

Notes

Acylimido Complexes of Tungsten(IV) Formed by Oxygen Atom Transfer to Nitrile- κ^2N,C Complexes

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Introduction

Oxyfunctionalization of coordinated nitriles is a potentially valuable strategy for the synthesis of pharmaceuticals, fine chemicals, and bulk industrial chemicals.^{1–3} Routes to heterocyclic compounds^{1–3} and the conversion of acrylonitrile to acrylamide⁴ are only two of the areas where this strategy may find important applications. Compared with well-established nitrile coupling, insertion, and reduction reactions,^{1–3} there are few well-defined examples of the oxyfunctionalization of coordinated nitriles. Reaction of coordinated nitriles with protic nucleophiles such as water and alcohols generates amidates and imido esters, respectively.⁵ An example is the base-catalyzed hydrolysis of $[M(NH_3)_5(RCN)]^{3+}$ ($M = Rh, Ir, Co, Ru$), which produces amidate complexes via nucleophilic attack of hydroxide on the nitrile carbon atom. The reactive oxozirconium complex ($\eta^5-C_5Me_5$)₂Zr(=O) undergoes a cycloaddition reaction with nitriles to form metallacycles via an intermediate azaoxametallacycle.⁶ Various heterocycles are also formed by the cyclization of nitrile ligands using halo alcohols. For example, *cis*- and *trans*-PtCl₂(RCN)₂ and *trans*-[Pt(R)(RCN)(PPh₃)₂]⁺ react with 2-chloroethanoate to yield five-membered 2-oxazoline complexes;⁷ in the latter case, free oxazolines are released upon reaction of the cationic product with chloride. Analogous 1,3-oxazine complexes can be prepared by reactions involving 3-chloro-1-propanoate.⁸

This paper reports the oxyfunctionalization of coordinated nitriles by oxygen atom transfer to the nitrile carbon atom. Specifically, it describes the synthesis and characterization of the acylimido-W(IV) complexes LW{NC(O)R}I(CO) [$L = \text{hydrotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$; $R = \text{Me, Et, Ph}$], formed by reaction of LWI(RCN)(CO)⁹ with pyridine *N*-oxide, and the X-ray crystal structure of the derivative LW{NC(O)Me}(SPh)(CO)· $\frac{1}{2}C_6H_{14}$. The conversion of nitrile ligands to imido ligands in related tungsten complexes has been reported by Templeton et al.,¹⁰ here, reactions of [LW(RCN)(CO)₃]⁺ with nucleophiles result in the formation of LW{N=C(Nu)R}(CO)₂ complexes (Nu = H, Et, OMe), which are protonated by HBF₄ to produce cationic imido-W(IV) complexes of the type [LW{NCH(Nu)R}(CO)₂]⁺. Templeton et al.¹¹ have also reported the generation of the acetylimido complex LW{NC(O)Me}Cl(CO) by reaction of LWN(CO)₂ with acetyl chloride, but to date no complex of this type has been structurally characterized.

Results and Discussion

Oxygen atom transfer to LWI(MeCN)(CO) was expected to produce LWOI(CO) in a manner analogous to the generation of LWSI(CO) by sulfur atom transfer to LWI(MeCN)(CO).⁹ However, reaction of LWI(MeCN)(CO) with pyridine *N*-oxide at 40 °C in acetonitrile/dichloromethane produces the blue-green, air-stable, diamagnetic acetylimido complex LW{NC(O)Me}I(CO) and only trace amounts of LWOI(CO). The complexes LW{NC(O)Et}I(CO) and LW{NC(O)Ph}I(CO) are readily prepared by analogous reactions involving LWI(EtCN)(CO) and LWI(PhCN)(CO), respectively. Higher reaction temperatures result in mixtures of unidentified (red) compounds and poor yields of the acylimido complexes. The complexes are soluble in chlorinated solvents, tetrahydrofuran, acetonitrile, and aromatic hydrocarbons but insoluble in alcohols and aliphatic hydrocarbons. Complexes such as LW(S₂PPh₂-S)(MeCN)(CO) and LW(SPh)(MeCN)(CO) do not react with pyridine *N*-oxide to give products of this type. However, LW{NC(O)Me}I(CO) reacts with sodium thiophenolate in refluxing tetrahydrofuran to yield blue, air-stable, diamagnetic LW{NC(O)Me}(SPh)(CO). In contrast to LW{NC(O)Me}I(CO), this complex shows a high solubility in most organic solvents with the exception of aliphatic hydrocarbons. All the complexes are very stable, as expected for imido complexes of this type, and fail to react with phosphines (PPh₃ or PMe₂Ph) to form phosphine oxides, even in refluxing toluene. This lack of reactivity is not consistent with the previous, tentative formulation of LW{NC(O)Me}I(CO) as an acetonitrile *N*-oxide complex.^{9a}

The infrared spectra of the compounds exhibit a single ν -(CO) band at ca. 1960–1940 cm⁻¹ and bands associated with

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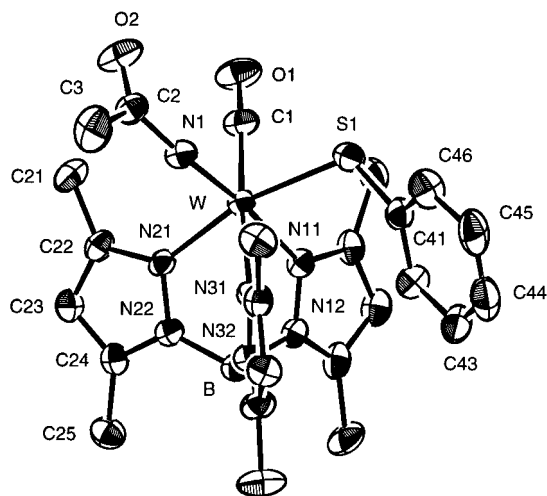


Figure 1. Molecular structure and atom-numbering scheme for LW{NC(O)Me}(SPh)(CO). The numbering of the pyrazole rings containing N(11) and N(31) parallels that shown for the ring containing N(21). Thermal ellipsoids are drawn at the 30% probability level.

the imido ligands at ca. 1680, 1260, and 1070 cm^{-1} . The band at 1680 cm^{-1} may be confidently assigned to the $\nu(\text{C}=\text{O})$ mode of the imido ligand, but the origins of the other bands are less certain. It is likely that the 1260 and 1070 cm^{-1} bands are due to vibrations involving the imido C–N and W–N fragments, respectively.¹² Assignment^{9a} of the 1680 and 1260 cm^{-1} bands to $\nu(\text{CN})$ and $\nu(\text{N}=\text{O})$ modes of an acetonitrile *N*-oxide¹³ ligand is no longer tenable in light of the complete characterization data now available. The fingerprint bands typically associated with the L and SPh⁻ ligands are also evident in the infrared spectra. The complexes exhibit ¹H and ¹³C{¹H} NMR spectra indicative of a single isomer possessing *C*₁ symmetry. Under *C*₁ symmetry, all the protonic groups of ligand L are inequivalent; six methyl resonances (with some coincidence) and three methine resonances are observed in ¹H NMR spectra. For LW{NC(O)Me}I(CO), the resonance at δ 2.15 can be assigned to the acetyl imido methyl group, as it was absent in the spectrum of the deuterated complex LW{NC(O)Me-*d*₃}I(CO). For LW{NC(O)Me}I(CO), ¹³C resonances at δ 24.84 and 181.88 may be assigned to the methyl and carbonyl carbon atoms, respectively, of the imido ligand; the former is observed as a septet in the spectrum of LW{NC(O)Me-*d*₃}I(CO), and the latter exhibits ¹⁸³W satellites (²*J*_{WC} = 35 Hz). A single metal–carbonyl resonance at δ 269.64 (¹*J*_{WC} = 171 Hz) is also observed. The NMR spectra of LW{NC(O)Me}(SPh)(CO) and LW{NC(O)Me-*d*₃}(SPh)(CO) exhibit similar features. Previously reported LW{NC(O)Me}Cl(CO) exhibits very similar NMR properties, most notably imido and carbonyl carbon resonances at δ 181.7 (²*J*_{WC} = 35 Hz) and δ 280.6 (¹*J*_{WC} = 177 Hz), respectively.¹¹ The assignment given for LW{NC(O)Et}I(CO) was assisted by two-dimensional (HMQC, HMBC) NMR methods. NOE experiments are consistent with solution structures having a syn arrangement of the imido and metal carbonyl groups, as observed in the solid state structure of LW{NC(O)Me}(SPh)(CO) (vide infra).

The structure of LW{NC(O)Me}(SPh)(CO) has been determined by X-ray diffraction. A view of the molecule and the atom-numbering scheme are shown in Figure 1, and selected bond distances and angles are given in Table 1. The complex

Table 1. Selected Bond Distances (Å) and Angles (deg) for LW{NC(O)Me}(SPh)(CO)

W–S(1)	2.381(3)	W–N(21)	2.189(10)	C(2)–O(2)	1.19(2)
W–N(1)	1.778(9)	W–N(31)	2.177(9)	C(2)–C(3)	1.48(2)
W–C(1)	1.991(13)	S(1)–C(41)	1.783(14)	C(1)–O(1)	1.15(2)
W–N(11)	2.290(9)	N(1)–C(2)	1.389(15)		
S(1)–W–N(1)	103.1(3)	S(1)–W–C(1)	84.2(4)		
S(1)–W–N(11)	87.2(3)	S(1)–W–N(21)	163.4(2)		
S(1)–W–N(31)	93.4(3)	N(1)–W–C(1)	85.3(5)		
N(1)–W–N(11)	167.3(4)	N(1)–W–N(21)	93.4(2)		
N(1)–W–N(31)	100.3(4)	C(1)–W–N(11)	88.5(4)		
C(1)–W–N(21)	97.5(5)	C(1)–W–N(31)	174.3(5)		
N(11)–W–N(21)	76.4(3)	N(11)–W–N(31)	86.3(3)		
N(21)–W–N(31)	83.3(3)	W–S(1)–C(41)	115.0(4)		
W–N(1)–C(2)	167.0(9)	N(1)–C(2)–O(2)	121.8(12)		
N(1)–C(2)–C(3)	117.1(13)	O(2)–C(2)–C(3)	121.1(14)		
W–C(1)–O(1)	175.3(12)				

exhibits a distorted octahedral structure, composed of a tungsten center coordinated by monodentate acetyl imido, carbonyl, and thiophenolate ligands, and a facially tridentate L ligand. The W–N(1) bond distance of 1.778(9) Å is typical of related tungsten imido complexes, as is the N(1)–C(2) distance of 1.389(15) Å.^{11,12} The acetyl carbonyl group is characterized by a C(2)–O(2) distance of 1.19(2) Å, and C(2) is trigonal and planar, indicative of sp² hybridization. The W–S(1) bond distance of 2.381(3) Å, W–S(1)–C(41) angle of 115.0(4)°, and the nonplanarity of the WSPH fragment are all consistent with an sp³-hybridized sulfur atom and the absence of any significant π -interactions between the tungsten and sulfur. The non-hydrogen atoms of the W{NC(O)Me}(CO) fragment are essentially planar [maximum deviation from plane = 0.063(10) Å for N(1)], and those of the NC(O)Me fragment are strictly planar, the tungsten atom being 0.16(2) Å out of this plane toward the sulfur atom. The W–N(1)–C(2) angle of 167.0(9)° brings the acetyl carbonyl group toward the carbonyl ligand. The precise positioning of the acetyl imido ligand reflects a degree of steric conflict between this group and the dimethylpyrazole group containing N(31). The carbonyl ligand approaches linearity with a W–C(1)–O(1) angle of 175(1)°. The W–N(11) bond [2.290(9) Å] is considerably lengthened relative to the other W–N(*n*1) bonds (average 2.183 Å) due to the trans influence of the imido ligand.¹² The phenyl group of the thiophenolate ligand occupies a cleft in the pyrazolyborate ligand fragment, its precise location being dictated by intermolecular interactions with the dimethylpyrazole groups of neighboring molecules. The lattice hexane molecules occupy channels parallel to the *a* direction.

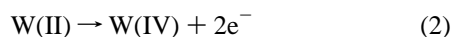
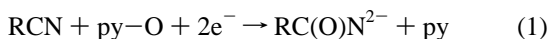
The orientation of the acyl imido ligands with respect to the metal carbonyl fragment can be rationalized by π -orbital overlap considerations; in the following discussion, we assume the *x*, *y*, and *z* axes lie approximately along the molecular W–N(1), W–S(1), and W–C(1)–O(1) directions, respectively. Here, the usual two over three arrangement of d orbitals appropriate for a strict octahedral field is modified by the disparity in ligand fields and by π -bonding and π -back-bonding interactions between tungsten and the imido and carbonyl ligands. Since it is orthogonal to the strong field imido ligand, the *d*_{yz} orbital will be stabilized relative to the other d orbitals and will be occupied by the d² electrons in this formally W(IV) complex. Consequently, this orbital becomes available for π -back-bonding to the carbonyl ligand, while the empty *d*_{xy} and *d*_{xz} orbitals become favorably disposed to π -donation from the imido ligand. The observed orientation of the imido carbonyl group with respect to these π -base interactions suggests that a molecular orbital delocalized over the W–N–C=O fragment, and involving the p_y orbitals of both C(2) and O(2), may contribute to the

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electronic structure of the molecule. The orbital in the xz plane may be delocalized across the $N(1)-W-C\equiv O$ unit. Similar electronic descriptions have been advanced for isoelectronic carbonyl-oxo- and carbonyl-thio-Mo(IV) and -W(IV) complexes.^{9,14} The diamagnetism of the complexes is consistent with the orbital description.

The reaction of pyridine N -oxide with the κ^2N,C nitrile complexes may be initiated by attack of the nucleophilic oxygen of the N -oxide on the electrophilic nitrile carbon center. This may result in transient formation of an N -oxide adduct which then undergoes an electronic rearrangement leading to the observed products. It is unknown whether a κ^2N,C nitrile or a transient monodentate (κN) nitrile ligand is attacked by the N -oxide. Attack on a *coordinated* nitrile ligand is consistent with the conversion of $LWI(MeCN-d_3)(CO)$ to $LW\{NC(O)Me-d_3\}I(CO)$ upon reaction with pyridine N -oxide in warm acetonitrile/dichloromethane. The oxygen atom transfer reaction results in a formal two-electron oxidation of the tungsten center from W(II) to W(IV) as expected from the coupling of half-reactions 1 and 2 (py = pyridine). Other recently reported three-



and four-electron κ^2N,C nitrile complexes¹⁵ may undergo similar reactions producing further examples of nitrile ligand oxyfunctionalization.

Experimental Section

Materials and Methods. All reactions were performed under an atmosphere of dinitrogen using dried, deoxygenated solvents and standard Schlenk techniques. Samples of $LWI(CO)_3$ ¹⁶ and $LWI(MeCN)(CO)$ ^{9a} were prepared by literature methods or slight modifications thereof, and all other reagents were analytical reagent grade or above. Solid state (KBr disk) and solution (CH_2Cl_2) infrared spectra were recorded on a Bio-Rad FTS 165 FTIR spectrophotometer. 1H and $^{13}C\{^1H\}$ NMR spectra ($CDCl_3$) were obtained using Varian Unity 300 and Varian Unity Plus 400 spectrometers. UV-visible spectra were recorded on a Hitachi 150-20 double-beam spectrophotometer. Microanalyses were performed by Atlantic Microlabs Inc, Norcross, GA.

$LW\{NC(O)Me\}I(CO)$. A solution of $LWI(MeCN)(CO)$ (1.00 g, 1.48 mmol) and pyridine N -oxide (0.56 g, 5.92 mmol) in acetonitrile/dichloromethane (1/1, 50 mL) was heated at 40 °C for 30 min and then cooled to room temperature. The deep blue reaction mixture was reduced to dryness and the residue chromatographed on silica gel using dichloromethane as eluent. The blue fraction was collected and evaporated to dryness. The compound was purified by recrystallization from dichloromethane/methanol, isolated by filtration, washed with methanol (5 mL), and dried *in vacuo*. Yield: 0.43 g, 42%.

Anal. Calcd for $C_{18}H_{25}BN_7O_2W$: C, 31.20; H, 3.64; N, 14.15. Found: C, 31.28; H, 3.67; N, 14.01. IR (CH_2Cl_2): $\nu(CO)$ 1963s, $\nu(C=O)$ 1673m cm^{-1} . IR (KBr): $\nu(BH)$ 2557w, $\nu(CO)$ 1955s, $\nu(C=O)$

1680m, $\nu(CN)$ 1544m, 1447m, 1415m, 1362m, 1261s, 1198m, 1069m, 1047m, 951w, 911w, 858w, 807w, 690w cm^{-1} . 1H NMR ($CDCl_3$): δ 2.15 (s, 3H, $C(O)CH_3$; absent for CH_3-d_3 analogue), 2.28, 2.34, 2.51, 2.52, 2.52, 2.74 (s, 6 \times 3H, 6 \times CH_3 of L), 5.70, 6.01, 6.11 (s, 3 \times 1H, 3 \times CH of L). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.23, 12.25, 12.72, 16.51, 17.61, 17.66 (6 \times CH_3 of L), 24.84 ($C(O)CH_3$; septet, $^1J_{DC}$ 20 Hz for CH_3-d_3 analogue), 107.46, 107.76, 108.42 (3 \times CH of L), 145.16, 145.71, 146.07, 152.52, 153.75, 153.79 (6 \times CMe of L), 181.88 ($^2J_{WC}$ 35 Hz, $NC(O)$), 269.64 ($^1J_{WC}$ 171 Hz, CO). Electronic spectrum (CH_2Cl_2): 810 (sh), 680 nm (ϵ 115 $M^{-1} cm^{-1}$).

$LW\{NC(O)Me\}(SPh)(CO)$. A suspension of $LW\{NC(O)Me\}I(CO)$ (0.41 g, 0.59 mmol) and sodium thiophenolate (0.20 g, 1.51 mmol) in tetrahydrofuran (40 mL) was refluxed for 10 min, whereupon the reaction mixture was reduced to dryness. The residue was treated with dichloromethane (50 mL), and the mixture was filtered. The filtrate was reduced to dryness, the residue was dissolved in dichloromethane, and the solution was column-chromatographed on silica gel using dichloromethane as eluent. The green-blue band was collected and evaporated to dryness, and the residue was recrystallized from dichloromethane/hexane. The blue crystalline solid was filtered off, washed with hexane (10 mL), and dried *in vacuo*. Yield: 0.15 g, 38%.

Anal. Calcd for $C_{24}H_{30}BN_7O_2SW$: C, 42.69; H, 4.48; N, 14.52; S, 4.75. Found: C, 42.75; H, 4.55; N, 14.57; S, 4.68. IR (CH_2Cl_2): $\nu(CO)$ 1960s, $\nu(C=O)$ 1650m cm^{-1} . IR (KBr): $\nu(BH)$ 2566w, $\nu(CO)$ 1960s, $\nu(C=O)$ 1647m, $\nu(CN)$ 1544m, 1449m, 1417m, 1368m, 1353m, 1265s, 1205m, 1067m, 1044m, 966w, 858w, 791w, 746w, 696w cm^{-1} . 1H NMR ($CDCl_3$): δ 1.99 (s, 3H, $C(O)CH_3$; absent for CH_3-d_3 analogue), 2.14, 2.28, 2.45, 2.46, 2.51, 2.65 (s, 6 \times 3H, 6 \times CH_3 of L), 5.65, 5.97, 6.01 (s, 3 \times 1H, 3 \times CH of L) 6.96–7.40 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.38, 12.45, 12.56, 15.85, 16.40, 16.41 (6 \times CH_3 of L), 23.81 ($C(O)CH_3$; septet, $^1J_{DC}$ 20 Hz, for CH_3-d_3 analogue), 107.31, 107.37, 108.34 (3 \times CH of L), 124.49, 127.55, 132.30, 144.10, 145.33, 145.84, 152.99, 153.74, 153.79, 154.17 (6 \times CMe of L and Ph), 180.75 ($^2J_{WC}$ 35 Hz, $NC(O)$), 264.78 ($^1J_{WC}$ 175 Hz, CO). Electronic spectrum (CH_2Cl_2): 743 (110), 588 (370), 378 nm (ϵ 6.7 \times 10⁴ $M^{-1} cm^{-1}$).

$LW\{NC(O)Et\}I(CO)$. A solution of $LWI(CO)_3$ (1.5 g, 2.17 mmol) in propionitrile (30 mL) was refluxed for 3 h to generate $LWI(EtCN)(CO)$.^{9c} Upon cooling, pyridine N -oxide (0.4 g, 4.18 mmol) was added and the mixture was heated at 40 °C for 1 h. The brown reaction mixture was reduced to dryness and the residue chromatographed on silica gel using dichloromethane as eluent. The green fraction was collected and evaporated to dryness. The compound was purified by recrystallization from dichloromethane/methanol, isolated by filtration, washed with methanol (5 mL), and dried *in vacuo*. Yield: 0.61 g, 40%.

Anal. Calcd for $C_{19}H_{27}BN_7O_2W$: C, 32.28; H, 3.84; N, 13.87. Found: C, 32.12; H, 3.84; N, 13.70. IR (CH_2Cl_2): $\nu(CO)$ 1965s, $\nu(C=O)$ 1648m cm^{-1} . IR (KBr): 2978w, 2930w, $\nu(BH)$ 2560w, $\nu(CO)$ 1944s, $\nu(C=O)$ 1678s, $\nu(CN)$ 1544m, 1448m, 1416m, 1384m, 1366m, 1345m, 1278w, 1202s, 1069m, 1047m, 858w, 793m, 691w, 640w cm^{-1} . 1H NMR ($CDCl_3$): δ 1.14 (t, 3H, CH_2CH_3), 2.25–2.58 (obscured m, 2H, CH_2CH_3), 2.29, 2.32, 2.52, 2.53, 2.73 (s, 6 \times 3H, 6 \times CH_3 of L), 5.70, 6.01, 6.12 (s, 3 \times 1H, 3 \times CH of L). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 8.17 (CH_2CH_3), 12.22, 12.22, 12.70, 16.48, 17.60, 17.69 (6 \times CH_3 of L), 31.44 (CH_2CH_3), 107.37, 107.72, 108.42 (3 \times CH of L), 145.06, 145.62, 145.92, 152.46, 153.76, 153.83 (6 \times CMe of L), 185.47 ($^2J_{WC}$ 34 Hz, $NC(O)$), 270.75 ($^1J_{WC}$ 172 Hz, CO). Electronic spectrum (CH_2Cl_2): 810 (sh), 662 (ϵ 106 $M^{-1} cm^{-1}$).

$LW\{NC(O)Ph\}I(CO)$. A solution of $LWI(CO)_3$ (0.8 g, 1.16 mmol) in benzonitrile (15 mL) was heated to 100 °C for 4 h to generate $LWI(PhCN)(CO)$.^{9c} Upon cooling, pyridine N -oxide (0.43 g, 4.5 mmol) was added, and the mixture was heated at 40 °C for 30 min. The deep blue reaction mixture was reduced to near dryness, the residue was dissolved in a minimum amount of dichloromethane, and the solution was treated with methanol (ca. 40 mL) and cooled to -4 °C for several days. The green solid isolated upon filtration was purified by column chromatography (silica/dichloromethane) and recrystallized from dichloromethane by addition of methanol. Yield: 0.31, 36%. The microanalysis was performed on the dichloromethane hemisolvate (confirmed by NMR).

Anal. Calcd for $C_{23.5}H_{28}BClIN_7O_2W$: C, 35.39; H, 3.54; N, 12.29.

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Table 2. Crystallographic Data for LW{NC(O)Me}(SPh)(CO) $\cdot\frac{1}{2}$ C₆H₁₄

empirical formula	C ₂₇ H ₃₇ BN ₇ O ₂ SW
fw	718.36
space group	P1
<i>a</i> , Å	9.640(3)
<i>b</i> , Å	12.344(6)
<i>c</i> , Å	14.471(12)
α , deg	80.83(7)
β , deg	89.50(6)
γ , deg	67.35(3)
<i>V</i> , Å ³	1566(2)
<i>Z</i>	2
ρ_{calcd} , g cm ⁻³	1.523
radiation (wavelength, Å)	Mo K α (0.710 73)
<i>T</i> , °C	293(1)
μ , cm ⁻¹	37.89
<i>R</i> ^a	0.0608
<i>R</i> _w ^b	0.1826

^a For $I > 2\sigma(I)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^b For all data, $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Found: C, 35.44; H, 3.54; N, 12.37. IR (CH₂Cl₂): $\nu(\text{CO})$ 1965s, $\nu(\text{C}=\text{O})$ 1650m cm⁻¹. IR (KBr): 2965w, 2927w, $\nu(\text{BH})$ 2557w, $\nu(\text{CO})$ 1962s, $\nu(\text{C}=\text{O})$ 1650m, 1596w, 1579w, $\nu(\text{CN})$ 1544m, 1488w, 1447m, 1415m, 1385w, 1366m, 1275s, 1199m, 1181m, 1066m, 1047m, 986w, 911w, 857w, 807m, 712m, 690w 643w, 639w cm⁻¹. ¹H NMR (CDCl₃): δ 2.24, 2.33, 2.59, 2.61, 2.61, 2.71 (s, 6 \times 3H, 6 \times CH₃ of L), 5.74, 6.01, 6.18 (s, 3 \times 1H, 3 \times CH of L), 7.45 (t, 2H, Ph), 7.56 (t, 1H, Ph), 8.10 (d, 2H, Ph). ¹³C{¹H} NMR (CDCl₃): δ 12.08, 12.10, 12.49, 16.12, 17.39, 17.51 (6 \times CH₃ of L), 107.11, 107.44, 108.30 (3 \times CH of L), 128.22, 130.38, 130.88 (ipso), 133.09 (Ph), 144.85, 145.63, 145.76, 152.78, 153.41, 153.68 (6 \times CMe of L), 176.30 (²J_{WC} 34 Hz, NC(O)), 272.41 (¹J_{WC} 172 Hz, CO). Electronic spectrum (CH₂Cl₂): 810 (sh), 678 (ϵ 109 M⁻¹ cm⁻¹).

Crystal Structure. Blue-green crystals of LW{NC(O)Me}(SPh)(CO) $\cdot\frac{1}{2}$ C₆H₁₄ were grown by slow diffusion of hexane into a diethyl ether solution of the complex. All other attempts to grow X-ray-quality crystals of this very soluble complex, or the other complexes at hand, were unsuccessful. A number of crystals were subjected to preliminary X-ray diffraction studies. All showed broad peaks suggestive of a degree of disorder; the best, a needle of approximate dimensions 0.76 \times 0.11 \times 0.08 mm, was selected for data collection. Intensity data were collected using an Enraf-Nonius CAD-4MachS single-crystal X-ray diffractometer using the $\omega/2\theta$ scan method, with Mo K α radiation (graphite crystal monochromator, $\lambda = 0.71073$ Å) at 293(1) K. Accurate values of the unit cell parameters and crystal orientation were obtained by a least-squares procedure from the angular settings of 25 carefully centered reflections. Crystallographic data are summarized in Table 2.

The structure was solved by using a combination of Patterson, direct

methods, and difference synthesis.^{17,18} After all non-hydrogen atoms had been located, four broad peaks of ~ 1.5 e Å⁻³ were found in the difference map, each separated from its neighbor by about 1.4 Å and related to another four peaks by a center of symmetry at (0, $\frac{1}{2}$, $\frac{1}{2}$). This was interpreted as being due to disordered hexane molecules which were asymmetrically distributed around the center of symmetry. Half of the hexane molecules had four carbons on one side of the center and two on the other, while the other half of the molecules had the reverse distribution. It was noted that the solvent molecules lie in a channel directed along the *a* axis and could lie in several different distributions around two centers of symmetry at (0, $\frac{1}{2}$, $\frac{1}{2}$) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). Attempts to include more components, such as 5:1 and 3:3 distributions, and distributions around ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), did not significantly improve the model. There were a number of other peaks of heights ~ 2 e Å⁻³, near the W, B, and C(21) atoms. It was possible to include only one of the peaks in the refinement, as a minor component of the W atom. No reliable positions for hydrogen atoms could be found in the difference maps, and none were included in the refinement. Full-matrix least-squares refinement on F^2 , using all data, was carried out with anisotropic displacement parameters applied to each of the non-hydrogen atoms, except for the atoms of the hexane molecule and the minor component of the disordered W atoms. The refinement converged with conventional R [$I > 2\sigma(I)$] and R_w (all data) of 0.0608 and 0.1826. The weighting scheme employed was of the type $w = [\sigma^2(F_o^2) + (0.0578P)^2 + 20.16P]^{-1}$. The final occupancy factors of the atoms of the hexane molecule were 0.5, and that of the minor component of the W atom was 0.013(2). In the final difference map, the maximum and minimum peak heights were 2.52 and -2.70 e Å⁻³.

The atomic scattering factors of all atoms were taken from ref 19; corrections were made for anomalous dispersion. Calculations were carried out on a Vaxstation 4000VLC computer system. Figure 1 was prepared using the program ORTEP.²⁰

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Supporting Information Available: An X-ray crystallographic file, in CIF format, is available on the Internet only. Access information is given on any current masthead page.

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