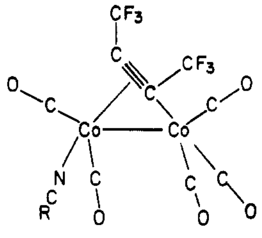
of $1^{\bullet -}$ generated electrochemically would prevent an efficient reaction by this means of activation.

We had considered that the preparation of 2 might involve carbonyl radicals,[31] but there was no evidence for this suggestion. Instead, the product from an AIBN-initiated reaction using 1 and $[Mo(CO)_3Cp]_2$ was the new labile derivative $[(CF_3)_2C_2]Co_2(CO)_5[NCC(CH_3)_2N_2C(CH_3)_2CN]$ (4). This formulation is based on analysis, mass spectra, and IR spectra. A structure in which the nitrile is coordinated in a pseudoequatorial position is suggested by the identical profile and energy of the $\nu$(CO) bands of 4 and those of $[(CF_3)_2C_2]Co_2(CO)_5(NCCH_3)$.[2]

## Conclusion

While this particular synthesis to give 2 does not represent another example of a ETC-catalyzed attack on a carbonyl substrate by a metal carbonyl nucleophile, it is clear that heteronuclear carbonyl complexes are accessible via this route even when the metal–metal bond in the reactant is "clamped" by an organic moiety. In the system described herein the chain is terminated because of a second reversible reductive charge transfer in the product. We are currently studying other systems where this problem is not met.



**4**, R ≡ CMe$_2$N$_2$CMe$_2$CN

**Registry No.** 1, 37685-63-5; 2, 102735-96-6; 3, 102735-97-7; 4, 102735-98-8; AIBN, 78-67-1; BPK, 119-61-9; $[Mo(CO)_3Cp]_2$, 12091-64-4; $PPh_3$, 603-35-0; Co, 7440-48-4; Mo, 7439-98-7.

**Supplementary Material Available:** Tables of positional and thermal parameters, structure factors, bond lengths and angles, and least-squares plane for 2 and a view of the second molecule of 2 (27 pages). Ordering information is given on any current masthead page.

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[31] A radical pathway has been demonstrated in the synthesis of some FeCo clusters. Horwitz, C. P.; Holt, E. M.; Shriver, D. F. *Organometallics* 1985, *4*, 1117.

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# Tungsten Carbonyl Isocyanide Carbene Complexes: A Structural and Spectroscopic Study of Three Types of Metal–Carbon Bonds in the Same Molecule

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The syntheses, spectroscopic characterization, and X-ray structural determinations of $(CO)_4W(C(OCH_3)(C_6H_5))(CNC_6H_4\text{-}p\text{-}CH_3)$ (1) and $(CO)_4W(C(OCH_3)(C_6H_5))(CNC(CH_3)_3)$ (2) are reported. Data from related complexes are also presented in order to compare differences in metal–carbon bonding in W–CO, W–$C_{CAR}$, and W–$C_{CNR}$ bonds in the complexes. The X-ray crystal structures of both molecules reveal that the carbene ligand is cis to the isocyanide ligand with W–CO distances significantly shorter than the other W–C distances in each complex. Crystal data for 1: space group *Pbca* (No. 61); $Z = 8$, $a = 21.172$ (3) Å, $b = 22.463$ (3) Å, $c = 8.322$ (2) Å; $V = 3957.9$ (9) Å$^3$; $R = 0.038$, $R_w = 0.030$. Crystal data for 2: space group $P2_1/n$ (No. 14); $Z = 4$, $a = 16.709$ (2) Å, $b = 9.425$ (2) Å, $c = 12.823$ (2) Å; $\beta = 111.52$ (3)°; $V = 1875.8$ (5) Å$^3$; $R = 0.047$, $R_w = 0.045$. Carbonyl force constants, $^{13}$CO chemical shifts, tungsten–carbon coupling constants, and metal–carbon bond lengths all indicate that carbon monoxide is as an overwhelming $\pi$ acid in the molecules. Both isocyanide ligands appear to be much weaker $\pi$ acceptors, while phenylmethoxycarbene is primarily a $\sigma$ donor.

## Introduction

Carbonyl, isocyanide, and carbene ligands all possess donor lone pairs and exhibit orbitals with proper symmetry for potential overlap with occupied $t_{2g}$ orbitals on a pseudooctahedrally coordinated low-valent transition-metal center. Thus all three ligand types are capable of dative bonding, an observation which has led many investigators to speculate on their comparative $\sigma$ donor/$\pi$ acceptor abilities.[1] Zerovalent transition-metal carbonyl carbenes have been the subject of theoretical, crystallographic, and spectroscopic studies,[2] while zerovalent transition-metal carbonyl isocyanides have been studied theoretically, spectroscopically, and electrochemically.[3]

Each ligand experiences different effects upon coordination, and while generalizations are probably not entirely appropriate, carbon monoxide is usually found to be more reactive when coordinated to zerovalent metals,[4] while coordinated isocyanides are ordinarily stabilized.[5] Of the

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[1] (a) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc. A* 1968, 642. (b) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* 1977, *99*, 2127. (c) Guy, M. P.; Guy, J. T.; Bennett, D. W. *J. Mol. Struct.* (*Theochem.*) 1985, *122*, 95.

[2] (a) Guy, J. T., Jr.; Guy, M. P.; Bennett, D. W. *J. Mol. Struct.* (*Theochem.*), in press. (b) Schubert, U. *Coord. Chem. Rev.* 1984, *55*, 261. (c) Bodner, G. M.; Kahl, S. B.; Bork, K.; Storhoff, B. N.; Wuller, J. E.; Todd, L. J. *Inorg. Chem.* 1973, *12*, 1071. (d) Kohler, F. H.; Kalder, H. J.; Fischer, E. O. *J. Organomet. Chem.* 1976, *113*, 11.

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three types of ligands, carbenes are certainly altered the most, transcending from ephemeral coordinatively unsaturated molecules to still coordinatively unsaturated but surprisingly stable ligands. While it would appear that this increased stabilization must arise from dative bonding with the metal, a situation necessary to ensure the integrity of the almost sacred tetravalency of carbon, there is increasing evidence that carbenes are unable to compete effectively with carbon monoxide for metal electron density.[6]

The relative $\pi$ acidities of carbonyl, aryl isocyanides, and alkyl isocyanides have been compared theoretically and experimentally, often resulting in conflicting assessments. Frontier molecular orbital studies show that alkyl isocyanides should behave as stronger bases, with carbon monoxide and aryl isocyanides the better $\pi$ acceptors. There has been some debate over the relative $\pi$ acidity of carbonyl and aryl isocyanide ligands,[1c] a situation which the frontier molecular orbital formalism is unable to resolve. While spectroscopic studies point to CO as the strongest $\pi$ acid, there are no crystal structures in the literature to provide metal–carbon bonding parameters—necessary pieces in this complex puzzle.

Even in the event that crystal structures of the mixed zerovalent metal isocyanide/carbonyl complexes become available the story will still be incomplete. A truly valid comparison of metal–ligand bonding between the three ligand types must come either from complexes which contain all three ligands attached to the same metal center or from complexes containing identical metals and ligands, excepting only the ligand under investigation. In this report we present the results of the synthesis, spectroscopic characterization, and crystal structure determination of two molecules: one containing carbonyls, a carbene, and an aryl isocyanide; the other containing carbonyls, a carbene, and an alkyl isocyanide.

## Experimental Section

**General Data.** All reactions were performed in a dry nitrogen atmosphere by using standard Schlenck techniques; solvents were dried and deoxygenated by using standard techniques. $W(CO)_6$, $(CH_3)_3OBF_4$, and $C_6H_5Li$ were purchased from Aldrich Chemical Co. and used without further purification. *p*-Tolyl isocyanide, *tert*-butyl isocyanide, (*p*-tolyl isocyanide)tungsten pentacarbonyl, and (*tert*-butyl isocyanide)tungsten pentacarbonyl were prepd. according to literature methods.[7,8] The synthesis and characterization of $(CO)_4W(C(OMe)(C_6H_5))(CNC_6H_4\text{-}p\text{-}CH_3)$ (1) has been previously reported.[5] Anal. Calcd: C, 45.04; H, 2.82; N, 2.63. Found: C, 45.31; H, 2.87; N, 3.02.

Proton-decoupled $^{13}C$ NMR spectra were recorded on a Bruker WH-250 spectrometer. All samples were dissolved in $CDCl_3$, which served as an internal reference. Chemical shifts are reported with respect to $Me_4Si$. Infrared spectra were recorded in Nujol mulls using a Nicolet MX1 FTIR instrument.

**Synthesis of $(CO)_4W(C(OMe)(C_6H_5))(CNC(CH_3)_3)$ (2).** Phenyllithium (4.8 mmol) in 10 mL of diethyl ether was added dropwise to a solution of 1.0 g of $(CO)_5WCNC(CH_3)_3$ in 35 mL of diethyl ether, and the resulting solution was stirred for 4 h. The solvent was removed via evaporation in a stream of dry nitrogen, leaving a dark orange-brown residue. Ten milliliters of carefully deoxygenated water, 2.5 mmol of $(CH_3)_3OBF_4$, and 20 mL of pentane were added to the residue in rapid succession. The resulting layers were separated, and a dark red product was extracted from the aqueous layer with 100 mL of pentane. The pentane solution was dried over $MgSO_4$, reduced in volume, and cooled to −60 °C. A dark red solid precipitate was recovered from the cold solution. Unreacted starting material was removed via vacuum sublimation, yielding 0.735 g (60%) of the purified product. Attempted further purification of the product on a silica gel column resulted in decomposition of the product. $^{13}C$ NMR: $C_{CAR}$, 322 ppm; CO (trans to carbene), 210 ppm; CO (trans to isocyanide), 204 ppm; CO (trans to CO), 201 ppm. IR ($cm^{-1}$): $\nu_{CN}$ 2141; $\nu_{CO}$ 2056 (w), 1956 (s), 1938 (s), 1916 (vs). Anal. Calcd: C, 40.91; H, 3.93; N, 2.81. Found: C, 40.69; H, 3.41; N, 2.74.

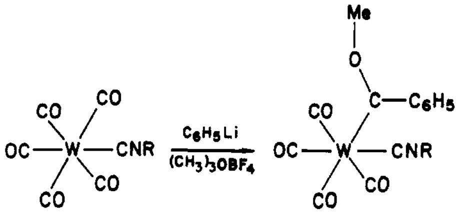
**Force Constant Calculations.** Normal coordinate analyses[9] of the vibrational spectra of the parent compounds were performed by assuming that significant vibrational coupling occurs only between C–N and C–O moieties on the molecule. Initial values were obtained by using the Cotton–Kraihanzel approximation,[10] but this constraint was removed for the final simplex optimization. Relaxation of the Cotton–Kraihanzel restriction resulted in only very small differences in calculated force constants (0.01–0.02 mdyn/Å). Final calculated and experimental stretching frequencies agreed within ± 0.1 $cm^{-1}$ with this method. For $(CO)_5WCNC_6H_5\text{-p-}CH_3$ (3) $\nu_{CN}$ occurred at 2141 $cm^{-1}$ ($A_1$) and the carbonyl stretching frequencies were assigned as follows ($cm^{-1}$): 2055 ($A_1$), 1979 ($B_1$), 1956 (E), and 1920 ($A_1$). For $(CO)_5WCNC(CH_3)_3$ (4) $\nu_{CN}$ occurred at 2155 $cm^{-1}$ ($A_1$) and the carbonyl stretching frequencies were assigned as follows ($cm^{-1}$): 2055 ($A_1$), 2063 ($B_1$), 1952 (E), and 1920 ($A_1$).[11]

**X-ray Crystal Structure Determinations.** Dark red crystals of $(CO)_4W(C(OMe)(C_6H_5))(CNC_6H_4\text{-}p\text{-}CH_3)$ and $(CO)_4W(C(OMe)(C_6H_5))(CNC(CH_3)_3)$ suitable for crystal study were obtained by recrystallization from pentane at −20 °C. Both crystals were anchored with epoxy in sealed quartz capillary tubes. Intensity data were collected on a Picker autodiffractometer automated by Krisel Control. Lattice constants for both solids were determined from least-squares refinement of centered angular data using software written in our laboratory. Crystal data and data collection parameters are given in Table II. Empirical absorption corrections were made by interpolation of psi-scan intensity data by using CAMEL*JOCKEY.[12] Both structures were solved and refined by using SHELX-76.[13] The tungsten atoms were located by using direct methods, and all other non-hydrogen atoms were located in successive difference Fourier maps. Hydrogen atom positions were calculated on the basis of idealized geometries for methyl and phenyl groups; methyl groups were refined as rigid groups.

## Results

**Formation of Metal Carbonyl Isocyanide Carbene Complexes.** $(CO)_4W(C(OMe)(C_6H_5))(CN\text{-}p\text{-tolyl})$ (1) and $(CO)_4W(C(OMe)(C_6H_5))(CN\text{-}t\text{-Bu})$ (2) as well as their (monomethylamino)phenylcarbene analogues, all resulted from nucleophilic attack at a carbonyl cis to the isocyanide ligand of a monosubstituted tungsten carbonyl complex, with subsequent methylation producing the coordinated carbene ligand:

$$CNR + W(CO)_6 \xrightarrow[CoCl_2\cdot 2H_2O]{\text{toluene, 25 °C}} (CO)_5W(CNR)$$



As with traditional methoxyaryl carbenes, an amino group will readily displace the methoxide moiety.

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[5] Guy, M. P.; Bennett, D. W. *Inorg. Chim. Acta* **1984**, *86*, L45.

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[9] McIntosh, D. F.; Peterson, M. R. *QCPE* **1900**, *9*(2977), **1900**, 342.

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[11] These assignments are in reasonable agreement with those reported by R. B. King in ref 3b.

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**Table I. $^{13}C$ NMR Data for Compounds of Tungsten Containing Carbonyl, Isocyanide, and Carbene Ligands**[a]

| | A | B | C | D |
|---|---|---|---|---|
| | $^{13}C$ Chemical Shifts (ppm/$Me_4Si$) | | | |
| $W(CO)_5CNC_6H_4CH_3$ | 194 | 197 | | |
| $W(CO)_5CNC(CH_3)_3$ | 194 | 196 | | |
| $W(CO)_4CNCH_4CH_3(C(OCH_3)C_6H_5$ | 199 | 203 | 208 | 321 |
| $W(CO)_4CNC(CH_3)_3(C(OCH_3)C_6H_5$ | 201 | 204 | 210 | 321 |
| $W(CO)_5C(OCH_3)C_6H_5$ | 197 | | 203 | 322 |
| $W(CO)_6$ | 191 | | | |
| | $^{13}C-^{183}W$ Coupling Constants (Hz) | | | |
| $W(CO)_5CNC_6H_4CH_3$ | 125 | 137 | | |
| $W(CO)_5CNC(CH_3)_3$ | 126 | 133 | | |
| $W(CO)_4CNC_6H_4CH_3(C(OCH_3)C_6H_5$ | 127 | 133 | 114 | 106 |
| $W(CO)_4CNC(CH_3)_3(C(OCH_3)C_6H_5$ | 127 | 138 | 113 | 107 |
| $W(CO)_5C(OCH_3)C_6H_5$ | 127 | | 115 | 105 |
| $W(CO)_6$ | 125 | | | |

[a] A = CO trans to CO; B = CO trans to isocyanide; C = CO trans to carbene; D = Carbene ligand.

The $^{13}C$ NMR spectra of all mixed carbonyl–isocyanide–carbene compounds synthesized in this manner exhibit the same pattern qualitatively, with three carbonyl resonances in a 2:1:1 integral ratio, consistent with the cis isomer. Thin-layer chromatography and $^{13}C$ NMR spectra of product solutions prior to purification showed no evidence for the formation of either a trans isomer or a modified isocyanide ligand, confirming that nucleophilic attack had occurred exclusively at the cis carbonyl, regardless of whether the coordinated isocyanide ligand contained an aliphatic or aromatic group.

The presence of even a single isocyanide ligand in the tungsten coordination sphere has a marked influence on reaction kinetics. In the absence of an isocyanide the reaction is generally facile, proceeding to completion in less than 30 min with essentially complete conversion of $W(CO)_6$ from a stoichiometric addition of phenyllithium. In contrast the synthesis of **1** and **2** from the monosubstituted tungsten isocyanide carbonyl complexes requires 3–4 h with use of excess phenyllithium to obtain reasonable yields of product. Even under these circumstances some starting material is always recovered. The formation of a carbene ligand from the bis(isocyanide)tungsten tetracarbonyl complexes takes place with even more difficulty. In this case the parent compound $(CO)_4W(CNR)_2$, R = *p*-tolyl or *tert*-butyl, undergoes nucleophilic attack only under more vigorous conditions, requiring 6–7 h and an even greater excess of phenyllithium to produce only moderate amounts of a product which still awaits complete characterization. The presence of a third isocyanide ligand in $W(CO)_3(CNR)_3$ results in a continuation of this trend, with even slower reactions occurring between phenyllithium and $(CO)_3W(CN\text{-}p\text{-tolyl})_3$ or $(CO)_3W(CN\text{-}t\text{-}Bu)_3$.

**Spectroscopic Characterization.** A normal mode analysis of **3** and **4** reveals that the carbonyl ligands cis to the coordinated isocyanide exhibit C–O stretching force constants of 15.96 and 15.95 mdyn/Å, respectively, with a value of 14.97 mdyn/Å for the carbonyls trans to the isocyanide in both complexes. In both compounds the CO stretching force constants assigned to the cis carbonyls are nearly 1 mdyn/Å greater than the corresponding force constants for the trans carbonyls.

$^{13}C$ NMR chemical shifts for major resonances from **1**–**4** and related compounds are included in Table I, along with $^{183}W-^{13}C$ coupling constants for the carbonyl and carbene ligands attached to each complex. The assignment of resonances for carbonyls at various coordination sites on a given complex could not be made from chemical shift data alone, and for this task the tungsten–carbon coupling constants allowed for unequivocal assignments to be made. In general we have found $J_{W-C}$ to vary only a few hertz for a given mode of substitution on various complexes, with much larger variations between different modes of substitution. Thus in the entire series of complexes under consideration $J_{W-C}$ is 126 ± 2 Hz for the carbonyls trans to other carbonyls and 114 ± 1 Hz for those trans to the methoxyphenylcarbene ligand. Because of the difference in the isocyanide ligands $J_{W-C}$ varies a bit more for the carbonyl ligand trans to each isocyanide, but for a given type of isocyanide ligand, little variation is observed. Thus for complexes **1** and **3**, containing p-tolyl isocyanide, $J_{W-C}$ differs by only 0.3 Hz for the carbonyl trans to the isocyanide, while the variation is only 1.2 Hz for carbonyls trans to *tert*-butyl isocyanide in **2** and **4**.

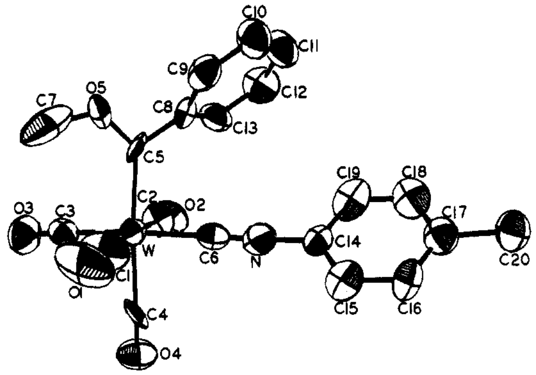

**Figure 1.** ORTEP drawing of $(CO)_4W(C(OCH_3)(C_6H_5))(CNC_6H_4\text{-}p\text{-}CH_3)$.

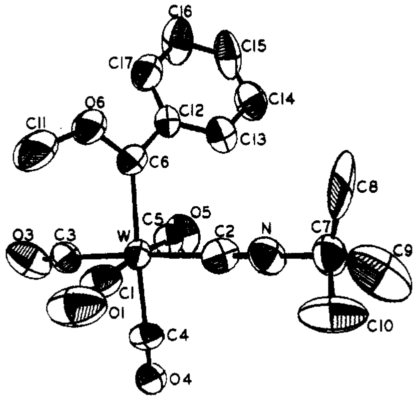

**Figure 2.** ORTEP drawing of $(CO)_4W(C(OCH_3)(C_6H_5))(CNC(CH_3)_3)$.

**X-ray Crystal Structure Determinations.** ORTEP diagrams of **1** and **2** are illustrated in Figures 1 and 2, respectively, and Tables II–VI list crystal data and data collection parameters, atomic coordinates, and selected bond lengths and angles. In both complexes carbonyl

**Table II. Crystal and Intensity Collection Data for $(CO)_4W(C(OCH_3)(C_6H_5))(CNC_6H_4\text{-}p\text{-}CH_3)$ (1) and $(CO)_4W(C(OCH_3)(C_6H_5))(CNC(CH_3)_3)$ (2)**

| | 1 | 2 |
|---|---|---|
| formula | $C_{20}H_{15}NO_5W$ | $C_{17}H_{17}NO_5W$ |
| mol mass, g/mol | 533.2 | 499.2 |
| space grp | *Pbca* (31) | $P2_1/n$ (14) |
| *a*, Å | 21.172 (3) | 16.709 (2) |
| b, Å | 22.463 (3) | 9.425 (2) |
| *c*, Å | 8.322 (3) | 12.823 (2) |
| $\alpha$, deg | 90.00 | 90.00 |
| $\beta$, deg | 90.00 | 111.52 (3) |
| $\gamma$, deg | 90.00 | 90.00 |
| *Z* | 8 | 4 |
| *V* Å$^3$ | 3957.9 | 1875.8 |
| linear abs coeff, cm$^{-1}$ | 56.38 | 59.35 |
| temp, K | 298 (5) | 298 (5) |
| cryst size, mm$^3$ | 0.4 × 0.3 × 0.2) | (0.3 × 0.2 × 0.4) |
| radiatn | Zr-filtered Mo K$\alpha$ ($\lambda$ = 0.71069 Å) | ($\lambda$ = 0.71069 Å) |
| $2\theta$ limits, deg | $4 < 2\theta < 50$ | $4 < 2\theta < 50$ |
| scan type | $\theta$–$2\theta$ | $\theta$–$2\theta$ |
| scan speed | variable | variable |
| bkgd time/scan time | 0.5 | 0.5 |
| unique refs | 2155 | 3365 |
| no. of parameters | 224 | 202 |
| *R* | 0.038 | 0.047 |
| $R_w$ ($w = 1/\sigma^2(\lvert F\rvert)$) | 0.030 | 0.045 |
| largest peak in final diff map, e/A$^3$ | 0.50 | 0.75 |

**Table III. Positional Parameters and Their Estimated Standard Deviations for $(CO)_4W(C(OCH_3)(C_6H_5))(CNC_6H_4\text{-}p\text{-}CH_3)$**

| atom | *x/a* | *y/b* | *z/c* | $U_{eq}$,[a] Å$^2$ |
|---|---|---|---|---|
| W | 0.55124 (3) | 0.60855 (3) | 0.20555 (8) | 0.05 |
| C1 | 0.4585 (11) | 0.1920 (8) | 0.3860 (25) | 0.09 |
| C2 | 0.4412 (9) | 0.0267 (7) | 0.1889 (24) | 0.07 |
| C3 | 0.5213 (9) | 0.0778 (9) | 0.4127 (23) | 0.06 |
| C4 | 0.5086 (7) | 0.1309 (8) | 0.1178 (25) | 0.06 |
| C5 | 0.3789 (8) | 0.0904 (8) | 0.4693 (23) | 0.05 |
| C6 | 0.3741 (9) | 0.1394 (9) | 0.1515 (21) | 0.06 |
| C7 | 0.4311 (13) | 0.1102 (11) | 0.7105 (26) | 0.13 |
| C8 | 0.3121 (9) | 0.0767 (8) | 0.4374 (22) | 0.04 |
| C9 | 0.2966 (8) | 0.0323 (9) | 0.3284 (23) | 0.07 |
| C10 | 0.2319 (11) | 0.0194 (9) | 0.2983 (25) | 0.08 |
| C11 | 0.1846 (9) | 0.0509 (11) | 0.3683 (27) | 0.08 |
| C12 | 0.1970 (9) | 0.0954 (9) | 0.4796 (26) | 0.08 |
| C13 | 0.2607 (10) | 0.1073 (9) | 0.5101 (20) | 0.06 |
| C14 | 0.2825 (9) | 0.1742 (9) | 0.9768 (21) | 0.06 |
| C15 | 0.2815 (9) | 0.2300 (8) | 0.9127 (23) | 0.06 |
| C16 | 0.2292 (10) | 0.2519 (9) | 0.8333 (21) | 0.06 |
| C17 | 0.1767 (9) | 0.2171 (10) | 0.8204 (23) | 0.06 |
| C18 | 0.1775 (10) | 0.1603 (11) | 0.8819 (25) | 0.07 |
| C19 | 0.2290 (13) | 0.1401 (8) | 0.9665 (24) | 0.07 |
| C20 | 0.1177 (8) | 0.2387 (9) | 0.7374 (22) | 0.09 |
| N | 0.3334 (8) | 0.1551 (7) | 0.0706 (20) | 0.07 |
| O1 | 0.4676 (8) | 0.2366 (6) | 0.4369 (20) | 0.13 |
| O2 | 0.4405 (7) | 0.9831 (5) | 0.1291 (17) | 0.10 |
| O3 | 0.5675 (6) | 0.0576 (6) | 0.4758 (17) | 0.09 |
| O4 | 0.5434 (6) | 0.1443 (6) | 0.0185 (16) | 0.08 |
| O5 | 0.3791 (5) | 0.0945 (6) | 0.6249 (17) | 0.07 |

[a] Anisotropically refined thermal parameters are given as equivalent isotropic parameters defined as $(^1/_3)[\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j]$.

**Table IV. Positional Parameters and Their Estimated Standard Deviations for $(CO)_4W(C(OCH_3)(C_6H_5))(CNC(CH_3)_3)$**

| atom | *x/a* | *y/b* | *z/c* | $U_{eq}$,[a] Å$^3$ |
|---|---|---|---|---|
| W | 0.38307 (3) | 0.41398 (5) | 0.10612 (4) | 0.05 |
| C1 | 0.0095 (9) | 0.0531 (13) | 0.6881 (13) | 0.05 |
| C2 | −0.1414 (9) | −0.1101 (14) | 0.5145 (11) | 0.06 |
| C3 | −0.1046 (10) | 0.2725 (13) | 0.6803 (12) | 0.06 |
| C4 | −0.0820 (8) | 0.1811 (14) | 0.4862 (10) | 0.05 |
| C5 | −0.2391 (10) | 0.1319 (16) | 0.5127 (12) | 0.06 |
| C6 | −0.1377 (9) | −0.0194 (13) | 0.7470 (11) | 0.06 |
| C7 | −0.1877 (11) | −0.3393 (14) | 0.4014 (13) | 0.07 |
| C8 | −0.2413 (14) | 0.2030 (21) | 0.2139 (15) | 0.10 |
| C9 | −0.2294 (19) | −0.4379 (18) | 0.4606 (17) | 0.15 |
| C10 | −0.1091 (5) | −0.4058 (19) | 0.3826 (23) | 0.14 |
| C11 | −0.2627 (13) | 0.1206 (20) | 0.7431 (17) | 0.11 |
| C12 | −0.0809 (9) | −0.1260 (12) | 0.8212 (12) | 0.05 |
| C13 | −0.0334 (10) | −0.2217 (14) | 0.7827 (12) | 0.06 |
| C14 | 0.0190 (11) | −0.3194 (15) | 0.8524 (15) | 0.08 |
| C15 | 0.0301 (13) | −0.3247 (17) | 0.9655 (18) | 0.10 |
| C16 | −0.0153 (12) | −0.2293 (21) | 1.0061 (15) | 0.09 |
| C17 | −0.0702 (11) | −0.1341 (16) | 0.9342 (14) | 0.07 |
| O1 | 0.0831 (8) | 0.0424 (11) | 0.7341 (11) | 0.09 |
| O3 | −0.0959 (9) | 0.3809 (11) | 0.7208 (11) | 0.11 |
| O4 | −0.0603 (6) | 0.2339 (9) | 0.4240 (7) | 0.07 |
| O5 | −0.3077 (9) | 0.1651 (15) | 0.4506 (10) | 0.11 |
| O6 | −0.1984 (7) | 0.0100 (10) | 0.7884 (8) | 0.07 |
| N | −0.1563 (8) | −0.2113 (11) | 0.4658 (10) | 0.06 |

[a] Anisotropically refined thermal parameters are given as equivalent isotropic parameters defined as $(^1/_3)[\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j]$.

**Table V. Selected Bond Lengths and Angles for $(CO)_4W(C(OCH_3)(C_6H_5))(CNC_6H\text{-}p\text{-}CH_3)$**

| | | | |
|---|---|---|---|
| | Bond Lengths, Å | | |
| W–C1 | 2.034 (18) | C2–O2 | 1.099 (20) |
| W–C2 | 2.043 (17) | C3–O3 | 1.199 (23) |
| W–C3 | 1.950 (19) | C4–O4 | 1.148 (23) |
| W–C4 | 2.004 (18) | C6–N | 1.149 (25) |
| W–C5 | 2.115 (18) | N–C14 | 1.398 (25) |
| W–C6 | 2.096 (19) | C5–O5 | 1.299 (24) |
| C1–O1 | 1.104 (23) | C5–C8 | 1.471 (25) |
| | Bond Angles, deg | | |
| C1–W–C2 | 176.3 (8) | C6–N–C14 | 178.0 (19) |
| C1–W–C3 | 93.3 (8) | N–C14–C15 | 120.8 (17) |
| C1–W–C4 | 88.8 (8) | W–C5–C8 | 126.2 (13) |
| C1–W–C5 | 89.6 (8) | O5–C5–W | 132.1 (12) |
| C1–W–C6 | 89.1 (8) | O5–C5C8 | 101.3 (14) |
| O1–C1–W | 175.7 (20) | C7–O5–C5 | 122.8 (15) |
| O2–C2–W | 176.3 (17) | C5–C8–C9 | 119.7 (16) |
| O3–C3–W | 175.6 (16) | W–C6–N | 178.3 (16) |
| O4–C4W | 178.9 (16) | | |

**Table VI. Selected Bond Lengths and Angles for $(CO)_4W(C(OCH_3)(C_6H_5))(CNC(CH_3)_3)$**

| | | | |
|---|---|---|---|
| | Bond Lengths, Å | | |
| W–C1 | 2.016 (13) | C3–O3 | 1.119 (17) |
| W–C2 | 2.136 (13) | C4–O4 | 1.106 (18) |
| W–C3 | 1.972 (13) | C5–O5 | 1.162 (18) |
| W–C4 | 2.033 (14) | C6–O6 | 1.338 (21) |
| W–C5 | 2.000 (14) | N–C7 | 1.466 (17) |
| W–C6 | 2.204 (15) | C2–N | 1.123 (17) |
| C1–O1 | 1.153 (18) | C6–C12 | 1.455 (17) |
| | Bond Angles, deg | | |
| C1–W–C2 | 96.2 (5) | O5–C5–W | 173.1 (16) |
| C1–W–C3 | 88.9 (6) | W–C2–N | 178.3 (13) |
| C1–W–C4 | 85.8 (6) | C2–N–C7 | 172.3 (16) |
| C1–W–C5 | 173.8 (7) | W–C6–C12 | 126.0 (12) |
| C1–W–C6 | 87.0 (6) | W–C6–O6 | 126.5 (8) |
| O1–C1–W | 175.7 (12) | O6–C6–C12 | 107.2 (13) |
| O3–C3–W | 177.4 (17) | C6–C12–C13 | 121.9 (14) |
| O4–C4–W | 177.9 (10) | | |

carbons are an average 0.1–0.2 Å closer to the metal center than the isocyanide or carbene carbons. In 1, the complex containing the aryl isocyanide ligand, the W–C$_{car}$ bond length is essentially identical (within experimental error) to the W–C$_{CNAr}$ bond length, while in 2, the complex containing the alkyl isocyanide ligand the W–C$_{car}$ bond length is measurably longer than the length of the W–C$_{CNR}$ bond. In 1 the dihedral angle between the C$_{phenl}$–C$_{car}$–OMe plane (C8,C5,O5) and the plane containing the two carbonyls trans to one another and the carbonyl trans to the carbene carbon (C1,W,C4) is 55°, while the analgous dihedral angle in **2** between the (C12,C6,O6) and (C1,W,C4,) planes is 31°. With the vector between the carbene carbon and the phenyl carbon attached to the carbene pointing toward the viewer, the plane of the phenyl ring is rotated 44 degrees counterclockwise to the $C_{phenl}$–$C_{car}$–OMe plane in 1 and clockwise 27 degrees in 2. In both complexes the geometry about oxygen is essentially trigonal and planar, with $C_{Me}$–O–$C_{CAR}$ bond angles of 123° and 125° for 1 and 2, respectively. $C_{CAR}$–O bond lengths of 1.30 (2) and 1.34 (2) Å for 1 and 2 indicate substantial multiple bonding between the methoxy oxygen and the carbene carbon in both complexes. Typical organic ethers exhibit C—O bond lengths of around 1.43 Å, while the C=O distances in ketones average about 1.22 Å,[14] suggesting that the C—OMe bonds in 1 and 2 have a bond order of roughly 1.5, somewhere between formally single and double carbon–oxygen bonds. Both isocyanides remain essentially linear, with a C–N–C angle of 172° in the coordinated alkyl isocyanide and 178° in the aryl isocyanide. The phenyl ring in the aryl isocyanide lies at an angle of 51° with respect to the (C1,W,C5) plane.

## Discussion

The new complexes $W(CO)_4(C(OMe)C_6H_5)(CNR)$, R = *tert*-butyl and *p*-tolyl, afford us the unique opportunity to compare directly the bonding between tungsten and the coordinated carbon atom of each type of ligand. Their formation results from preferential nucleophilic attack at coordinated carbonyl, with isocyanides inert toward nucleophilic addition in all the mixed carbonyl isocyanides investigated. The pronounced lack of reactivity of the coordinated isocyanide ligands is somewhat unexpected, with simple frontier molecular orbital considerations suggesting that the isocyanides are better $\sigma$ donors and less effective $\pi$ acceptors than carbon monoxide. This effect alone should render the coordinated isocyanide carbon more positive than that on carbon monoxide and subsequently more susceptible to nucleophilic attack. It follows that the reactivities of the two types of ligands must be due in large part to the type of heteroatom bonded to the coordinated carbon. The linearity of the isocyanides indicates that the "lone pair" electron density on nitrogen is delocalized onto the carbon, and the relative reactivities imply that this occurs to a greater extent than delocalization of similar electron density from oxygen onto the carbonyl carbon. In both 1 and 2 the tungsten–isocyanide carbon bond length is about 0.1 Å longer than the M–CO bonds in the same complex, while the tungsten–carbon bond to the alkyl isocyanide ligand is essentially the same length as the bond between tungsten and the aryl isocyanide carbon. This suggests increased electron–electron repulsion between the metal and the isocyanide carbon in both molecules, as would be the case with increased electron donation from the nitrogen atom to the coordinated carbon. The propensity for carbon monoxide to maintain consistently shorter metal–carbon bonds is convincing evidence that CO is the strongest $\pi$ acceptor of the three ligand types, especially in light of its extremely weak Lewis basicity.[15] As more carbon monoxide ligands are replaced with isocyanides, less $\pi$ density is removed from the metal center, and there are fewer carbonyls to compete for this excess charge. As the remaining carbonyls remove more of this charge from the metal center, they become increasingly negative in the process, making them less susceptible to attack by strong nucleophiles, as observed experimentally in this study.

A potential flaw in the above argument arises from the notion that aryl isocyanides are often considered to have similar or even more pronounced $\pi$ acidities than carbon monoxide.[16] However, as we have previously shown,[1c] these considerations failed to take into account that the highest occupied molecular orbital on the aryl isocyanide ligand has $\pi$ symmetry and significant contributions from atomic orbitals on the coordinated carbon, along with an orientation which should impede $\pi$ donation from occupied metal frontier orbitals. Thus while there are apparently major differences in the bonding of alkyl and aryl isocyanides coordinated to high-valent metals,[17] the differences appear to be much smaller in the low-valent tungsten complexes in this study, at least to the extent that such differences are reflected in the comparative metal–carbon bond lengths. The structural data presented here provides no indication that aryl isocyanides are substantially better $\pi$ acids than alkyl isocyanides, while carbon monoxide is clearly a stronger $\pi$ acid than either type of isocyanide.

Further evidence for this argument comes from the consistent observation that strong nucleophiles attack carbonyls cis to the isocyanide in the monosubstituted parent complexes. The carbonyl trans to the isocyanide competes with the isocyanide ligand for $\pi$ density, while the cis carbonyls compete with one another. Thus the trans carbonyl gains relatively more $\pi$ density, making it less susceptile to attack by an incoming nucleophile. This results in preferential attack at one of the carbonyl ligands cis to the isocyanide. This analysis is supported by a comparison of the cis and trans CO stretching force constants in which the larger force constants are ascribed to the carbonyl ligands cis to the isocyanide ligand. This reflects a smaller degree of $\pi$-back-bonding from the metal into the cis carbonyl $\pi^*$ frontier orbitals, imparting more positive character to the cis carbonyl carbons[18] and increasing their susceptibility to nucleophilic attack.

An extension of the analysis of force constants assigned to the various carbonyl ligands in 1 and 2 would be useful in describing the bonding of each ligand, but we have been unable to unequivocally assign the vibrational spectra of the two complexes. Fortunately, we are able to assign $^{13}C$ resonances to the various carbonyl groups as described above. For carbonyls in very similar chemical environments it has been shown that the chemical shift downfield from $Me_4Si$ is a measure of $\pi$ donation to that carbon from the metal center.[19] The $^{13}C$ spectra of *1* and *2* allow us to compare the relative amounts of $\pi$-back-bonding to each type of carbonyl in the complexes (see Table I). For the most part this should be a function of the total amount of d–$\pi$ electron density available and the ability of a given CO to compete for $\pi$ density with the ligand trans to that CO. In both complexes the carbonyl trans to the carbene carbon experiences the greatest downfield shift and the carbonyl trans to an isocyanide ligand is next, with resonances of the carbonyls trans to one another shifted upfield with respect to resonances from all other carbonyls. This further supports the premise that carbon monoxide is the strongest $\pi$ acid of the three ligand types, with isocyanides and carbenes unable to compete effectively with CO for $\pi$-electron density from the metal. Also note that $^{13}CO$ chemical shifts differ only slightly between the complexes containing p-tolyl isocyanide and *tert*-butyl isocyanide,

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[14] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; p 108.

[15] For example, while $H_3NBH_3$ is a stable molecule, $OCBH_3$ decomposes spontaneously at room temperature.

[16] Saillard, J. Y.; Beuze, A. L.; Simonneaux, G.; Maux, P. L.; Jaouen, G. J. *J. Mol. Struct.* (*Theochem.*) **1981**, *86*, 149.

[17] Mialki, W. S.; Wood, T. E.; Walton, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 7107.

[18] Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1692.

[19] Buchner, W.; Schenk, W. A. *J. Magn. Reson.* **1982**, *48*, 148.

another indication that the two types of isocyanides behave similarly when coordinated to low-valent metal centers. The small comparative increase in the downfield shifts observed for the *tert*-butyl isocyanide complex occurs for all of the CO's, rather than those exclusively trans to the isocyanide ligand. This would appear to suggest that the alkyl isocyanide places somewhat more electron density on the metal center than does the aryl isocyanide, with the resulting increased electrostatic repulsion uniformly expanding the d orbitals and allowing increased $\pi$-electron density for all the carbonyls attached to the metal. The notion that alkyl isocyanides have a greater net donor effect than aryl isocyanides is consistent with the results of electrochemical studies previously described by Connor et al.[20] and might provide an explanation for the longer metal–carbene bond length in **2**. Since the carbene ligand in both complexes is apparently the weakest $\pi$ acid, the metal–carbene bond is probably best described as a $\sigma$ bond resulting from "donation" of the carbene lone pair into the $\sigma$ framework of the complex.[6] Any increase in electron density into this framework would serve to retard the donation of the carbene electrons, resulting in an increase in the metal–carbene distance.

Although the partitioning of bonding electron density into "$\sigma$" and "$\pi$" components is fundamentally artificial, chemists have found such approximations useful in discussing the structure, reactivity, and spectroscopy of transition-metal complexes, particularly those containing carbonyl ligands. One problem in such an approach lies in the inherent difficulty in determining whether a given spectroscopic trend is due primarily to differences in $\pi$ acidity, $\sigma$ donation, or some indeterminate combination of both. For example, in the use of CO stretching frequencies as an indicator of relative amounts of charge on a given metal center and/or the ability of a series of ligands to attract $\pi$-electron density from the metal, variations in $\nu_{CO}$ are usually ascribed to differences in $\pi$-back-bonding, with $\sigma$ contributions totally ignored. Such is also the case with the use of $^{13}C$ NMR chemical shifts as bonding probes, indicating a need for a spectroscopic measurement that is known to be dominated by either $\sigma$ or $\pi$ contributions to a given chemical bond. Fortunately, in cases where metal–carbon coupling constants can be measured, we are provided with such a tool.

The magnitude of the spin–spin coupling constant across one bond is ordinarily dominated by the Fermi contact contribution, arising from currents (i.e., electron density) at the bonding nuclei.[21] In the LCAO approximation only s-type atomic orbitals are nonzero at the nucleus, such that the metal–carbon coupling constant is a sensitive indicator of the "s" character in a given metal–carbon bond. The hybrid orbitals involved in the metal–ligand $\sigma$ framework contain a high degree of "s" character, and as a result an increase in metal–ligand $\sigma$ bonding will tend to increase the magnitude of the Fermi contact term and subsequently lead to an increase in the metal–carbon coupling constant.[22] Coupling constants for carbonyl ligands are especially susceptible to changes in charge at the metal center since the ligated carbons are close to the metal center, making the spherically distributed electron density near the nucleus easier to perturb. In this study we have employed tungsten–carbon coupling constants in order to measure perturbations in tungsten–carbon $\sigma$ bonds trans to the various ligands under consideration. We have found that these perturbations can be ascribed to a "trans influence" effected by ligands trans to a given ligand, where we refer to "trans influence" as the ability of a ligand, L, to weaken the bond between the metal and the ligand, L′, which is trans to L.[23]

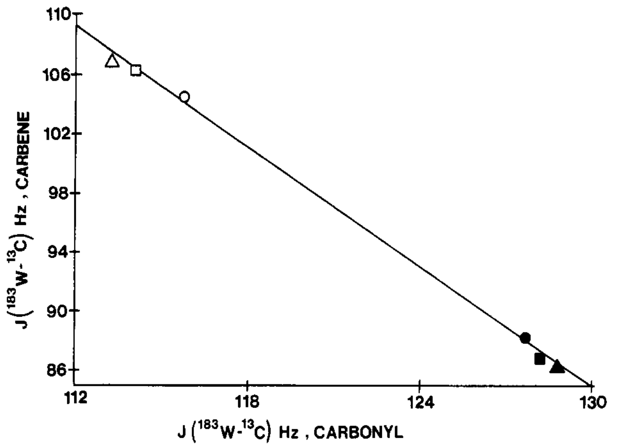

**Figure 3.** Plot of $^{13}C$–$^{183}W$ coupling constants for the carbene and the carbonyl trans to the carbene: $W(CO)_4(C(OMe)C_6H_5)$(CN-*t*-Bu) (△), $W(CO)_4(C(OMe)C_6H_5)$(CN-*p*-tolyl) (□), $W(CO)_5C(OMe)C_6H_5$ (○), $W(CO)_5C(NHMe)C_6H_5$ (●), $W(CO)_4(C(NHMe)C_6H_5)$(CN-*p*-tolyl) (■), and $W(CO)_4(C(NHMe)C_6H_5)$(CN-*t*-Bu) (▲). Correlation coefficient = 0.999.

A long standing model for metal–carbon bonding in metal carbonyls describes the bond as "synergistic", with the $\sigma$ bond strengthened as increased $\pi$ bonding occurs.[24] Thus the shorter M–CO distance coupled with the large fraction of carbon "s" character on the sp-hybridized carbon results in the correspondingly large tungsten–carbon coupling constants observed for coordinated carbonyls in general. Unfortunately, a direct comparison of $J_{W-C}$ between ligated carbenes and carbonyls is not possible, since the carbon "s" character is markedly different in the two ligands (i.e., $sp^2$ vs. $sp^3$), but the trans influence described above tells us a great deal about differences in metal–carbon bonding for the three ligand types. It is particularly interesting to note that carbonyl ligands trans to carbene ligands exhibit smaller values of $J_{W-C}$ than carbonyls cis to carbenes, while carbonyls trans to isocyanides exhibit the highest values of $J_{W-C}$.

The apparent increase in the $\sigma$ interaction between the metal and the carbonyl trans to an isocyanide ligand probably arises from an increase in M–CO $\pi$ bonding as indicated in the $^{13}C$ chemical shift of the carbonyl carbon, producing a stronger dative bond, including a strengthening of the $\sigma$ component of the M–CO bond. In the face of strong theoretical and experimental evidence[1c,3b,c] it is preposterous to imply that that CO is inherently a better $\sigma$ donor than isocyanide ligands, and it is more reasonable to assume that the $\sigma$ interaction of a given isocyanide is not sufficiently strong to overcome CO's tendency for synergistic bonding. On the other hand it is clear from the smaller value of $J_{W-C}$ for the carbonyl trans to a carbene that the carbonyl has the poorest $\sigma$ interaction with the metal, *in spite of a greater $\pi$ interaction*. It is likely that this is a result of the very strong $\sigma$ interaction that the carbene has with the metal. This causes charge polarization away from the isocyanide toward the trans carbonyl,

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[20] Connor, J. A.; Jones, E. M.; McEwen, G. K.; Lloyd, M. K.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1246.

[21] Jesson, J. P. In *NMR of Paramagnetic Molecules*; La Mar, G. N., Horrocks, D. W., Jr., Holm, R. H., Eds.; Academic Press: New York, 1973; p 5.

[22] Buchner, W.; Schenk, W. A. *Inorg. Chem.* **1984**, *23*, 132, and references therein.

[23] Appleton, T. G.; Clard, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

[24] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry: A Comprehensive Text*, 4th ed.; Wiley: New York, 1980; p 83.

tending to repel the carbonyl lone pair to an extent where increases in $\pi$ bonding cannot completely compensate. In contrast to the isocyanide case, the $\sigma$ trans influence of the carbene is sufficiently strong to disrupt the $\sigma/\pi$ synergism that is normally observed for coordinated carbon monoxide. A graphic illustration of this interdependence is seen if Figure 3, in which $J_{W-C}$ for the carbene carbon is plotted vs. $J_{W-C}$ for the carbonyl trans to the carbene for a series of complexes. These data strongly indicate that an increase in $\sigma$ density between the metal and carbene carbon imposes a corresponding decrease in M–CO bonding to the trans carbonyl.

A structural comparison of **1** and **2** reveals little difference between corresponding M–CO and M–CNR bond lengths in the two complexes, and yet the metal–carbene distance in **1** is shorter than in **2**. Since the only difference between the two complexes is the type of coordinated isocyanide, it is evident that the nature of the M–CNR bond in the two complexes must be different, despite the similar M–CNR bond lengths. Somewhat paradoxically, the relative lengthening of the metal–carbene bond in **2** is not reflected strongly in the spectroscopic data. That both complexes exhibit parallel $^{13}C$ chemical shifts and tungsten–carbon coupling constants suggests that the excess electron density from the *tert*-butyl isocyanide ligand resides principally in the d orbitals on the metal. Thus neither the metal or ligand carbon atoms experience significant changes in "s" character, and large differences in $^{13}C-^{183}W$ coupling constants are not observed. As a result the carbonyl trans to the alkyl isocyanide exhibits a tungsten–carbon coupling constant only 5 Hz greater than that for the carbonyl trans to the aryl isocyanide, with $J_{W-C}$ for the more distant carbene ligand essentially unchanged. If this excess electron density resided soley in the $\sigma$ framework, all the ligands should be repelled from the metal center, increasing the tungsten–carbon distance and decreasing any tungsten–carbon $\pi$ bonding. Since the symmetry of the molecule has been lowered considerably, d orbital mixing must result in delocalization of the excess charge on the metal into both the $\sigma$ and $\pi$ systems, allowing ligands capable of $\pi$ bonding to compensate for the increased repulsion and retain their original metal–carbon distance and metal–ligand $\pi$ electron density. It therefore appears that the isocyanide ligands are at least capable of $\pi$ bonding to the extent of being able to accommodate excess charge at the metal center, a phenomenon which certainly must occur in stable metal complexes containing a majority of isocyanide ligands (e.g., $W(CNR)_6$). If this scenario is correct, the carbonyl and isocyanide ligands will suffer little net effect from small amounts of added charge at the metal center, while the carbene ligand, a much weaker $\pi$ acid, is unable to compensate for increased electrostatic repulsion in the $\sigma$ framework.

The carbenes on both complexes lie at angles which make overlap of the available p orbital on the ligands with d orbitals on the metal less likely, providing further evidence that there is little $\pi$ bonding to the carbene ligands. Somewhat surprisingly, this is also observed with the aryl group on coordinated *p*-tolyl isocyanide. Aromatic isocyanides have been described as better $\pi$ acceptors because of their ability to distribute the accepted charge density over the $\pi$ system of the ring.[25] The shorter N–C14 bond length in **1** compared to the N–C7 bond in **2** suggests that the $\pi$ system of the ring does interact with the CN $\pi$ system, and yet the ligand shows no tendency to maximize $\pi$ interactions with the metal by aligning this $\pi$ system with appropriate symmetry orbitals on the metal center.

## Conclusions

It is apparent from the preceding discussion that the bonding scheme is quite complex in the mixed tungsten carbonyl isocyanide carbene complexes, and yet a comparative bonding picture begins to emerge from an overall analysis of the data. The most striking feature of all the complexes under consideration is the relative tenacity of carbon monoxide for $\pi$-electron density. Even though carbene and isocyanide ligands are capable of $\pi$ bonding to the metal, isocyanides appear to behave only as weak $\pi$ acids and carbenes do not seem to $\pi$ bond to any significant extent when carbonyl is share the tungsten coordination sphere. The bonding of carbene and isocyanide ligands to tungsten appear to be predominantly in "$\sigma$" character, with the ligands appropriately considered relatively strong Lewis bases in comparison to carbon monoxide.

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**Supplementary Material Available:** Tables of structure factors, positional parameters, and anisotropic temperature factors for 1 and 2 (24 pages). Ordering information is given on any current masthead page.

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[25] Essenmacher, G. J., Triechel, P. M. *Inorg. Chem.* **1977**, *16*, 800.