEt_3)$  (1)

Bond Lengths (Å)			
W-C1	1.973 (15)	C1-O1	1.153 (17)
W-C2	2.060 (18)	C2-O2	1.114 (17)
W-C3	2.065 (12)	C3-N3	1.168 (15)
W-C4	2.023 (16)	C4-O4	1.125 (16)
W-C5	2.004 (12)	C5-O5	1.155 (15)
W-P	2.537 (3)	N3-C10	1.386 (15)
C10-C11	1.377 (18)	C10-C12	1.376 (17)
Bond Angles (deg)			
C1-W-C2	90.0 (5)	C4-W-C5	89.3 (6)
C1-W-C3	89.5 (5)	C4-W-P	91.5 (4)
C1-W-C4	87.9 (6)	C5-W-P	89.8 (4)
C1-W-C5	92.0 (5)	W-C1-O1	179.4 (12)
C1-W-P	178.1 (4)	W-C2-O2	177.8 (13)
C2-W-C3	91.1 (5)	W-C3-N3	176.1 (12)
C2-W-C4	177.8 (5)	W-C4-O4	177.5 (14)
C2-W-C5	91.5 (5)	W-C5-O5	178.1 (13)
C2-W-P	90.5 (4)	C3-N3-C10	169.2 (14)
C3-W-C4	88.1 (5)	C11-C10-N3	120.0 (11)
C3-W-C5	177.0 (5)	C12-C10-N3	121.4 (11)
C3-W-P	88.7 (4)	C12-C10-C11	118.5 (11)

**Table V.** Selected Bond Lengths and Angles for  $W(CO)_4(PPh_3)CNPhNCW(CO)_4(PPh_3)$  (2)

Bond Lengths (Å)			
W-C1	1.982 (14)	C1-O1	1.150 (14)
W-C2	2.048 (14)	C2-O2	1.133 (15)
W-C3	2.084 (11)	C3-N3	1.134 (12)
W-C4	2.032 (15)	C4-O4	1.129 (14)
W-C5	1.998 (13)	C5-O5	1.152 (13)
W-P	2.544 (3)	N3-C10	1.440 (14)
C10-C11	1.356 (17)	C10-C12	1.363 (17)
Bond Angles (deg)			
C1-W-C2	88.2 (5)	C4-W-C5	92.1 (5)
C1-W-C3	93.3 (4)	C4-W-P	92.0 (3)
C1-W-C4	87.7 (5)	C5-W-P	91.8 (3)
C1-W-C5	86.1 (5)	W-C1-O1	176.8 (11)
C1-W-P	177.8 (3)	W-C2-O2	175.2 (12)
C2-W-C3	87.8 (5)	W-C3-N3	177.0 (10)
C2-W-C4	174.6 (5)	W-C4-O4	178.0 (12)
C2-W-C5	91.2 (5)	W-C5-O5	175.9 (11)
C2-W-P	92.2 (3)	C3-N3-C10	175.8 (10)
C3-W-C4	92.1 (5)	C11-C10-N3	119.3 (11)
C3-W-C5	178.8 (4)	C12-C10-N3	119.8 (12)
C3-W-P	88.9 (3)	C12-C10-C11	120.9 (11)

be 169.2 (1.4)° for **1** and 175.8 (1.0)° for **2**, compared to 178.6 (4)° for the free diisocyanide ligand. The plane of the phenyl ring of the ligand in each complex lies at a significant torsional angle with respect to the bisecting  $M(L)_4$  planes in the pseudooctahedral complexes to which the ligands are coordinated. In **1** the smallest torsional angle with respect to such a plane is 36.8°, while the ligand is similarly rotated 43.1° in **2**. It is interesting to note here that **1** and **2** pack in the same space group and the similarity of their intracell arrangements suggests that they are probably subject to similar packing forces, both in kind and in degree.

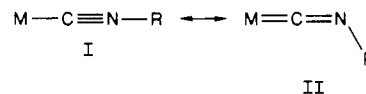
**Spectroscopic Characterization.**  $^{13}C$  NMR data for  $CNC_6H_4NC$ , **1**, and **2** are given in Tables VI and VII. The carbonyl resonances for CO trans to the phosphine are readily identified as those exhibiting the largest value of  $^2J_{PC}$ , the two-bond  $^{31}P$ - $^{13}C$  coupling constant. The remaining carbonyl carbon resonances were readily assigned on the basis of integral ratios. Chemical shifts for specific carbonyl carbons followed the trend (trans to CO) < (trans to CNR) < (trans to  $PR_3$ ), with the carbonyls trans to a phosphine ligand exhibiting the largest downfield shifts. Infrared stretching frequencies for the compounds  $CNC_6H_4NC$ , **1**, **2**, and **3** are reported in Table VIII. Assignments are based on expected band intensities and comparison with similar compounds in the literature. In other work we have noted that aryl isocyanides experience only small shifts to higher frequencies when coordinated to  $M(CO)_5$  fragments.<sup>6</sup> Compounds **1** and **2**, which contain a diisocyanide coordinated

to  $M(PR_3)(CO)_4$  fragments, experience larger shifts to lower frequencies, 21  $cm^{-1}$  for **1** and 17  $cm^{-1}$  for **2**.

## Discussion

When coordinated to the same zerovalent metal center, aryl isocyanides exhibit C-N stretching frequencies typically 30–50  $cm^{-1}$  higher than those of analogues complexes containing aryl isocyanides.<sup>13</sup> Despite the obvious differences in the bonding which must accompany such deviations, C-N bond lengths in both types of complexes are almost identical.<sup>14</sup> This implies that C-N bond lengths are relatively insensitive to changes that occur upon coordination. As stated in the Introduction, no direct X-ray crystallographic comparison has been made between CO or CNR ligands before and after coordination prior to this report, although calculations and microwave studies indicated that the C-O bond lengths are about the same for free and coordinated CO. In the work reported here, direct X-ray structural comparisons of C-N bond lengths in a free aryl diisocyanide ligand with two complexes of the ligand indicate that the story is essentially the same for coordinated isocyanides, attesting to the strength of the C-X triple bond. Within the tolerance limits of room-temperature crystal structure data, alterations in C-N and C-O bonding do not appear to be reflected in their experimentally determined bond lengths.

In complexes containing only CO and CNR, M-CO bond lengths are consistently shorter than M-CNR bond lengths, reflecting the greater  $\pi$ -acidity of the CO ligand. Addition of an organophosphine ligand to the coordination sphere appears to provide sufficient electron density to enhance  $\pi$ -bonding between the metal and isocyanide ligand, resulting in M-CNR bond lengths nearly as short as the longest M-CO bond lengths in both complexes. The phenyl rings in both complexes exhibit in-plane bends, with **1**, the complex containing  $PEt_3$ , showing the largest deviation from linearity—10.8°. We have shown in previous theoretical work that the total energy and  $\pi$ -acidity of aryl isocyanides is not significantly altered with moderate in-plane bends,<sup>15</sup> since the  $p_z$  overlap population remains effectively unchanged. It is possible that these deviations are the result of packing forces, but the similarity in the packing environment of both molecules strongly suggests that the reasons are more electronic than steric. When the metal coordination sphere contains a single aryl isocyanide ligand and a number of carbon monoxide ligands, C-N-R angles are close to 180°. When the metal is completely surrounded with isocyanide ligands, stronger  $\pi$  donors, isocyanides often deviate considerably from linearity. For example, the C-N-R angle in  $Cr(CNC_6H_5)_6$  is 172.9°.<sup>16</sup> Increased charge density at the metal center may be responsible for this, since the contribution from resonance structure II would be expected to increase as M-L  $\pi$  bonding is enhanced:



It follows from this that the presence of a sufficiently strong base should cause an otherwise linear aryl isocyanide to bend in a similar fashion. Phosphines may fill this role, in which case the stronger base would cause the greatest deviation from  $sp$  hybridization at the isocyanide nitrogen. The 10–20- $cm^{-1}$  shifts observed in the infrared spectra for **1** and **2** compared to spectrum of the free ligand are consistent with increased M-L  $\pi$  bonding for both complexes. The complex containing triethylphosphine experienced a larger shift than the complex containing triphenylphosphine, indicating more M-CNR back-bonding in **1** than in **2**. This supports the notion that the larger bend in **1** is due to increased back-bonding. Further evidence of increased back-bonding in the phosphine-containing compounds comes from a comparison of  $^{13}C$  NMR chemical shifts for  $W(CO)_5CNC_6H_4NCW(CO)_5$ <sup>6</sup> with those for **1** and **2**. The isocyanide resonance

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Table VI. <sup>13</sup>C Chemical Shift Data (ppm, TMS)

	CO <sup>a</sup>	CO <sup>b</sup>	CO <sup>c</sup>	C <sup>d</sup>	C <sup>e</sup>	C <sup>f</sup>
CNPhNC				167.6	126.8	127.6
W(CO) <sub>5</sub> CNPhNCW(CO) <sub>5</sub> <sup>g</sup>	193.5	195.5		156.2	127.6	127.1
W(CO) <sub>4</sub> (PEt <sub>3</sub> )CNPhNCW(CO) <sub>4</sub> (PEt <sub>3</sub> )	199.3	201.7	202.7	164.7	127.4	127.1
W(CO) <sub>4</sub> (PPh <sub>3</sub> )CNPhNCW(CO) <sub>4</sub> (PPh <sub>3</sub> )	199.5	202.1	202.6	165.4	127.2	126.9

<sup>a</sup>CO trans to CO. <sup>b</sup>CO trans to isocyanide. <sup>c</sup>CO trans to phosphine. <sup>d</sup>Isocyanide. <sup>e</sup>Quaternary carbon of phenyl ring. <sup>f</sup>Phenyl carbons. <sup>g</sup>Reference 6.

Table VII. NMR Coupling Constants

	<sup>1</sup> J <sub>CW</sub> , Hz				<sup>2</sup> J <sub>CP</sub> , Hz			
	CO <sup>a</sup>	CO <sup>b</sup>	CO <sup>c</sup>	C <sup>d</sup>	CO <sup>a</sup>	CO <sup>b</sup>	CO <sup>c</sup>	C <sup>d</sup>
W(CO) <sub>5</sub> CNPhNCW(CO) <sub>5</sub> <sup>e</sup>	126.0	<i>f</i>						
W(CO) <sub>4</sub> (PEt <sub>3</sub> )CNPhNCW(CO) <sub>4</sub> (PEt <sub>3</sub> )	124.2	129.2	145.9	119.5	7	6	21	9
W(CO) <sub>4</sub> (PPh <sub>3</sub> )CNPhNCW(CO) <sub>4</sub> (PPh <sub>3</sub> )	125.8	<i>f</i>	<i>f</i>	<i>f</i>	7	6	24	9

<sup>a</sup>CO trans to CO. <sup>b</sup>CO trans to isocyanide. <sup>c</sup>CO trans to phosphine. <sup>d</sup>Isocyanide. <sup>e</sup>Reference 6. <sup>f</sup>Not observed.

Table VIII. Infrared Stretching Frequencies in the C≡O and C≡N Region (cm<sup>-1</sup>)

	C≡N	C≡O
CNPhNC	2128 (s)	
W(CO) <sub>5</sub> CNPhNCW(CO) <sub>5</sub> <sup>a</sup>	2130 (m)	2047 (m), 2034 (sh), 1974 (sh), 1955 (s)
W(CO) <sub>4</sub> (PEt <sub>3</sub> )CNPhNCW(CO) <sub>4</sub> (PEt <sub>3</sub> )	2107 (m)	1992 (m), 1900 (sh), 1880 (s)
W(CO) <sub>4</sub> (PPh <sub>3</sub> )CNPhNCW(CO) <sub>4</sub> (PPh <sub>3</sub> )	2111 (m)	1999 (m), 1926 (sh), 1907 (s), 1884 (s)

<sup>a</sup>Reference 6.

for the compound lacking phosphine ligands occurs at 156.2 ppm, about 8 ppm upfield from the <sup>13</sup>CNR resonances in **1** and **2**. <sup>13</sup>C chemical shifts are dominated by the paramagnetic term that, for MCO and MCNR, takes the approximate form

$$\sigma_p = -[K(1/\langle\Delta E\rangle)\langle r^{-3}\rangle_{2p}](Q_{CC} + Q_{CM} + Q_{CX})$$

where X = O or NR,  $K = (e^2h^2)/(2m^2c^2)$ ,  $\langle\Delta E\rangle$  is the average electronic excitation energy,  $\langle r^{-3}\rangle_{2p}$  is the mean inverse cube radius of the 2p<sub>x</sub> orbital on the coordinated carbon, and Q<sub>CX</sub> is formulated from the bond-order density matrix elements for atoms C and X.<sup>17</sup> In general,  $\sigma_p$  is dominated by Q<sub>MC</sub>.<sup>18</sup> As M-C π bonding increases, Q<sub>MC</sub> increases and  $\sigma_p$  becomes more negative, resulting in a net shift downfield, as observed when CO is formally replaced with PR<sub>3</sub>.

It is interesting to note that a single phosphine ligand is apparently able to effect a CNR bend similar to that resulting from a number of isocyanides in the M(0) coordination sphere. An analysis of <sup>183</sup>W-<sup>13</sup>C coupling constants provides a simple explanation. The magnitude of the spin-spin coupling constant is dominated by Fermi contact, a function of spherically symmetric ("s") electron density at the nucleus.<sup>19</sup> Thus, for coordinated atoms with the same fraction "s" character, <sup>1</sup>J<sub>WC</sub> serves as a comparative measure of π density in the metal-ligand bond. As shown in Table VII the carbonyl trans to the phosphine in **1** and **2** experiences the largest value for <sup>1</sup>J<sub>WC</sub>, with <sup>1</sup>J<sub>WC</sub> for carbonyls trans to an isocyanide slightly larger than that for carbonyls trans to another CO. This is entirely consistent with the notion that

aryl isocyanides are somewhat more effective as σ donors and that phosphines are significantly more effective. Thus the contribution of "excess" electron density to the metal center from a single phosphine is essentially the same as that from several isocyanides, consistent with the in-plane bend observed for both bimetallic complexes.

Finally, in light of our intended use of bridging aryl diisocyanides as charge-transfer agents, the torsional angle with respect to one of the pseudooctahedral ML<sub>4</sub> planes in **1** and **2** would seem to indicate less than optimal configurations for M→CN→ring π bonding, since maximum overlap would occur with the ring and ML<sub>4</sub> fragment coplanar with one another. However, theoretical investigations of carbene carbonyl complexes have shown that the p<sub>π</sub> orbital on the carbene is exposed to metal electron density that is approximately cylindrically symmetric.<sup>20</sup> In an analogous manner, the π frontier orbital on the aryl isocyanide should "see" only minor perturbations from cylindrical symmetry at the metal center, and the rotational barrier about the M-CNR bond would be expected to be small even though back-bonding is occurring.

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**Registry No.** **1**, 115321-34-1; **2**, 115321-35-2; [W(CO)<sub>4</sub>(PEt<sub>3</sub>)Cl]<sup>-</sup>[Et<sub>4</sub>N]<sup>+</sup>, 80191-30-6; [W(CO)<sub>4</sub>(PPh<sub>3</sub>)Cl]<sup>-</sup>[Et<sub>4</sub>N]<sup>+</sup>, 60938-97-8.

**Supplementary Material Available:** Tables of thermal parameters, hydrogen positions, and angles and distances associated with the phenyl rings and ethyl groups (20 pages); listings of calculated and observed structure factors (25 pages). Ordering information is given on any current masthead page.

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