

^{13}C , ^{17}O , and ^{14}N NMR Spectroscopic Studies of a Series of Mixed Isocyanide/Carbonyl Complexes of Tungsten: $\text{W}(\text{CO})_{6-n}(\text{CNR})_n$ ($\text{R} = \textit{tert}$ -Butyl, p -Tolyl; $n = 1-3$)

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^{13}C , ^{17}O , and ^{14}N NMR spectra for the tungsten isocyanide complexes $\text{W}(\text{CO})_{6-n}(\text{CNR})_n$ ($\text{R} = \textit{tert}$ -butyl, p -tolyl; $n = 1-3$) have been obtained and the magnitudes of the corresponding chemical shifts utilized as a probe of differences in electronic structure. Comparisons of $\delta(^{17}\text{O})$ with $\delta(^{13}\text{CO})$ and of $\delta(^{14}\text{N})$ with $\nu(\text{CN})$, $\delta(^{13}\text{CN})$, or $\delta(^{13}\text{CO})$ are shown to confirm the better net donor ability of the aliphatic isocyanide over the aromatic isocyanide and illustrate an increased amount of charge density available at the metal center when CO is successively replaced with CNR. Marked differences in ^{14}N quadrupolar relaxation times are observed between aromatic and aliphatic isocyanides, suggesting that the aromatic ring is involved in the M-L π system.

Introduction

The coordination chemistry of isocyanides continues to be an area of intense interest.¹ Superficially isocyanide ligands are carbon monoxide analogues capable of participating in synergistic bonding with low-valent transition-metal centers. In contrast to CO, they are structurally versatile and equally capable of coordinating to high-valent transition metals. This versatility can be exploited in synthetic strategies designed to produce complexes with varying electronic properties, thus creating a need for an understanding of the nature of the metal-ligand bond in such complexes. In particular, aryl isocyanides and alkyl isocyanides exhibit markedly differing spectroscopic properties and reactivities as ligands.² Metal-carbon and carbon-nitrogen bond lengths in both types of complexes are remarkably similar, yet C-N stretching frequencies and metal reduction potentials differ considerably.³ Apparent contradictory observations such as this create an unclear picture of the differences between alkyl and aryl isocyanides and more importantly the reasons for these differences. The obvious difference between these two ligand types is the aromatic ring, which can participate in M-L π bonding while the aliphatic group in alkyl isocyanides cannot. In spite of this, crystallographic studies support earlier vibrational work in implying that the ring does not appear to be involved to any significant extent in M-L π bonding.⁴

Thus far, primary tools for analysis of transition-metal isocyanide complexes have included vibrational spectroscopy, electrochemical methods, and X-ray crystallography.⁵ As mentioned above, these techniques have often yielded results for which conflicting conclusions have been drawn with regard to the nature of the isocyanide ligand as it bonds to low-valent transition-metal centers.^{3,4} In principle, NMR spectroscopy should provide more direct information regarding electronic structure and metal-ligand bonding. ^{13}C NMR studies of coordinated isocyanides have been conducted with limited success, but they are often hampered by relaxation effects and lack of NOE, which tend to preclude detection of the isocyanide carbon resonance.⁶ It has been suggested that ^{17}O NMR may be even more sensitive than ^{13}C chemical shifts as a probe for metal carbonyl π bonding,⁷ and previous studies by several groups have demonstrated the sensitivity of C^{17}O NMR chemical shifts to differences in electronic structure between metal carbonyls.⁸ If such interpretations are to be useful, they should at least be self-consistent. Thus, the determination of ^{17}O resonances for a series of metal carbonyl/isocyanide complexes should corroborate traditional bonding interpretations arising from ^{13}C NMR data.

The ^{14}N nucleus has been used much more sparingly as a probe, due undoubtedly to its large quadrupole moment, which renders most compounds containing nitrogen unsuitable for ^{14}N studies because the resonance is simply too broad to be observed. Isocyanides are an important exception in that they contain nitrogen in a relatively symmetric electronic environment, which results in a smaller interaction of the nuclear magnetic quadrupole with

Table I. ^{13}C Chemical Shifts for 1-6 (ppm)

	CO^a	CO^b	CN
$\text{W}(\text{CO})_3(\text{CNC}_6\text{H}_4\text{CH}_3)_3$		203	160
$\text{W}(\text{CO})_4(\text{CNC}_6\text{H}_4\text{CH}_3)_2$	197	200	156
$\text{W}(\text{CO})_5\text{CNC}_6\text{H}_4\text{CH}_3$	194	196	151
$\text{W}(\text{CO})_3(\text{CNC}(\text{CH}_3)_3)_3$		205	151
$\text{W}(\text{CO})_4(\text{CNC}(\text{CH}_3)_3)_2$	198	201	144
$\text{W}(\text{CO})_5\text{CNC}(\text{CH}_3)_3$	195	197	140

^a CO trans to CO. ^b CO trans to isocyanide.**Table II.** ^{17}O Chemical Shifts for 1-6 (ppm, Relative to H_2O)

	CO^a	CO^b
$\text{W}(\text{CO})_3(\text{CNC}_6\text{H}_4\text{CH}_3)_3$		346
$\text{W}(\text{CO})_4(\text{CNC}_6\text{H}_4\text{CH}_3)_2$	348	347
$\text{W}(\text{CO})_5\text{CNC}_6\text{H}_4\text{CH}_3$	351	351
$\text{W}(\text{CO})_3(\text{CNC}(\text{CH}_3)_3)_3$		338
$\text{W}(\text{CO})_4(\text{CNC}(\text{CH}_3)_3)_2$	344	343
$\text{W}(\text{CO})_5\text{CNC}(\text{CH}_3)_3$	350	348

^a CO trans to CO. ^b CO trans to isocyanide.**Table III.** ^{14}N Chemical Shifts for 1-6 (ppm, Relative to Et_4NO_3)

	CN	CN
$\text{W}(\text{CO})_3(\text{CNC}_6\text{H}_4\text{CH}_3)_3$	158.1	$\text{W}(\text{CO})_3(\text{CNC}(\text{CH}_3)_3)_3$ 174.2
$\text{W}(\text{CO})_4(\text{CNC}_6\text{H}_4\text{CH}_3)_2$	159.4	$\text{W}(\text{CO})_4(\text{CNC}(\text{CH}_3)_3)_2$ 176.3
$\text{W}(\text{CO})_5\text{CNC}_6\text{H}_4\text{CH}_3$	160.3	$\text{W}(\text{CO})_5\text{CNC}(\text{CH}_3)_3$ 178.6

the electric field gradient.⁹ Thus, not only are isocyanide ^{14}N resonances observable, but their line widths prove to be extremely sensitive to perturbations in the symmetry of the electric field about nitrogen.

In this report we demonstrate the utility of ^{13}C , ^{17}O , and ^{14}N NMR data in providing information regarding the relative donor/acceptor abilities of *tert*-butyl and *p*-tolyl isocyanides in a

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series of complexes consisting of varying numbers of these ligands coordinated to a low-valent tungsten center. The results of these studies serve as a basis for an analysis of the differences between aromatic and aliphatic isocyanide ligands coordinated to low-valent transition metals.

Experimental Section

The complexes $W(CO)_3(CNC_6H_4CH_3)_3$ (1), $W(CO)_4(CNC_6H_4CH_3)_2$ (2), $W(CO)_3CNC_6H_4CH_3$ (3), $W(CO)_3(CNC(CH_3)_3)_3$ (4), $W(CO)_4(CNC(CH_3)_3)_2$ (5), and $W(CO)_5CNC(CH_3)_3$ (6) were synthesized with all the isocyanides cis to each other according to published procedures.¹⁰ All NMR spectra were recorded on a Bruker WM-250 FT spectrometer at ambient temperatures. Proton-decoupled ^{13}C spectra were recorded in dry oxygen-free $CDCl_3$ solutions with $CDCl_3$ as an internal reference. Chemical shifts are reported for compounds 1–6 in Table I. Chemical shifts are reported relative to TMS ($(CH_3)_4Si$), with downfield chemical shifts considered positive. ^{17}O NMR spectra were recorded in 15 mm o.d. tubes containing H_2O in an insert, which served as an external reference. Chemical shifts are reported for compounds 1–6 in Table II. In order to eliminate acoustic ringing effects for the observation of this nucleus, a spin-echo Fourier transform pulse sequence was utilized incorporating a 120- μs pulse delay between 90° pulses. It was not necessary to use such a sequence for the acquisition of ^{14}N NMR data, with spectra readily acquired in 15 mm o.d. tubes and referenced with respect to the $^{14}NH_4^+$ signal of NH_4NO_3 (insert). Chemical shifts are reported for compounds 1–6 in Table III. The presence of the quadrupole moment results in the dominance of quadrupolar relaxation rather than the usual dipole-dipole mechanism. In the ideal limit the relaxation rates T_1^{-1} and T_2^{-1} are equal and in this case equivalent to the quadrupolar relaxation rate T_q^{-1} , expressed as

$$T_q^{-1} = \frac{3}{8} [(e^2qQ)^2] \hbar^{-2} (1 + \eta^2/3) \tau_c$$

where eq = effective electric field gradient, eQ = quadrupole moment of the observed nucleus, η = asymmetry parameter, and τ_c = rotational correlation time. In isocyanides, it is the highly symmetric charge distribution that effectively reduces the electronic field gradient at the nitrogen center and is manifested experimentally in terms of a reasonably narrow line width in the observed ^{14}N resonance. In the expression for T_q^{-1} , the asymmetry parameter η is negligible for highly symmetric molecules such as isocyanides (η was determined independently to be zero for compounds such as CH_3CN ¹¹). The rotational correlation term is largely a function of molar volume and viscosity and should not be very different for the dilute concentrations of the complexes. Since T_2 and T_q are essentially identical, T_q is effectively measured from the line width of the experimentally observed resonances.

Results and Discussion

The paramagnetic term in Ramsey's equation dominates the chemical shift for atoms with $2p\pi$ electrons.¹² An approximate formulation of the paramagnetic term derived by Karplus and Pople provides a useful rationalization of chemical shift trends involving π -acceptor ligands:¹³

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

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

$$Q_{AB} = \frac{1}{3} \delta_{AB} (\sum_{\mu} P_{\mu A \mu B}) - \frac{2}{3} \sum_{\mu \neq \nu} P_{\mu A \mu B} P_{\nu A \nu B} + \frac{2}{3} \sum_{\mu \neq \nu} P_{\mu A \nu B} P_{\nu A \mu B}$$

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.¹⁴ For ^{13}CO NMR, $\sigma_p = -[K(1/\langle\Delta E\rangle)\langle r^{-3}\rangle_{2p}](Q_{CC} + Q_{MC} + Q_{CO})$, where $K = (e^2\hbar^2)/(2m^2c^2)$. While the $\langle\Delta E\rangle$ and $\langle r^{-3}\rangle_{2p}$ terms

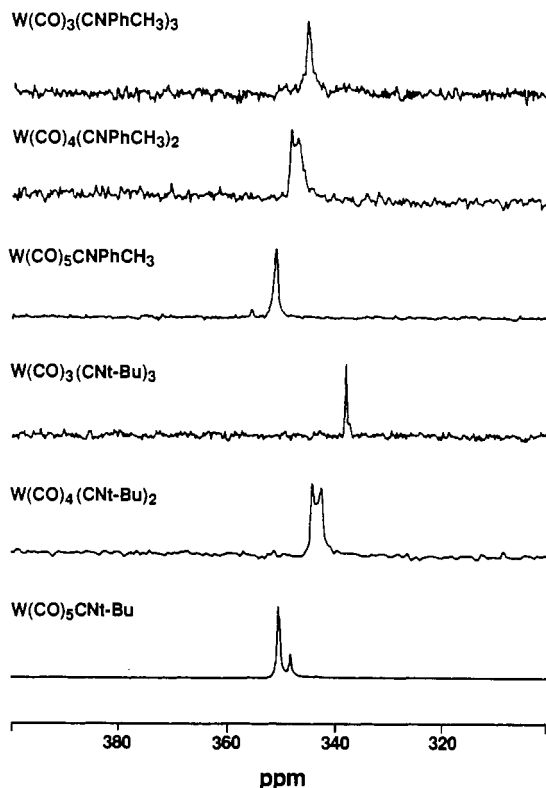


Figure 1. ^{17}O NMR spectra of 1–6.

affect the absolute values of the chemical shifts, they generally have secondary effects that fail to account for observed trends in series of complexes.^{8b} An increase in $M-C$ π bonding results in an increase in Q_{MC} and a subsequent decrease in Q_{CO} . Since the major perturbation occurs in the $M-C$ π bond, it is not surprising that Q_{MC} dominates the ^{13}C chemical shift.¹⁵ Isocyanides are generally considered to be stronger Lewis bases than carbon monoxide, and this is reflected in the increasing downfield shift of ^{13}CO resonances as carbonyl ligands are replaced with isocyanide ligands. Chemical shifts for the complexes containing alkyl isocyanides occur further downfield than those for the aryl isocyanide complexes with the same degree of carbonyl substitution, supporting the notion that alkyl isocyanides supply more charge density to the metal center than aryl isocyanides. This is consistent with frontier molecular orbital considerations which indicate that alkyl isocyanides should be stronger σ donors while aryl isocyanides are better π acids. Carbonyl groups are the predominant π acceptors in complexes containing isocyanides, with $M-CO$ bond lengths significantly shorter than $M-CNR$ lengths. As indicated previously, $M-C$ and $C-N$ bond lengths vary little among isocyanides coordinated to the same zerovalent metal, regardless of whether R = aryl or alkyl. In spite of the apparent similarity of the $M-C$ bonding in such complexes, ^{13}CNR chemical shifts provide further evidence that the electronic nature of the $M-C$ bonds in both types of complexes is different. We have previously rationalized this as a fortuitous cancellation of effects in which the stronger basicity of the alkyl isocyanide is compensated for by the stronger π acidity of the aryl isocyanide.⁵ The ^{13}CNR resonances in Table I are consistent with this argument. In this case $\sigma_p = -[K(1/\langle\Delta E\rangle)\langle r^{-3}\rangle_{2p}](Q_{CC} + Q_{MC} + Q_{CN})$, and although there is some risk in drawing a comparison between CO and CNR , it seems reasonable that Q_{MC} will again be the dominant contributor. Increased isocyanide substitution results in a downfield trend similar to that observed for ^{13}CO , and perhaps more importantly, the aryl isocyanide resonances are all 9–11 ppm further downfield than those of the corresponding alkyl isocyanides. This suggests that the aryl isocyanide ligands are stronger π

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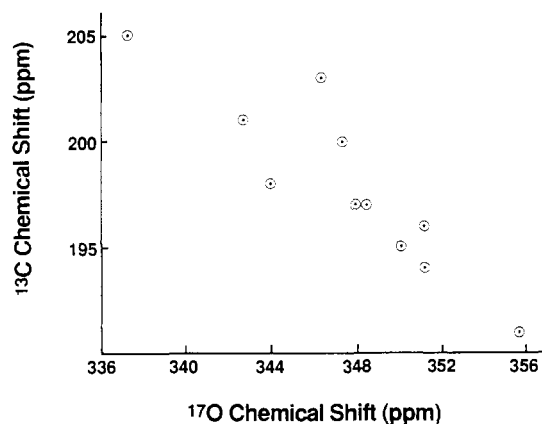


Figure 2. Plot of ^{13}C vs ^{17}O chemical shifts for 1-6 and $\text{W}(\text{CO})_6$.

acceptors, clearly implicating the ring in the M-C π -bonding scheme.

^{17}O NMR spectra for $\text{W}(\text{CO})_5(\text{CN-}t\text{-Bu})$ (1) ($t\text{-Bu}$ = *tert*-butyl), $\text{W}(\text{CO})_4(\text{CN-}t\text{-Bu})_2$ (2), $\text{W}(\text{CO})_3(\text{CN-}t\text{-Bu})_3$ (3), $\text{W}(\text{CO})_5(\text{CN-}p\text{-Tol})$ (4) ($p\text{-Tol}$ = *p*-tolyl), $\text{W}(\text{CO})_4(\text{CN-}p\text{-Tol})_2$ (5), and $\text{W}(\text{CO})_3(\text{CN-}p\text{-Tol})_3$ (6) are shown in Figure 1. For ^{17}O , $\sigma_p = -[K(1/\langle\Delta E\rangle)\langle r^{-3}\rangle_{2p}](Q_{\text{OO}} + Q_{\text{CO}})$, such that an increase in M-C π bonding results in a decrease in Q_{CO} , and with no Q_{MC} term, the chemical shift is less negative; i.e., it occurs further upfield.^{16,14,8b} In general, as carbonyl ligands are replaced with isocyanide ligands, remaining carbonyl ^{17}O resonances move upfield as predicted from an increase in available electron density for M-CO π bonding. Figure 2 illustrates the strong correlation between ^{17}O and ^{13}C chemical shifts for these complexes, again demonstrating that the alkyl isocyanide ligand provides more charge density for CO π bonding than the aryl isocyanide.

To our knowledge there has been only one prior report of ^{14}N NMR chemical shifts of organometallic isocyanide complexes.¹⁷ From the results of this study, it was concluded that increasing the number of isocyanide ligands about a metal center results in a shift to lower fields and may suggest a greater amount of metal-to-ligand π bonding as estimated from C-N stretching frequencies. ^{14}N NMR spectra of 1-6 are shown in Figure 3. In this case, $\sigma_p = -[K(1/\langle\Delta E\rangle)\langle r^{-3}\rangle_{2p}](Q_{\text{NN}} + Q_{\text{CN}} + Q_{\text{NC}})$, and in the absence of a Q_{MC} term, the decreasing Q_{CN} term would be expected to result in an upfield trend as M-CNR π bonding increases in a manner analogous to that of the ^{17}O chemical shift for metal carbonyls. However, this interpretation is complicated in aryl isocyanides by a potential π interaction between the nitrogen and the aromatic ring to which it is attached (Q_{NC}). Ab initio calculations on the free aromatic ligand indicate that the LUMO, the frontier orbital participating in the π bond, is antibonding with respect to the C(terminal)-N bond and bonding with respect to the C(aryl)-N bond.¹⁸ Thus, Q_{CN} and Q_{NC} should have opposite effects on the ^{14}N chemical shift. The M-C-N π bond arises largely from the polarization of charge density on the metal toward electronegative nitrogen, and since there is no effective source of charge in the portion of the isocyanide frontier orbital centered on the ring, the Q_{CN} term might be expected to dominate. This view is supported by the observation that the ^{14}N chemical shifts for the aryl isocyanide complexes are 14-18 ppm further upfield than those for the alkyl isocyanides. It appears that the major effect of the ring is to lower electron-electron repulsion at the nitrogen to the extent that it is capable of attracting more charge density from the metal, thus increasing the predominance of the Q_{CN} term. The Q_{NC} term will be less affected since electron density attracted into the ring will not remain isolated in the N-C(aryl) bond as much as increased M-L density will remain localized in the C(terminal)-N bond. The ^{14}N res-

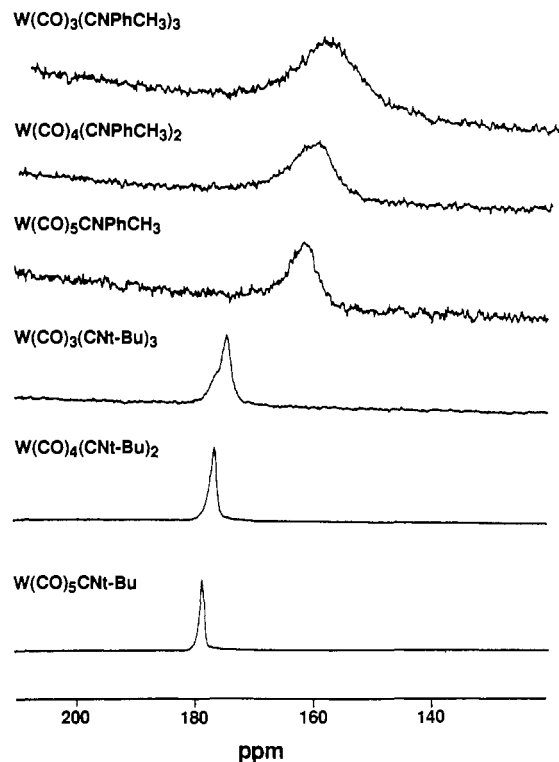


Figure 3. ^{14}N NMR spectra of 1-6.

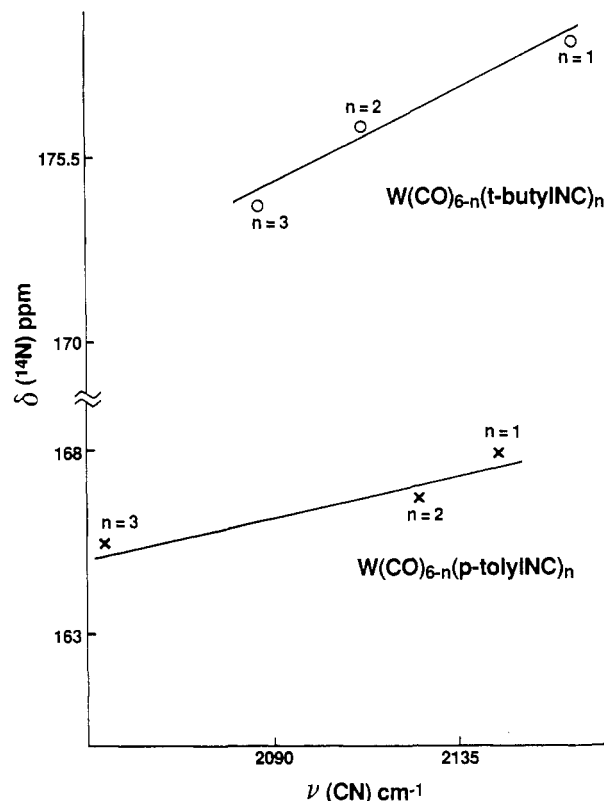


Figure 4. Plot of $\delta(^{14}\text{N})$ versus ν_{CN} for 1-6.

onances for coordinated aryl and alkyl isocyanides exhibit striking differences, both in chemical shifts and in line shape, and provide further evidence that there is more M-CNR π bonding in coordinated aryl isocyanides than in their alkyl counterparts. Figure 4 is a plot of $\delta(^{14}\text{N})$ versus ν_{CN} for 1-6. It appears from this comparison that C-N stretching frequencies are also a reasonable indicator of M-CNR π bonding, provided that comparisons are made between complexes containing the same metal and same type of isocyanide ligand. Figure 5 is a plot of $\delta(\text{C}^{14}\text{NR})$ versus

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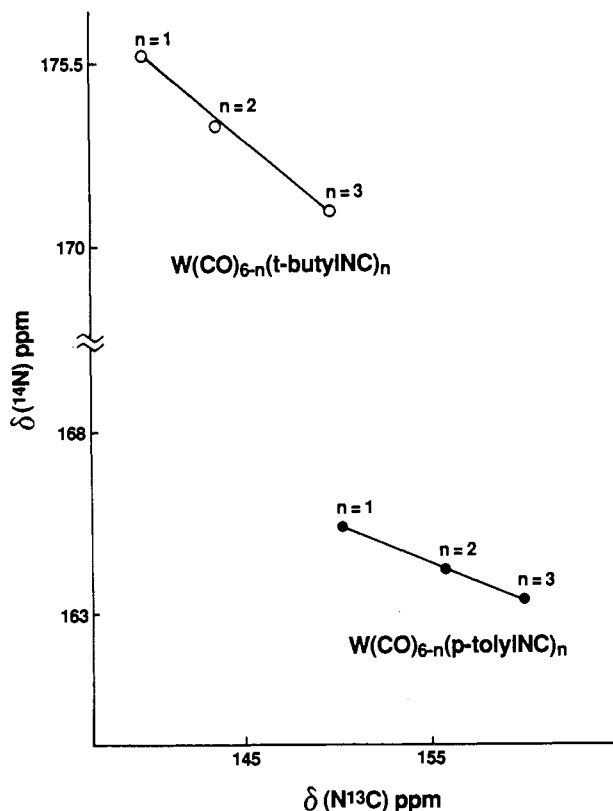


Figure 5. Plot of $\delta(\text{C}^{14}\text{NR})$ versus $\delta(\text{N}^{13}\text{CNR})$ for 1-6.

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

While all of the data cited so far have supported the increased π -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}N nucleus

may become an asset, in that its relaxation mechanism is dominated by the interaction of the large ^{14}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}N resonance at all. With little π 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}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}C NMR, ^{17}O NMR, and ^{14}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,¹⁹ but other factors may also be important, and further experimental and theoretical work is clearly warranted to determine the role of ^{14}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}C NMR, ^{31}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 π -acids is evident in the large number of crystal structures of such complexes and the routine use of M—C, C \equiv O, and C \equiv N stretching frequencies, ^{13}CO , C^{17}O , and C^{14}N chemical shifts, M—CO and M—CN charge-transfer bands, etc. as probes of both geometric and electronic

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