Communication between Metal Centers in Tungsten(0)-Tungsten(II) Complexes Bridged by 1,4-Diisocyanobenzene: Is the Ligand π System Involved?

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The ability of the aromatic diisocyanide ligand 1,4-diisocyanobenzene to act as a mediator for charge polarization between W(0) and W(II) centers was investigated. A series of bridged complexes were synthesized which contained W(0)-W(0), W(0)-W(II), and W(II)-W(II) metal centers, coupled by CNC_6H_4NC. C-N stretching vibrations for the W(0) ends of the molecules were actually at higher energies than those for the W(II) ends. Infrared and multinuclear NMR studies indicated that the W(0)-W(II) molecules were effectively unperturbed hybrids of the W(0)-W(0) and W(II)-W(II) molecules. In contrast, the MLCT band of the binuclear complexes is red-shifted 1221 cm^{-1} compared to that of the mononuclear complexes, indicating that the π system is involved in M-L-M bonding and *should* telegraph differences in charge from one metal center to the other through charge polarization across the ring. The apparent contradiction is resolved in the X-ray photoelectron spectra of the W(0)-W(II) complexes, which exhibit nearly identical W(4f) chemical shifts for the two tungsten centers, indicating that the metals are in very similar electronic environments.

Introduction

Isocyanide ligands are unique in their ability to coordinate strongly to transition metals encompassing the entire spectrum of oxidation states. For example, stable isocyanide complexes of tungsten occur in oxidation states varying from 0 to +6. In general, isocyanides stabilize low-valent complexes by participating as π-acceptor ligands, thus lowering charge density at the low-valent metal center and delocalizing it toward the electronegative nitrogen atom on the nitrile functionality. While isocyanides coordinate to low-valent metals in a manner analogus to that of other π-acceptor ligands such as CO and N_2, they are significantly stronger bases. Thus isocyanides coordinate to high-valent transition metals as strong σ donors. In addition, aryl isocyanides can *provide* charge density to metal centers in high oxidation states by participating as π-donor ligands. It is this dual capability of aryl isocyanides which led us to propose that the aromatic ring might serve to mediate charge density polarization between high- and low-valent transition metals, thus acting as a communication link between them.

In order to investigate this hypothesis, the bridged complexes $(CO)_5WCNC_6H_4NCW(CO)_5$ (**1**), $(CO)_4(PPh_3)WCNC_6H_4NCW(PPh_3)(CO)_4$ (**2**), $Br_2(PEt_3)_2(CO)_2WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (**3**), $(CO)_5WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (**4**), and $(CO)_4(PPh_3)WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (**5**), Ph = C_6H_5 and Et = C_2H_5, were synthesized and analyzed with spectroscopic techniques designed to test variations in charge density at each metal center resulting from the presence of the bridging aromatic system. The spectroscopic behavior of coordinated carbon monoxide has long been utilized as a probe to assess charge density variations in transition metal complexes. The most utilized spectroscopic method for this purpose has been infrared spectroscopy, which has often shown subtle differences in carbonyl stretching frequencies between complexes containing the same metal center and similar coordination environments. This results from M-L π donation, which is often considered to be a measure of the net charge on the metal. ^{13}CO NMR chemical shifts are also sensitive to the amount of charge density in the M-L π bond, and changes in them usually correlate well with shifts in CO stretching frequencies. For complexes with ligands containing π systems, Karplus and Pople[1] have shown that the dominant paramagnetic term for the chemical shift due to nucleus A is approximated by

$$\sigma_p = -[(e^2\hbar^2)/(2m^2c^2\langle\Delta E\rangle)\langle r^{-3}\rangle_{2p}]\sum_B Q_{AB}$$

where $\langle\Delta E\rangle$ = the average electronic excitation energy over all states, $\langle r^{-3}\rangle_{2p}$ = mean inverse cube of the 2p orbital radius associated with nucleus A, and Q_{AB} is determined from the charge density bond order matrix:

$$Q_{AB} = {}^4/_3\delta_{AB}(\sum_{\mu} P_{\mu A\nu B}) - {}^2/_3\sum_{\mu\neq\nu} P_{\mu A\mu B}P_{\nu A\nu B} + {}^2/_3\sum_{\mu\neq\nu} P_{\mu A\nu B}P_{\nu A\mu B}$$

where δ_{AB} is the Kronecker δ, μ and ν are valence atomic orbitals on A and B, and *P* is an element of the density matrix. For ^{13}CO ligands coordinated to transition metals, $\sigma_p = -[K\langle\Delta E\rangle^{-1}\langle r^{-3}\rangle_{2p}](Q_{CC} + Q_{MC} + Q_{CO})$, where $K = (e^2\hbar^2)/(2m^2c^2)$. A modest increase in M-C π bonding causes an increase in Q_{MC} and a smaller decrease in Q_{CO}; thus Q_{MC} dominates the ^{13}C chemical shift. As charge density increases on the transition metal, the carbonyl resonances shift downfield as Q_{MC} increases. Spectra related to the isocyanide ligand also provide information about the charge at the metal center; we have shown strong correlations between putative charge densities and C-N stretching frequencies, ^{13}C NMR chemical shifts, and ^{14}N NMR chemical shifts and band shapes.[2] Isocyanide ^{13}CNR chemical shifts also tend to be dominated by Q_{MC} in a manner analogous to that for ^{13}CO chemical shifts. For ^{14}N NMR, $\sigma_p = -[K\langle\Delta E\rangle^{-1}\langle r^{-3}\rangle_{2p}](Q_{NN} + Q_{CN} + Q_{NC})$, with no Q_{MC} term. Thus the major contributor is the Q_{CN} term, which decreases with increasing charge density at the metal center (as the C-N bond weakens); this tends to cause an upfield movement of the ^{14}N resonance.

Single-crystal X-ray diffraction studies of $(CO)_4PEt_3WCNC_6H_4NCWPEt_3(CO)_4$ indicate that the addition of the phosphine ligand introduces so much charge onto the complex that back-bonding actually results in significant bending of the

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Table I. Infrared Stretching Frequencies of **1–5** and Related Compounds in the C≡N and C≡O Stretching Regions (cm^{-1})

compound	ν_{CN}		ν_{CO}					
CNC_6H_4NC		2128						
$(CO)_5WCNC_6H_4NC$	2130	2144			1925		1990	2056
$(CO)_4(PPh_3)WCNC_6H_4NC$	2109	2118	1898		1942	1953	2005	
$W(CO)_3(PEt_3)_2Br_2$			1894		1921			
$(CO)_5WCNC_6H_4NCW(CO)_5$		2132			1925		1990	2055
$(CO)_4(PPh_3)WCNC_6H_4NCW(PPh_3)(CO)_4$	2111		1884	1907	1926		1999	
$Br_2(PEt_3)_2(CO)_2WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$	2083		1870		1928			
$(CO)_5WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$	2092	2141	1873		1926	1950	1992	2056
$(CO)_4(PPh_3)WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$	2094	2110		1913			2003	

isocyanide C–N–C bonds as it deviates from sp toward sp^2 hybridization.[3] It follows that the addition of a high-valent end to replace one of the W(0) moieties should allow for delocalization of this excess charge across the ring. The nature of the π bond in carbonyl and isocyanide ligands allows for a fairly straightforward rationalization of chemical shift trends. The analysis of ^{31}P chemical shifts is less informative as a semiquantitative means of assessing electron density at the metal center, but ^{31}P resonances are nonetheless quite sensitive to changes in the charge density, albeit often in a somewhat unpredictable manner. Still, it was anticipated that the mixed-valent complexes **4** and **5** would exhibit differences in the ^{31}P resonances when compared to **3** and **2**.

We began these studies with the working hypotheses that electron density would be polarized away from the W(0) end of **4** or **5** toward the W(II) end and that the subsequent shifts in charge would result in a downfield movement of ^{13}CO resonances on the low-valent end and corresponding increases in CO stretching frequencies. We expected opposite effects for the carbonyls on the high-valent end. We also anticipated that the CN moieties on the isocyanide ligand bonded to the different metals would behave similarly and that ^{31}P resonances would be altered by the polarization of charge density across the ring. What we discovered was something quite different! The picture which emerges from these studies sheds light on the nature of charge density at metal centers in neutral complexes containing metals in varying oxidation states and provides a warning to investigators who routinely use electron counting and oxidation numbers as a qualitative measure of "electron richness" or "electron deficiency".

Experimental Section

General Reagents and Procedures. All reactions were performed in a dry nitrogen atmosphere by using standard Schlenk techniques. $W(CO)_6$ was purchased from Strem Chemicals; 1,4-diaminocyclohexane was supplied by Du Pont; Et_4NCl, Br_2, PPh_3, PEt_3, and 1,4-diaminobenzene were purchased from Aldrich Chemical Co.; all were used without further purification. CNC_6H_4NC,[4] $CNC_6H_{10}NC$,[4] $Et_4N[W(CO)_5Cl]$,[5] $Et_4N[W(CO)_4(PPh_3)Cl]$,[6] $WOCl_4$,[7] and $W(CO)_3(PEt_3)_2Br_2$[8] (**7**) were prepared as described in the literature. The synthesis and characterization of $(CO)_4(PPh_3)WCNC_6H_4NCW(PPh_3)(CO)_4$ (**2**) have been previously reported.[3] Infrared spectra were recorded from KBr pellets on a Nicolet MX-1 FTIR spectrometer. Proton-decoupled ^{13}C and ^{31}P NMR spectra were recorded on a Bruker WH 250-MHz spectrometer in $CDCl_3$, which was used as an internal standard for ^{13}C NMR spectra, and 85% H_3PO_4 was used as an external reference for the ^{31}P NMR spectra. The ^{14}N NMR spectra were recorded on a 500-MHz GE-9 spectrometer. Electronic absorption spectra were obtained on a Hewlett-Packard 8451 A spectrometer. X-ray photoelectron spectra were obtained on a VG Scientific, Ltd., ESCALAB 200 spectrometer with a Mg/Al twin anode. Mg Kα radiation was used as the X-ray excitation source. Samples were prepared by dissolving the compounds in an appropriate solvent and drying them in vacuo in the sample chamber. The carbon 1s binding energy at 285.0 eV was used as a chemical shift reference.

Synthesis of $(CO)_5WCNC_6H_4NCW(CO)_5$ (1). 1,4-Diisocyanobenzene (5 mmol) in 50 mL of ethanol was added to a solution of $Et_4N[W(CO)_5Cl]$ (10 mmol) in 100 mL of ethanol, and the resulting solution was stirred for 5 h. The product precipitated from solution and was collected by vacuum filtration. The product was then rinsed several times with anhydrous ethanol and diethyl ether and dried under vacuum. Anal. Found (calcd): C, 27.13 (27.86); H, 0.60 (0.52); N, 3.39 (3.61).

Synthesis of $Br_2(PEt_3)_2(CO)_2WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (3). $W(CO)_3(PEt_3)_2Br_2$ (20 mmol) and CNC_6H_4NC (10 mmol) were stirred in diethyl ether (100 mL) for 1 h. The product was collected by removing the solvent by vacuum. Anal. Found (calcd): C, 30.73 (30.90); H, 4.63 (4.61); N, 1.97 (2.00). ^{31}P NMR δ (ppm): –3.3 d (PEt_3), –11.0 d (PEt_3).

Synthesis of $(CO)_5WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (4). $(CO)_5WCNC_6H_4NC$ (10 mmol) and $W(CO)_3(PEt_3)_2Br_2$ (10 mmol) were stirred in diethyl ether (150 mL) for 3 h. The solvent was reduced under vacuum and the product precipitated with pentane; it was then vacuum-filtered off and recrystallized from diethyl ether. Anal. Found (calcd): C, 30.23 (29.80); H, 3.38 (3.15); N, 2.51 (2.58). ^{31}P NMR δ (ppm): –3.3 d (PEt_3), –11.0 d (PEt_3).

Synthesis of $(CO)_4(PPh_3)WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (5). **5** was prepared in a manner identical with that for **4**, substituting $(CO)_4(PPh_3)WCNC_6H_4NC$ for $(CO)_5WCNC_6H_5NC$. Anal. Found (calcd): C, 40.83 (40.90); H, 3.81 (3.82); N, 2.18 (2.17). ^{31}P NMR δ (ppm): 22.8 s (PPh_3), –3.3 d (PEt_3), –11.0 d (PEt_3).

Synthesis of $(CO)_5WCNC_6H_4NC$ (6). $Et_4N[W(CO)_5Cl]$ (10 mmol) and CNC_6H_4NC (40 mmol) were stirred in ethanol (300 mL) at 50 °C for 1 h. The solvent was reduced to 25 mL in vacuo and the product precipitated out of solution. It was then vacuum-filtered off and purified by repeated washings with cold ethanol and pentane. Anal. Found (calcd): C, 33.77 (33.80); H, 0.99 (0.87); N, 6.31 (6.06).

Synthesis of $(CO)_5WCNC_6H_{10}NC$ (8). This complex was prepared in a manner similar to that for **6**, substituting $CNC_6H_{10}NC$ for CNC_6H_4NC, and the solution was stirred at room temperature. Anal. Found (calcd): C, 32.64 (34.08); H, 2.21 (2.20); N, 5.92 (6.12).

Synthesis of $(CO)_5WCNC_6H_{10}NCW(CO)_5$ (9). This complex was prepared in a manner identical with that for **1**, substituting $CNC_6H_{10}NC$ for CNC_6H_4NC. Anal. Found (calcd): C, 29.12 (27.65); H, 1.44 (1.29); N, 3.67 (3.58).

Synthesis of $(CO)_4(PPh_3)WCNC_6H_4NC$ (10). (10). This complex was prepared in a manner identical with that for **6**, substituting $Et_4N[W(CO)_4(PPh_3)Cl]$ for $Et_4N[W(CO)_5Cl]$. Anal. Found (calcd): C, 52.66 (53.50); H, 2.83 (2.79); N, 4.05 (4.08). ^{31}P NMR δ (ppm): 22.8 s (PPh_3).

Synthesis of $(CO)_4(PPh_3)WCNC_6H_4NC\cdot WOCl_4$. $(CO)_4(PPh_3)WCNC_6H_4NC$ (10 mmol) in 30 mL of toluene was added dropwise to a solution of $WOCl_4$ (10 mmol) in 30 mL of toluene, and the mixture was stirred at 25 °C for 2 h. The product that precipitated upon addition of hexane (60 mL) was filtered off and washed several times with hexane. IR (cm^{-1}): ν_{CN} 2110 s, 2160 sh, ν_{CO} 1922 s, 1956 sh, 1979 vs, 2043 s. ^{31}P NMR δ (ppm): 46.6 s (PPh_3).

Results and Discussion

Infrared Spectroscopic Studies. Frequencies of major absorption bands in the carbonyl and isocyanide stretching regions in the infrared for compounds **1–5** and related species are given in Table I. As we have discussed in earlier work,[9] C–N stretching frequencies in aromatic isocyanide ligands undergo relatively small

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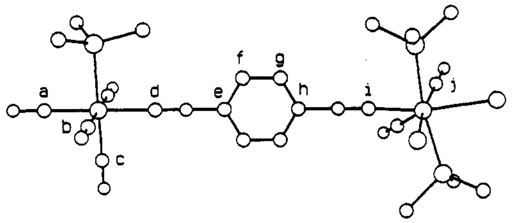
Table II. ^{13}C NMR Resonances for **1**–**5** and Related Compounds (ppm, TMS)[a]



	C^aO	C^bO	C^cO	C^dN	C^e	C^f	C^g	C^h	NC^i	C/O
CNC_6H_4NC				167.5	126.9	127.6	127.6	126.9	167.5	
$W(CO)_6$	191.5	191.5	191.5							
$(CO)_5WCNC_6H_4NC$	195.5	193.5	193.5	n	n	127.9	127.7	n	n	
$(CO)_4L'WCNC_6H_4NC$	202.0	199.3	202.4	165.7	n	127.0	127.4	n	167.1	
$W(CO)_3L_2Br_2$										n
$(CO)_5WCNC_6H_4NCW(CO)_5$	195.5	193.5	193.5	156.2	127.1	127.6	127.6	127.1	156.2	
$(CO)_4L'WCNC_6H_4NCWL'(CO)_4$	202.1	199.5	202.6	165.4	127.2	126.9	126.9	127.2	165.4	
$Br_2L_2(CO)_2WCNC_6H_4NCW(CO)_2L_2Br_2$				n	128.5	126.0	126.0	128.5	n	n
$(CO)_5WCNC_6H_4NCW(CO)_2L_2Br_2$	195.4	193.6	193.6	n	n	128.0	126.2	n	n	n
$(CO)_4L'WCNC_6H_4NCW(CO)_2L_2Br_2$	202.0	199.4	202.5	165.8	n	127.3	125.5	n	n	n

[a] n = not observed; L = triethylphosphine; L′ = triphenylphosphine.

changes upon coordination to zerovalent metal centers; the effects of increased metal to ligand back-donation are largely compensated for by lone pair ligand to metal polarization. Aliphatic isocyanides are weaker π acids and exhibit often substantial increases in C–N stretching frequencies upon coordination. Coordination of CNC_6H_4NC to form $(CO)_5WCNC_6H_4NC$ results in two C–N stretching frequencies, one which remains essentially identical to that for the free ligand and the other experiencing a 16-cm^{-1} increase. Thus the $W(CO)_5$ moiety appears to be dominated by the electron-withdrawing capacity of the carbonyl ligands. The introduction of a phosphine ligand in $(CO)_4(PPh_3)WCNC_6H_4NC$ reverses this effect by saturating the metal center with charge and increasing M–L back-bonding. The result is a 19-cm^{-1} decrease in the C–N stretching frequency. This is also reflected in the carbonyl stretching frequencies, which are generally lower in the monometallic complex containing the phosphine.

The heterobimetallic molecules show only small variations in ν_{CN}. The W(0) *and* the W(II) ends both appear to experience about 10-cm^{-1} shifts to higher energies in comparison with their homobimetallic analogues. More importantly, it is evident that the "low-valent" and "high-valent" ends of the molecule tend to retain their identity in the heterobimetallic molecules. All molecules containing a W(0) moiety display carbonyl and isocyanide stretching frequencies characteristic of the homobimetallic zerovalent (W(0)–W(0)) complexes. Similarly, molecules containing a W(II) moiety display frequencies characteristic of the W(II)–W(II) complexes. It is important here to note that the C–N stretching frequency of the end of the ligand coordinated to W(II) ranges from 2083 to 2094 cm^{-1}, while the end of the ligand coordinated to "low-valent" W(0) exhibits C–N stretching frequencies ranging from 2110 cm^{-1} (on the electron-rich phosphine-containing moiety) to 2144 cm^{-1} in $(CO)_5WCNC_6H_4NC$. The lower frequencies are indicative of greater back-donation from the metal, and/or lower σ donation onto the metal, implying that there is *more* electron density on the W(II) metal centers than there is on the W(0) centers. Such considerations presume that there is little coupling between uncoordinated C–N and coordinated C–N stretching vibrations, allowing ν_{CN} to be treated as an independent "group" frequency. If there is substantial coupling, then the increased mass of the –NC–W(II) end might serve to lower the frequency in comparison with the –NC–W(0) end. M–C and C–N force constants are generally observed to differ significantly, suggesting that the coupling will be quite weak, but this cannot be known with certainty in the absence of a complete (but prohibitive) normal-coordinate analysis.

NMR Spectroscopic Studies. ^{13}C NMR resonances for **1**–**5** and related compounds are given in Table II. The isocyanide carbons and quaternary carbons in the ring experience no NOE enhancement and are often not observed. The seven-coordinate W(II) moiety is also apparently fluxional, and no ^{13}CO resonances were observed for the "high-valent" end of any of the molecules in this study. The coordination of CNC_6H_4NC into the W(0) homobimetallic molecules resulted in insignificant changes in the ^{13}C resonances on the ring. The resonances due to the isocyanide carbons in **1** experienced an 11 ppm upfield shift upon coordination, while those in **2** shifted only about 2 ppm upfield. The Q_{MC} term should be larger for the molecule containing the phosphine ligands, due to a substantial increase in charge density at the metal center. Thus the ^{13}CN resonance for **2** would be downfield with respect to the ^{13}CN resonance for **1**.

In the heterobimetallic molecules the ^{13}CO resonances were virtually identical to those in the homobimetallics. The ^{13}CN resonance for **4** was not observed but was found to be identical in **2** and **5**. The carbon atoms coordinated to the W(0) end of the molecule appear to be indifferent to the moiety on the other side of the ring! Resonances due to the ring carbons on the bridging ligand of the W(II) homobimetallic molecule are shifted upfield in comparison with those of the W(0) homobimetallics. The ring carbons on **5** do exhibit small shifts, with the resonances due to the carbon atoms closest to the W(II) end shifting upfield and those due to the carbon atoms close to the W(0) end shifting downfield. This is consistent with a slight increase in charge density on the W(0) end and a decrease at the W(II) end of the heterobimetallic molecule in comparison with the homobimetallic analogs. While this seems contrary to intuition, it is entirely consistent with the lower C–N stretching frequencies observed for the W(II) moiety in comparison with the W(0) C–N stretching frequencies.

^{14}NC resonances for **1**, **3**, and **4** are shown in Figure 1. The resonance of the nitrogen atom on the W(II) ends of **3** and **4** is significantly broader than that associated with the W(0) ends of **1** and **3**, indicating the lower symmetry of the electric field gradient on the seven-coordinate portion of the molecules.[2] The broadness of the peaks makes it impossible to assess any slight differences, but it is clear that very little difference exists between the nitrogen atoms on the heterobimetallic molecule in comparison with the homobimetallic analogs. Again, one end of the molecule appears to be insensitive to the presence of the other end.

The apparent lack of communication between the metal centers is seen most graphically in a comparison of ^{31}P NMR spectra of the homobimetallic and heterobimetallic molecules. Figure 2 illustrates the ^{31}P resonances of **2**, **3**, and **5**. The W(0)–W(II)

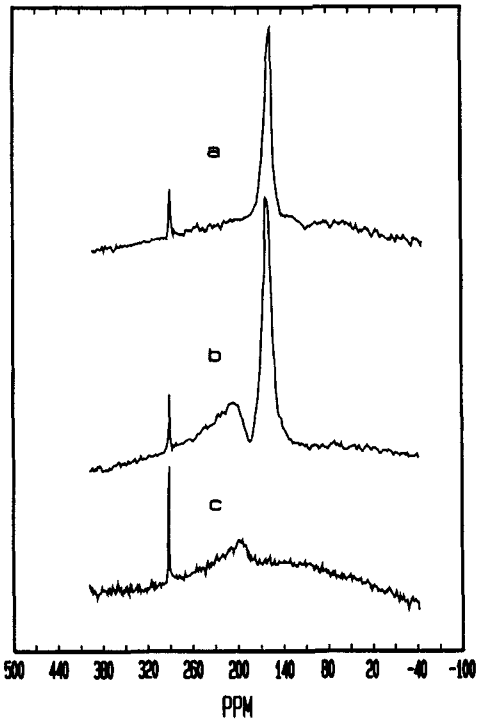


Figure 1. ^{14}NC resonances for (a) $(CO)_5WCNC_6H_4NCW(CO)_5$ (**1**), (b) $(CO)_5WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (**4**), and (c) $Br_2(PEt_3)_2(CO)_2WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (**3**). The sharp resonance at 290 ppm is dissolved N_2.

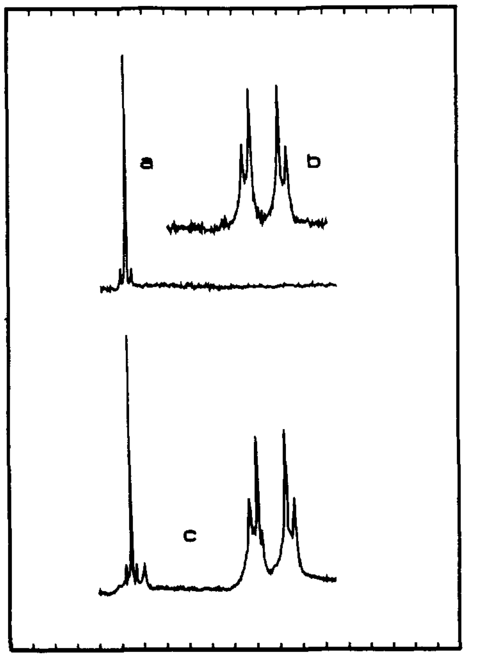


Figure 2. ^{31}P resonances for (a) $(CO)_4(PPh_3)WCNC_6H_4NCW(PPh_3)(CO)_4$ (**2**), (b) $Br_2(PEt_3)_2(CO)_2WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (**3**), and (c) $(CO)_4(PPh_3)WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (**5**).

spectrum appears to consist of a 50/50 contribution of the W(0)–W(0) and W(II)–W(II) molecules. On the basis of these traditional NMR and infrared spectroscopic techniques, we are apparently led to the conclusion that the W(0) and W(II) ends of the heterobimetallic molecules are almost completely uncoupled, irrespective of the ligand π system.

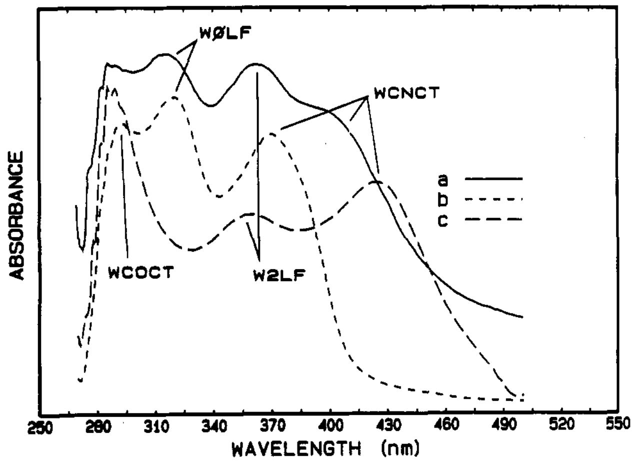


Figure 3. Electronic absorption spectra of (a) $(CO)_5WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (**4**), (b) $(CO)_5WCNC_6H_4NCW(CO)_5$ (**1**), and (c) $Br_2(PEt_3)_2(CO)_2WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (**3**). WCOCT refers to metal to CO charge transfer, W0LF to ligand field transitions localized on the W(0) end, W2LF to ligand field transitions localized on the W(II) end, and WCNCT to metal to ligand charge transfer into the bridging ligand π^* system.

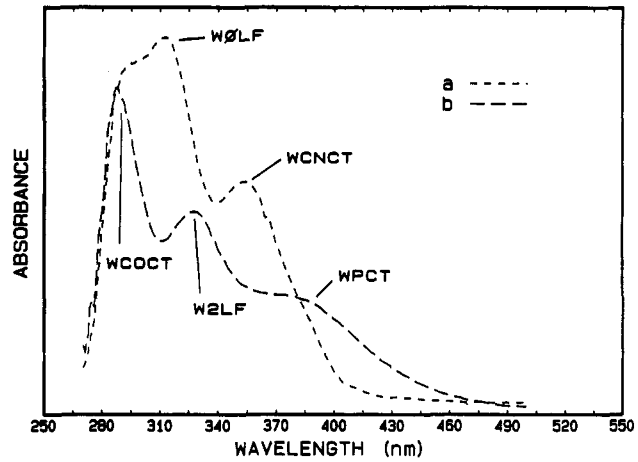


Figure 4. Electronic absorption spectra of (a) $(CO)_5WCNC_6H_4NC$ and (b) $W(CO)_3(PEt_3)_2Br_2$. WCOCT refers to metal to CO charge transfer, W0LF to ligand field transitions localized on the W(0) end, W2LF to ligand field transitions localized on the W(II) end, WCNCT to metal to ligand charge transfer into the bridging ligand π^* system, and WPCT to metal to phosphine charge transfer.

Electronic Absorption Spectroscopic Studies. Figure 3 illustrates electronic absorption spectra of **1**, **3**, and **4**; Figure 4 shows electronic absorption spectra of the monometallic precursor molecules, $(CO)_5WCNC_6H_4NC$ (**6**) and $W(CO)_3(PEt_3)_2Br_2$ (**7**). $W \rightarrow \pi^*(CO)$ charge-transfer bands are observed in all complexes in the 280–295-nm region. The assignments were based on the metal to carbonyl absorption maximum observed at 290 nm in $W(CO)_6$.[10] Ligand field (LF) transitions were assigned on the basis that they should have transition energies similar to those observed in $W(CO)_6$ at 314 and 334 nm. These bands also exhibit negligible solvatochromic shifts, a characteristic of d–d transitions.[11] The LF bands in these molecules are significantly more intense than those observed in $W(CO)_6$, since they are allowed transitions in a noncentrosymmetric environment about the coordinated metal. The ligand field transitions on the W(0) end of molecules **1**, **4**, and **6** occur in the 310–325-nm region and experience only slight shifts, since they are effectively in the same coordination environments in all complexes. The LF transitions are at lower energies on the W(II) ends than on the W(0) end. This indicates that the bromine ligands donate substantial π-electron density to the metal center, therefore lowering the ligand field splitting. Additionally, while the LF transitions on the W(II) ends of **3** and **4** occur at nearly the same frequency,

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(10) Beach, N. A.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5713.
(11) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 1139.

the transition in **7** is at a higher frequency. In this comparison, the coordination environment of W(II) in **7** differs from that of **3** and **4**, in that **7** contains a carbonyl ligand in place of an isocyanide ligand. CO is a better π acceptor than CNR,[12] and **7** should therefore exhibit an increase in ligand field splitting over **3** and **4**. Tungsten to isocyanide charge-transfer bands were assigned on the basis of transitions observed in $W(CNR)_6$.[13] A weak and very broad band is observed for **7**, perhaps containing a combination of W → P metal to ligand charge-transfer (MLCT) and Br → W ligand to metal charge-transfer (LMCT) bands. The band is apparently masked by the strong tungsten to isocyanide charge-transfer band(s) in **4**. The $W \rightarrow \pi^*(CNR)$ absorption occurs at 27 027 cm^{-1} in **1** and at 23 585 cm^{-1} in **3**. The MLCT band involving the bridging ligand is not characteristic of either homonuclear analog but appears as a broad band about midway between the $W \rightarrow \pi^*(CNR)$ MLCT bands of the homonuclear complexes, at approximately 25 000 cm^{-1} for complex **4**. Lees and co-workers observed similar results in the heteronuclear complex $(CO)_5WpyzRe(CO)_4Cl$.[14] Given that occupied metal orbitals remain effectively constant over the range of complexes with similar coordination environments, as with Lees' complexes, the π^* systems on the ligands are very different for **1**, **3**, and **4**. This strongly suggests that the ligand π^* system is influenced by the W(0) and W(II) ends of the molecule and that this effect is delocalized over the entire ring rather than localized in the C–N π^* region. The delocalization of the π^* system on the bridge clearly points to a delocalized and *occupied* π system, primed to sense charge differences between both ends of the molecule.

This effect is illustrated dramatically when the monometallic $(CO)_5WCNC_6H_4NC$ is transformed into a binuclear complex. Addition of a second $W(CO)_5$ moiety to the free isocyanide functionality of **6** results in a dramatic red shift in the $W \rightarrow \pi^*(CNR)$ MLCT band from 28 248 cm^{-1} in **6** to 27 027 cm^{-1} in **1**. Lees and co-workers also observed this phenomenon when comparing the electronic spectra of $(CO)_5Wpyz$ and $(CO)_5WpyzW(CO)_5$.[14] The lowering in energy of the π^* system on the ring strongly implies that electrons in the ligand π molecular orbitals are much more delocalized on the bimetallic complex than on the monometallic precursor, resulting in increased resonance stabilization in the bimetallic molecule. The transition is from a largely "metal-like" state to a "ligand-like" state, and the localization of the ground-state electron density on metals in the same effective coordination environment would render these localized ground states approximately equivalent in energy. The lowering of energy of the transition must therefore arise from a "ligand-like" excited state. This hypothesis is readily tested by replacing the aromatic ligand with a saturated analog, $CNC_6H_{10}NC$. The lack of a π system should isolate one end of the molecule from the other, and the red shift should not occur upon binucleation of the monometallic analog of **6** containing this ligand. The monometallic $(CO)_5WCNC_6H_{10}NC$ (**8**) and the bimetallic $(CO)_5WCNC_6H_{10}NCW(CO)_5$ (**9**) were synthesized and their electronic spectra were recorded; the results are shown in Figure 5. As predicted, the MLCT transitions occur at effectively the same wavelength, providing convincing evidence that the ligand π system in 1,4-diisocyanobenzene is capable of interacting with metal centers and electronically coupling them in the complexes under investigation in this study. At this stage we are faced with an obvious contradiction: there exists a π system intimately involved in the metal–ligand–metal bonding of **4** and **5**, yet a spectroscopic analysis of the ligands attached to each metal center indicates that their environments are insensitive to differences in the oxidation state of the metal on the other side of the bridging ligand. This contradiction is finally resolved by directly observing the W(0) and W(II) centers in both heterobimetallic and homobimetallic complexes.

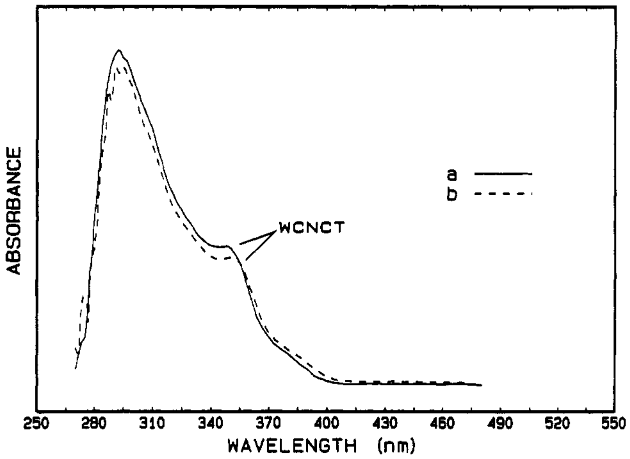

Figure 5. Electronic absorption spectra of (a) $(CO)_5WCNC_6H_{10}NCW(CO)_5$ (**9**) and (b) $(CO)_5WCNC_6H_{10}NC$ (**8**). WCNCT refers to metal to ligand charge transfer into a π^* molecular orbital localized mainly on the isocyanide (CN) moiety.

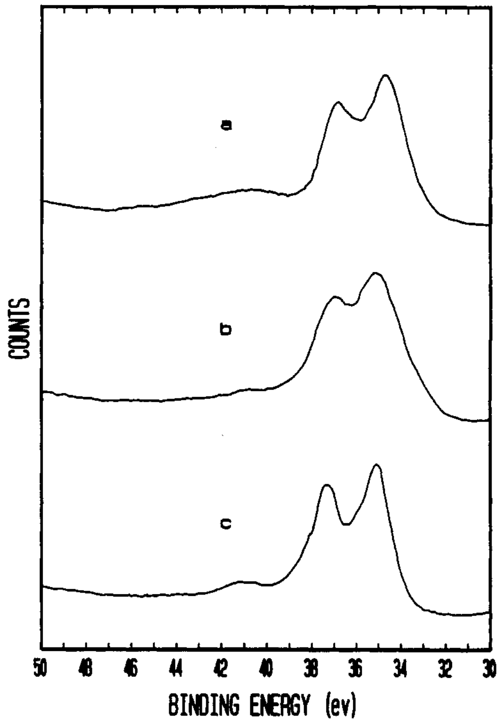

Figure 6. W(4f) X-ray photoelectron spectra of (a) $(CO)_5WCNC_6H_4NCW(CO)_5$ (**1**), (b) $(CO)_5WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (**4**), and (c) $Br_2(PEt_3)_2(CO)_2WCNC_6H_4NCW(CO)_2(PEt_3)_2Br_2$ (**3**).

X-ray Photoelectron Spectroscopic Studies. The 4f electrons of tungsten are very diffuse and especially sensitive to ligand perturbations. Chemical shifts of the 4f electrons are used routinely to identify the various oxidation states of tungsten. The 4f electrons in a given tungsten atom exhibit two peaks corresponding to the two spin–orbit states. Thus, if there is a lack of coupling between two different metal centers in the heterobimetallic complexes, this should be reflected in two sets of 4f binding energies, one corresponding to the W(0) center and the other to the W(II) center. W(4f) X-ray photoelectron spectra of **1**, **3**, and **4** are shown in Figure 6. The spectra dramatically reveal the reason for the lack of ligand perturbations: the metals to which they are attached have very similar average charge densities. The binding energies are remarkably close to one another for the three complexes, so close that the peaks are effectively unresolved in the heterobimetallic complexes.

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[12] Guy, M. P.; Guy, J. T.; Bennett, D. W. *THEOCHEM* **1985**, *122*, 95.

[13] Mann, K. R.; Cimolino, M.; Geoffrey, G. L.; Hammond, G. S.; Orio, A. A.; Albertia, G.; Gray, H. B. *Inorg. Chim. Acta* **1976**, *16*, 97.

[14] Zulu, M. M.; Lees, A. J. *Organometallics* **1989**, *8*, 955.

The anticipated shift was based on the hypothesis that the "high-valent" W(II) end of a heterobimetallic molecule would polarize charge away from the "low-valent" end across the π system of the bridging ligand. This can occur only if there is a reasonable difference in electronegativity between the metals, and the XPS data indicate clearly that this is not the case. Spectral indications of ligand environments are effectively unchanged because the metal centers to which the ligands are attached are effectively unchanged.

Spectroscopic Perturbations in $(CO)_4(PPh_3)WCNC_6H_4NC\cdot WOCl_4$. It is perhaps not so surprising that the formal W(0) and W(II) metal centers are in similar electronic environments. After all, W(0) carbonyl complexes would not exist if the carbonyl ligands were not strongly electron-withdrawing, and the W(II) centers in these complexes contain four strong donor ligands: two bromine and two phosphine ligands. If the π system of the bridging ligand is capable of supporting charge polarization between metal centers, then the replacement of the W(II) center with one in a much higher oxidation state should serve to induce the perturbations that we have been looking for.

We have succeeded in synthesizing a complex in solution resulting from the reaction of $(CO)_4(PPh_3)WCNC_6H_4NC$ and $WOCl_4$. The complex is extremely air-sensitive and to date we have been unable to isolate it in sufficient purity for elemental analysis. Nevertheless, solid-state infrared spectra provide strong evidence that the complex is $(CO)_4(PPh_3)WCNC_6H_4NCWOCl_4$. The appearance of a sharp absorption at 997 cm^{-1} and lack of a broad band at 875 cm^{-1} are consistent with the conversion of the polymeric bridged oxygen atoms (W–O–W) in $WOCl_4$ to terminal oxygen atoms (W═O).[15] Only one band is observed in the 340-cm^{-1} region, suggesting that the chlorine atoms lie in a plane and are not trans to the W═O group.[15c] These observations indicate that the complex has local C_{4v} symmetry, consistent with a $WOCl_4L$ ($L = CNC_6H_4NCW(PPh_3)(CO)_4$) structure.

The putative W(0)–W(VI) complex exhibits a 2110-cm^{-1} C–N stretching frequency characteristic of low-valent aryl isocyanide complexes, shifted to slightly higher energy in comparison to that of $(CO)_4(PPh_3)WCNC_6H_4NC$. This is probably due to the delocalization of electron density away from the C–N bonding region of the W(0) end in the M–L–M $d\pi$–$p\pi^*$–$d\pi$ molecular orbital. More significantly, the W(0)–W(VI) complex exhibits a second C–N stretching frequency at 2160 cm^{-1}. The 42-cm^{-1} shift to higher frequencies is typical of isocyanide ligands coordinated to W(VI) centers.[16] Carbonyl stretching frequencies are 14–38 cm^{-1} higher in the heterobimetallic complex than they are in the W(0)–W(0) complex, consistent with a shift in charge density away from the W(0) center. ^{13}C and ^{31}P NMR spectra provide more dramatic evidence that the W(VI) end has had a substantial effect on the W(0) portion of the molecule. Observed ^{13}CO resonances shift by as much as 16 ppm, while the ^{31}P resonance on the W(0) end of the W(0)–W(VI) complex shifts downfield 25 ppm. Thus charge perturbations across the ring are observed when the differences between the two metal centers become pronounced.

Concluding Remarks

The lesson here is an important one: comparative oxidation states for transition metals tell us little about the charge density at the metal centers. In the case cited here the "low-valent" metal appears to be *at least* as positively charged as the "high-valent" center. The comparative C–N stretching frequencies indicate that, if anything, the W(0) ends of the bimetallic molecules are less able to contribute π-electron density to the isocyanide ligand than the W(II) ends. In any event, the bridging aromatic ligand is involved in a M–L–M π system which appears capable of transmitting electronic information from one end of the molecule to the other, provided that there is a sufficient difference in charge density between the metals to which the bridging ligand is coordinated.

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(15) (a) Crouch, P. C.; Fowles, G. W. A.; Marshall, P. R.; Walton, R. A. *J. Chem. Soc. A* **1968**, 1634. (b) Fowles, G. W. A.; Frost, J. L. *J. Chem. Soc. A* **1966**, 1634. (c) Canterford, J. H.; Colton, R.; Tomkins, I. B. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 471.

(16) Guy, J. T.; Bennett, D. W. *Inorg. Chim. Acta* **1985**, *96*, L83.