Equilibrium between Ylidene and Isocyanide Complexes: Synthesis and Crystal Structure of *cis*-(*N*-Methyl-1,2-dihydrobenzoxazol-2-ylidene)-(triphenylphosphine)tetracarbonyltungsten

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Summary: Reaction of 2-(trimethylsiloxy)phenyl isocyanide (1) with $[W(THF)(CO)_5]$ gives the complex $[W(1)(CO)_5]$ (2a). Hydrolysis of the Si-O bond leads to the formation of an equilibrium between complexes with a 2-hydroxyphenyl isocyanide (3a) or a 1,2-dihydrobenzoxazol-2-ylidene ligand (4a), which lies mostly on the side of the ylidene complex 4a. Substitution of one cis-CO ligand in 2a for $P(C_6H_5)_3$ enhances metal-toligand ($d \rightarrow p$) π -back-bonding and shifts the equilibrium toward the isocyanide complex 3e. The equilibrium can again be shifted toward the ylidene complex by deprotonation and alkylation of the ylidene nitrogen to give (N-methyl-1,2-dihydrobenzoxazol-2-ylidene)(triphenylphosphine)tetracarbonyltungsten (4f) which was characterized by single-crystal X-ray structure analysis.

Introduction

Reaction of coordinated isocyanides with nucleophiles constitutes the oldest method for the preparation of heteroatom-stabilized carbene complexes,¹ and many examples for this reaction can be found in the literature.² However, this reaction normally only works with isocyanides that are coordinated to late or oxidized transition metals. In this case the isocyanide carbon is not deactivated for nucleophilic attack by $(d \rightarrow p)\pi$ -back-bonding from the metal center. The isocyanide carbon in $[W(CNCH_2CH_5OH)(CO)_5]$, for example, is stabilized against intramolecular nucleophilic attack by the hydroxyl oxygen,³ while the same ligand reacts spontaneously to give complexes with the oxazolidin-2-ylidene ligand when coordinated to Pd(II).⁴

Results and Discussion

Different behavior was observed for the aromatic ligand 2-(trimethylsiloxy)phenyl isocyanide⁵ when coordinated to a $W(CO)_5$ or $Fe(CO)_4$ fragment (Scheme 1). Complexes of type 2 react after hydrolysis of the Si-O bond to give a mixture of isocyanide complexes, 3 and complexes with a 1,2-dihydrobenzoxazol-2-ylidene ligand,





4.^{6,7} The equilibrium between complexes 3 and 4 resides mostly on the side of the ylidene complexes 4. Driving force for the enhanced ylidene formation, compared to the aliphatic ligand 2-hydroxyethyl isocyanide,³ is the high stability of the formed ylidene ligand with an aromatic five-membered ring.⁶ In this contribution we report an example for the selective shift of the equilibrium between isocyanide and ylidene complexes to the side of the isocyanide complex by changing of the electronic properties of the metal center or to the side of the ylidene by a reaction at the coordinated ligand.

In a mixture of complexes 3 and 4, the isocyanide complexes 3 can be identified by the N=C IR absorption $(\tilde{\nu}_{\rm NC} = 2132 - 2169 \,{\rm cm}^{-1})$ while complexes of type 4 show a strong IR absorption for the N-H bond around $\tilde{\nu} =$ 3430 cm⁻¹. The OH resonance for complexes of type 3 is found between 5.6 and 6.1 ppm in the ¹H NMR spectrum, while the NH resonance for complexes of type 4 appears around 10.5 ppm. Comparison of the integrals for these two resonances allows to determine the relative abundance of the components in a mixture of complexes of types 3 and 4. Spectroscopic data for some complexes of the types 3 and 4 are summarized in Table 1.

The reactivity of coordinated carbonyl or isocyanide ligands can be related to the IR absorption frequencies or the force constants of the CO or CN bonds.⁸ The force constant can be directly correlated with the positive

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 Table 1. Physical and Spectral Data for Mixtures of Complexes 3 and 4



ML _x	complex	ratio, %					
		isocyanide 3	ylidene 4	$\frac{1 \text{H N}}{OH}$	$\frac{MR, \delta}{NH} IR, \frac{1}{\nu, cm}$	IR, ν , cm ⁻¹	k(CN), ¹ Nm ⁻¹
W(CO) ₅	3a/4a	15	85	5.63	10.43	2141	1746
Mo(CO) ₅	3b/4b	24	76	6.08	10.64	2137	1739
Cr(CO) ₅	3c/4c	29	71	5.85	10.44	2132	1731
Fe(CO) ₄	4d	0	100		10.95	2169 ^a	1791
cis-[W(CO) ₄ - PPh ₃]	3e	100	0	6.50		2117	1706

^a Wave number for the 2-(trimethylsiloxy)phenyl isocyanide derivative **2d**; the 2-hydroxyphenylisocyanide derivative of type **3** was not isolated (Scheme 1).

charge on the carbon atom, e.g., with its susceptibility for nucleophilic attack.⁹ In the series of the pentacarbonyl complexes 3a-c, the N=C stretching absorption is found at the lowest wavenumber for the chromium complex 3c (Table 1). The force constant for the N = Cbond was calculated according to the method of Cotton¹⁰ with corrections for the mass difference of CO vs CN. The lowest force constant was calculated for 3c indicating that this isocyanide complex is partly stabilized by metal-to-ligand $(d \rightarrow p)\pi$ -back-bonding against intramolecular nucleophilic attack. Thus the chromium complex shows the smallest ylidene: isocyanide ratio (2:1). A slightly larger force constant was calculated for the tungsten complex 3a. This difference is sufficient to cause a much stronger tendency of the coordinated isocyanide ligand to give the ylidene complex 4a (ylidene:isocyanide ratio 6:1). In contrast to the aliphatic 2-hydroxyethyl isocyanide [$k(NC) \ge 1800 \text{ N m}^{-1}$ for intramolecular ylidene formation¹¹], a much stronger tendency for ylidene formation is observed with the aromatic 2-hydroxyphenyl isocyanide. Intramolecular nucleophilic attack is dominant at force constants as low as 1731 N m⁻¹ (Table 1), which shows again that not only the activation of the isocyanide carbon-indicated by the N=C force constant-but also the stability of the resulting ylidene determine the course of the reaction.^{6,7}

No isocyanide complex of type **3** was detected by IR or ¹H NMR spectroscopy upon hydrolysis of the Si–O bond in the iron complex **2d**. Only formation of the ylidene complex **4d** was observed. This becomes plausible if the force constant for the 2-(trimethylsiloxy)phenyl isocyanide complex **2d** [$k(NC) = 1791 N m^{-1}$] is considered. This force constant should not change significantly upon hydrolysis of the Si–O bond. It is significantly higher than the value calculated for **3a** (1746 N m⁻¹) which already reacts mostly to give the ylidene complex **4a**.

Not only the type of transition metal but also its electronic properties as determined by the coordinated ligands influence the position of the equilibrium between isocyanide and ylidene complexes. The stability of the coordinated isocyanide ligand in complex **3a** is greatly enhanced by substitution of a good π -acceptor (CO) for a good σ -donor (PPh₃) at the tungsten atom. The complex **2e** (Scheme 2) reacts after hydrolysis of the Si-O bond almost exclusively to give the isocyanide complex **3e**. The ylidene complex **4e** could not be detected by IR or ¹H NMR spectroscopy. The introduction of a σ -donor leads to enhanced (d \rightarrow p) π -backbonding, and the force constant for the N=C bond in **3e** shrinks to 1706 N m⁻¹ (Table 1). This low value indicates a complete deactivation of the isocyanide carbon in **3e** for intramolecular nucleophilic attack and explains why no ylidene complex **4e** could be identified spectroscopically.

Even the electronically stabilized isocyanide complex **3e** can be converted into a ylidene derivative. This requires removal of the trace amounts of 4e from the reaction mixture which will cause the equilibrium to shift to the right side (Scheme 2). Removal of 4e is best achieved by alkylation of the ylidene nitrogen^{6,7} (Scheme 2). This alkylation prevents the back-reaction of the ylidene to the isocyanide complex and shifts the equilibrium completely to the side of the N-alkylated ylidene complex 4f. However, an alternative mechanism is conceivable for the reaction of a mixture of 3e/4e with strong bases and MeI. First, the strong base deprotonates the hydroxyl group in 3e. Now the phenolate oxygen attacks the isocyanide carbon atom under formation of a coordinated iminoacyl. This ligand is then alkylated with MeI to give 4f. In both cases the reaction product is the same. An electronically stabilized complex with a 2-hydroxyphenyl isocyanide ligand is completely converted into a complex with an N-methylated 1,2-dihydrobenzoxazol-2-ylidene ligand.

The molecular structure of **4f** was established by X-ray diffraction analysis. Scheme 2 shows an ORTEP diagram of **4f**. The tungsten atom is coordinated in a distorted octahedral fashion by one ylidene, four CO carbons, and a triphenylphosphine ligand. Bond distances and angles in **4f** compare well with equivalent parameters in **4a**⁶ and its N-methylated derivative.⁶

In summary, we present an aromatic isocyanide ligand with a strong tendency to form ylidene complexes by intramolecular nucleophilic attack when attached to electron-poor transition metal fragments. Coordination to electron-rich transition metal fragments prevents the ylidene formation and leads to electronically stabilized complexes with the 2-hydroxyphenyl isocyanide ligand. The isocyanide complex can be converted into ylidene complexes by reaction with strong bases followed by alkylation of the ylidene nitrogen atom. These reactions might prove useful for the synthesis of ylidenes of early transition metals, e.g., Ti(IV), from isocyanide complexes, and corresponding investigations are under way.

Experimental Section

General Comments. All manipulations were performed in an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use. ¹H and ¹³C NMR spectra were recorded on a Bruker AM 270 spectrometer. Infrared spectra were taken in KBr on a Perkin-Elmer 983 instrument. Elemental analyses (C,H,N) were performed at the Freie Universität Berlin on a Heraeus CHN-rapid elemental analyzer. Mass spectra (EI, 70 eV) were recorded on a Varian

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Scheme 2. Stabilization of 2-Hydroxyphenyl Isocyanide on a *cis*-[W(CO)₄(PPh₃)] Fragment and Molecular Structure of 4f²



^a Selected bond distances (Å) and angles (deg): W-P, 2.542(2); W-C1, 2.196(6); W-C27, 2.029(8); W-C28, 2.005(8); W-C29, 1.986(7); W-C30, 1.998(8); O1-C1, 1.373(8); O1-C8, 1.381(8); N-C1, 1.334(9), N-C2, 1.467(8); N-C3, 1.387(8); P-W-C1, 88.8(2); P-W-C27, 94.8(2); P-W-C28, 90.2(2); P-W-C29, 89.7(2); P-W-C30, 179.0(2); C1-W-C27, 84.8(3); C1-W-C28, 93.9(3); C1-W-C29, 176.1(2); C1-W-C30, 92.2(3); C27-W-C28, 174.9(3); C27-W-C29, 91.7(3); C27-W-C30, 85.4(3); C28-W-C29, 89.7(3); C28-W-C30, 89.7(3); C29-W-C30, 89.3(3); C1-O1-C8, 109.8(5); C1-N-C2, 124.5(6); C1-N-C3, 112.3(5); C2-N-C3, 123.2(6); W-C1-O1, 119.8(4); W-C1-N, 135.2(5); O1-C1-N, 105.1(5).

MAT 711 instrument. 2-(Trimethylsiloxy)phenyl isocyanide (1) was synthesized as previously described.⁵ The syntheses of the tungsten complexes $2a-4a^6$ and the iron complexes $2d-4d^7$ have been described. The molybdenum and chromium complexes 2b-4b and 2c-4c, respectively, were prepared in an analogous manner. Selected spectroscopic data for these complexes are summarized in Table 1.

Synthesis of $\{W(CNC_6H_4-2-OH)[P(C_6H_5)_3](CO)_4\}$ (3e). $cis-[N(C_2H_5)_4]{WBr[P(C_6H_5)_3](CO)_4}^{12}$ (8.03 g, 10.5 mmol) was dissolved in 200 mL of dry ethanol under argon. To this solution was added 2.0 g (10.5 mmol) of 2-(trimethylsiloxy)phenyl isocyanide (1), and the yellow reaction mixture was stirred for 12 h under argon as described by Rommel.¹³ The presumably formed 2-(trimethylsiloxy)phenyl isocyanide complex 2e could not be isolated since this reaction was carried out in ethanol and partial hydrolysis of the Si-O bond of the ligand already occurred under these conditions. A catalytic amount of KF (100 mg) was added, and the reaction mixture was stirred at room temperature for an additional 18 h. Then all solvents were removed in vacuo, and the solid yellow residue was purified by column chromatography (neutral Al₂O₃, eluent CH₂Cl₂/hexane, 1:2, v:v). Complex 3e was isolated as a yellow powder in 42% yield. Anal. Calcd for $C_{29}H_{20}NO_5PW$ (M_r = 677.31): C, 51.43; H, 2.98; N, 2.07. Found: C, 50.35; H, 3.18; N, 2.53. ¹H NMR (270 MHz, CDCl₃): δ 7.62–6.64 (m, 19H, Ar-H), 6.50 (s, br, 1H, OH). ¹³C[¹H] NMR (67.89 MHz, CDCl₃): δ 203.5 (d, ²J_{PC} = 24 Hz, CO trans to P), 202.9 (d, ${}^{2}J_{PC} = 7$ Hz, CO trans to isocyanide),

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199.7 (d, ${}^{2}J_{PC} = 7$ Hz, ${}^{1}J_{WC} = 126$ Hz, CO trans to CO), 163.8 (d, ${}^{2}J_{PC} = 9$ Hz, Ar-NC), 152.27 (C-OH), 135.7 (d, ${}^{1}J_{PC} = 39$ Hz, P-C), 133.1 (d, ${}^{2}J_{PC} = 12$ Hz, P-C-C), 129.8 (P-C-C-C-C), 128.3 (d, ${}^{3}J_{PC} = 9$ Hz, P-C-C-C), 128.0, 126.6, 120.1, 116.7 (Ar-C), 116.2 (Ar-C-NC). IR ($\bar{\nu}$): 2117 (m, CN), 2009 (s, CO), 1895 (vs, br, CO). LRMS (m/z, rel intensity): 677 (M⁺⁺, 7.1), 649 (M⁺⁺ - CO, 4.3), 621 (M⁺⁺ - 2 CO, 5.9), 593 (M⁺⁺ - 3 CO, 9.7), 565 (M⁺⁺ - 4 CO, 3.0), 558 (M⁺⁺ - CNC₆H₄-2-OH, 4.5), 262 [P(C₆H₅)₃⁺⁺, 100].

Synthesis of $\{W[CN(CH_3)C_6H_4-2-O][P(C_6H_5)_3](CO)_4\}$ (4f). 3e (1.0 g, 1.5 mmol) was dissolved in 50 mL of dry DMF under argon. The solution was cooled to -40 °C, and 190 mg (1.7 mmol) of KO-t-Bu was added as a solid. The reaction solution was stirred for 3 h at -40 °C, and then 92 μ L (1.5 mmol) of MeI was added via a syringe. The reaction mixture was allowed to warm up to room temperature and stirred at this temperature for 3 h. Then the DMF was removed in vacuo, and the yellow residue was recrystallized from CH₂Cl₂ to give 0.91 g (89%) of 4f as bright yellow, slightly air-sensitive crystals. ¹H NMR (270 MHz, CDCl₃): δ 7.72-7.01 (m, br, 19H, Ar-H), 3.67 (s, 3H, N-CH₃). ${}^{13}C[{}^{1}H]$ NMR (67.89 MHz, CDCl₃): δ 221.8 (d, ²*J*_{PC} = 9 Hz, NCO), 208.9 (d, ²*J*_{PC} = 5 Hz, CO trans to ylidene), 207.1 (d, ${}^{2}J_{PC} = 25$ Hz, CO trans to P), 202.7 (d, ${}^{2}J_{PC} = 8$ Hz, CO trans to CO), 152.1 (Ar-C), 136.1 (d, ${}^{1}J_{PC} = 37$ Hz, P-C), 133.0 (d, ${}^{2}J_{PC} = 12$ Hz, P-C-C), 129.3 (Ar-C and P-C-C-C-C), 128.0 (d, ${}^{3}J_{PC} = 9$ Hz, P-C-C-C), 124.4, 124.1, 110.3, 109.7 (Ar-C). IR (v): 2067 (m, CO), 1893 (s, CO), 1869 (vs, CO), 1847 (s, CO). LRMS (m/z rel intensity): 691 (M^{•+}, 3.3), 663 ($M^{\bullet+}$ - CO, 2.7), 635 ($M^{\bullet+}$ - 2 CO, 5.6), 607 ($M^{\bullet+}$ - 3 CO, 4.4), 262 [P(C_6H_5)₃)⁺, 100].

X-ray Crystallographic Analysis of 4f. Yellow platelike

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crystals of 4f were grown from CH_2Cl_2 at -26 °C. Selected crystallographic details: size of data crystal, 0.62 \times 0.38 \times 0.18 mm; formula, $C_{30}H_{22}NO_5PW$; M = 691.34 amu; triclinic, space group $P\bar{1}$; a = 10.032(2) Å, b = 10.258(2) Å, c = 16.580(4)Å; α = 79.12(2)°, β = 78.78(2)°, γ = 64.57(2)°; V = 1500.8(6) Å³; $\rho_{exp} = 1.55$ g/cm³, $\rho_{calc} = 1.530$ g/cm³; Mo Kα radiation ($\lambda =$ 0.71073 Å, monochromator graphite), μ (Mo K α) = 40.18 cm⁻¹; 3908 symmetry independent diffraction data were measured at 20(3) °C in the 2θ range 2-45°; structure solution with Patterson and Fourier methods; refinement of positional parameters of all non-hydrogen atoms with anisotropic thermal parameters; hydrogens on calculated positions [d(C-H)]= 0.95 Å] with $B_{eq(H)} = 1.3B_{eq(C)}$; R = 3.32, $R_w = 4.75$ for 3501 absorption-corrected (correction range 1.0/0.723) structure factors $F_0^2 \ge 3\sigma(F_0^2)$ and 343 refined parameters. Neutral atomic scattering factors¹⁴ were used, and all scattering factors were corrected for anomalous dispersion.¹⁴ All calculations were carried out with the MolEn program package.¹⁵

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Supplementary Material Available: Listings of X-ray data collection and refinement data, positional and thermal parameters, and bond lengths and angles for **4f** (8 pages). Ordering information is given on any current masthead page.

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