group 4 metal $Cp^*M(R)_2(L)_n^+$ and $Cp_2M(R)L^+$ derivatives[5,33] can be prepared and studied.

Acknowledgment. This work was supported by NSF grant CHE-9022700. R.F.J. gratefully acknowledges a Sloan Foundation Research Fellowship (1989–1991) and Union Carbide Research Innovation Awards (1989, 1990). Valuable discussions with G. Hlatky concerning the preparation of $C_2B_9H_{13}$ and with P. T. Wolczanski concerning solution molecular weight measurements are appreciated.

Supplementary Material Available: Complete listings of bond distances, bond angles, H atom positional parameters, and anisotropic thermal parameters for 1 and 2 (13 pages). Ordering information is given on any current masthead page.

OM920160M

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Reactivity of $Cp^*W(O)_2(CH_2SiMe_3)$ toward *p*-Tolyl Isocyanate: Cycloaddition Reactions of Tungsten–Oxo and –Imido Linkages[1,2]

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Treatment of $Cp^*W(O)_2(CH_2SiMe_3)$ with *p*-tolyl isocyanate under appropriate experimental conditions leads to the formation of $Cp^*W(O)(NC_6H_4\text{-}p\text{-}Me)(CH_2SiMe_3)$ (1), $Cp^*W(NC_6H_4\text{-}p\text{-}Me)_2(CH_2SiMe_3)$ (2), or $Cp^*W(NC_6H_4\text{-}p\text{-}Me)[N(C_6H_4\text{-}p\text{-}Me)C(O)N(C_6H_4\text{-}p\text{-}Me)](CH_2SiMe_3)$ (3). Each of the complexes 1–3 is derived in a sequential manner from its precursor by incorporation of an additional *p*-tolyl isocyanate fragment or molecule. The spectroscopic properties of these organometallic imido complexes are consistent with their possessing three-legged (1 and 2) and four-legged (3) piano-stool molecular structures. These conclusions have been confirmed by single-crystal X-ray crystallographic analyses of 2 and 3. Crystal data for 2: triclinic, $a = 15.095$ (3) Å, $b = 18.583$ (4) Å, $c = 10.828$ (2) Å, $\alpha = 95.01$ (2)°, $\beta = 107.01$ (2)°, $\gamma = 89.02$ (2)°, $Z = 4$, space group $P\bar{1}$, $R_F = 0.033$, $R_{wF} = 0.031$ for 5463 reflections with $I \geq 3\sigma(I)$. Crystal data for 3: monoclinic, $a = 14.5279$ (11) Å, $b = 10.447$ (7) Å, $c = 11.6482$ (13) Å, $\beta = 105.170$ (6)°, $Z = 2$, space group $P2_1$, $R_F = 0.058$, $R_{wF} = 0.081$ for 2479 reflections with $I \geq 3\sigma(I)$. The formation of complex 3 involves the *net* [2 + 2] cycloaddition of the N=C bond of *p*-tolyl isocyanate across one of the tungsten–imido links of complex 2, $Cp^*W(NC_6H_4\text{-}p\text{-}Me)_2(CH_2SiMe_3)$.

Introduction

The study of transition-metal imido complexes and other compounds having metal–ligand multiple bonds is currently in a period of rapid growth.[3-5] Imido complexes are of particular interest both as new reagents[6] and as heterogeneous or homogeneous catalysts for various organic conversions. For instance, metal–imido species have been invoked as intermediates during the ammoxidation of propylene.[7-9] Such species also appear to be involved in the catalytic cycles of a variety of metalloenzymes.[3,4] In light of the versatile reactivity exhibited by transition-metal–imido complexes, determination of their characteristic properties in various chemical environments is warranted.

We have previously described the synthesis, characterization, and some reactivity of metal–dioxo and metal–alkylidene–oxo complexes of the types A and B.[10] It was, therefore, of interest to us to determine whether the analogous metal–imido complexes (type C) could also be prepared.[11,12]

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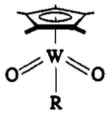
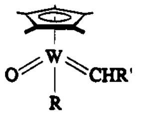
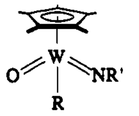
(11) We have previously synthesized one such imido oxo complex, namely CpW(O)(N-*o*-tolyl)(*o*-tolyl), by exposure of its diaryl nitrosyl precursor $CpW(NO)(o\text{-tolyl})_2$ as a solid to deaerated water vapor.[12] To date, this conversion remains unique.



A



B



C

A common method for the synthesis of compounds containing metal–imido linkages involves the reaction of alkyl or aryl isocyanates with metal–oxo complexes.[3,4,13] Reactions of this type are believed to proceed via a metallacyclocarbamate intermediate, a few examples of which have been isolated and structurally characterized.[3,5c,h,14]

This paper describes the outcomes of the reactions of Cp*W(O)$_2$(CH$_2$SiMe$_3$) with *p*-tolyl isocyanate. To date we have discovered that these reactions under appropriate experimental conditions lead to the sequential formation of Cp*W(O)(NC$_6$H$_4$-*p*-Me)(CH$_2$SiMe$_3$) (1), Cp*W(NC$_6$H$_4$-*p*-Me)$_2$(CH$_2$SiMe$_3$) (2), and Cp*W(NC$_6$H$_4$-*p*-Me)[N(C$_6$H$_4$-*p*-Me)C(O)N(C$_6$H$_4$-*p*-Me)](CH$_2$SiMe$_3$) (3). The present work demonstrates that not only do the tungsten–oxo links in Cp*W(O)$_2$(CH$_2$SiMe$_3$) undergo cycloaddition reactions with *p*-tolyl isocyanate but so does one of the tungsten–imido linkages in Cp*W(NC$_6$H$_4$-*p*-Me)$_2$(CH$_2$SiMe$_3$) (2).

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions using an atmosphere of dinitrogen. Conventional Schlenk techniques and a Vacuum Atmospheres Co. Dri-Lab Model HE-43-2 drybox were employed for the manipulation of air- and moisture-sensitive compounds.[15,16] The *p*-MeC$_6$H$_4$N=C=O reagent was purchased from Aldrich Chemical Co. and was used as received. Cp*W(O)$_2$(CH$_2$SiMe$_3$) was prepared by the published procedure.[17] Solvents were dried according to conventional procedures,[18] distilled, and deaerated with argon prior to use.

Infrared spectra were recorded on a Nicolet 5DX FT-IR instrument which was internally calibrated with a He/Ne laser. All ^{1}H and ^{13}C NMR spectra were obtained on a Varian Associates XL-300 spectrometer, and the chemical shifts of the observed resonances are reported in parts per million (ppm) downfield from Me$_4$Si referenced to the residual proton signal (^{1}H) or natural-abundance carbon signal (^{13}C) of C$_6$D$_6$. Ms. M. Austria, Ms. L. Darge, and Dr. S. O. Chan assisted in the collection of the NMR spectra. Low-resolution mass spectra were recorded at 70 eV on a Kratos MS50 spectrometer using the direct-insertion method by Dr. G. K. Eigendorf and the staff of the UBC Mass Spectrometry Laboratory. Elemental analyses were performed by Mr. P. Borda of this department.

Preparation of Cp*W(O)(NC$_6$H$_4$-*p*-Me)(CH$_2$SiMe$_3$) (1). Cp*W(O)$_2$(CH$_2$SiMe$_3$) (0.64 g, 1.46 mmol) was dissolved in hexanes (100 mL) in a 300-mL heavy-walled glass bomb. A hexanes (10 mL) solution of *p*-MeC$_6$H$_4$N=C=O (750 μL, ~6.0 mmol) was added to the bomb. The colorless reaction mixture was degassed using several freeze–pump–thaw cycles and was left under vacuum. The reaction vessel and its contents were heated to 140 °C for 1 week. The reaction vessel and solution were then cooled to 0 °C, and the atmosphere was removed in vacuo. The reaction mixture was then returned to the 140 °C oil bath for 2 days more. At the end of this time, a ^{1}H NMR spectrum of the final bright orange reaction mixture in C$_6$D$_6$ indicated complete consumption of the organometallic reactant. The final solution was taken to dryness in vacuo to obtain an orange oil. The oil was dissolved in hexanes (1.5 mL), and the solution was transferred by syringe to the top of a Florisil column (60–100 mesh, 2 × 20 cm) made up in hexanes. Elution of the column with hexanes (100 mL) yielded a pale yellow eluate, which was discarded. Elution of the column with hexanes/Et$_2$O (1:1, 300 mL; then 1:4, 100 mL) afforded a brilliant yellow solution, which was taken to dryness. The residue was crystallized from hexanes at −30 °C to obtain 390 mg (52% yield) of 1 as an analytically pure yellow powder. No solvent or combination of solvents could be found that produced crystals of 1. Anal. Calcd for C$_{21}$H$_{33}$NOSiW: C, 47.82; H, 6.31; N, 2.66. Found: C, 47.65; H, 6.39; N, 2.80. IR (Nujol mull): $\nu_{\mathrm{W=O}}$ 891 (vs) cm^{-1}; $\nu_{\mathrm{Si-Me}}$ 1241 (m) cm^{-1}; also 1496 (vs), 1346 (vs), 1105 (w), 1030 (w), 986 (m), 950 (m), 854 (ms), 832 (ms), 818 (m), 743 (w), 717 (m), 684 (w) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 6.96 (s, 4 H, C$_6$*H*$_4$), 2.13 (s, 3 H, C$_6$H$_4$C*H*$_3$), 1.78 (s, 15 H, C$_5$(C*H*$_3$)$_5$), 0.61 (d, 1 H, J_{HH} = 12.9 Hz, C*H*$_a$H$_b$), 0.51 (d, 1 H, J_{HH} = 12.9 Hz, CH$_a$*H*$_b$), 0.36 (s, 9 H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 154.32 (C$_{\mathrm{ipso}}$), 133.57 (C$_{\mathrm{para}}$), 129.29 (C$_{\mathrm{meta}}$), 124.67 (C$_{\mathrm{ortho}}$), 115.19 (*C*$_5$(CH$_3$)$_5$), 22.27 (*C*H$_2$), 21.12 (C$_6$H$_4$*C*H$_3$), 10.69 (C$_5$(*C*H$_3$)$_5$), 1.81 (Si(*C*H$_3$)$_3$). Low-resolution mass spectrum (probe temperature 80 °C): *m/z* 527 (P$^+$), 512 (P$^+$ − Me).

The air stability of 1 was demonstrated by dissolving a sample of 1 in reagent-grade acetone and allowing the resulting yellow solution to evaporate to dryness under ambient conditions. The remaining yellow solid exhibited physical properties which were identical with those displayed by 1.

Elution of the above column with THF (100 mL) produced an orange eluate, which was concentrated under reduced pressure until a white powder started to form in the flask. The flask was then placed in a freezer to complete the precipitation of the white powder. The powder was isolated by filtration, washed with Et$_2$O (20 mL), and dried in vacuo. Elemental analysis confirmed that this white solid was principally polymeric (*p*-MeC$_6$H$_4$NCO)$_x$. Anal. Calcd for C$_8$H$_7$NO: C, 72.17; H, 5.30; N, 10.52. Found: C, 72.52; H, 6.17; N, 10.39.

Preparation of Cp*W(NC$_6$H$_4$-*p*-Me)$_2$(CH$_2$SiMe$_3$) (2). This complex, like 1 above, was synthesized from Cp*W(O)$_2$(CH$_2$SiMe$_3$) (0.35 g, 0.80 mmol) and *p*-MeC$_6$H$_4$N=C=O (250 μL, ~2.0 mmol), except that the reaction was effected at 125 °C for 20 days. The final reaction solution was taken to dryness to obtain an orange tar, which was extracted with pentane (3 × 20 mL). The combined orange extracts were filtered through Celite (1 × 2 cm), concentrated to ~10 mL in vacuo, and placed in a freezer at −30 °C. After 1 week, orange crystals of 2 and some yellow powder of 1 had formed. The orange crystals were mechanically separated from 1 and were twice recrystallized from pentane. In this manner 107 mg (23% yield) of analytically pure 2 as orange crystals was isolated. The relatively low yield of 2 can be attributed primarily to the difficulty associated with separating 2 from small quantities of 1. Anal. Calcd for C$_{28}$H$_{40}$N$_2$SiW: C, 54.54; H, 6.54; N, 4.54. Found: C, 53.73; H, 6.49; N, 4.39. IR (Nujol mull): $\nu_{\mathrm{Si-Me}}$ 1240 (mw) cm^{-1}; also 2274 (m), 1662 (s), 1501 (s), 1344 (m), 1333 (m), 1297 (vs), 850 (m), 829 (ms), 815 (ms), 800 (mw) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 7.11 (m, 8 H, C$_6$*H*$_4$), 2.26 (s, 6 H, C$_6$H$_4$C*H*$_3$), 1.93 (s, 15 H, C$_5$(C*H*$_3$)$_5$), 0.65 (s, 2 H, J_{WH} = 9.0 Hz, C*H*$_2$), 0.37 (s, 9 H, Si(C*H*$_3$)$_3$). Low-resolution mass spectrum (probe temperature 80 °C): *m/z* 616 (P$^+$), 601 (P$^+$ − Me).

Preparation of Cp*W(NC$_6$H$_4$-*p*-Me)[N(C$_6$H$_4$-*p*-Me)C(O)N(C$_6$H$_4$-*p*-Me)](CH$_2$SiMe$_3$) (3). This complex was also synthesized from Cp*W(O)$_2$(CH$_2$SiMe$_3$) (0.33 g, 0.75 mmol) and *p*-MeC$_6$H$_4$N=C=O (~1.0 mL, ~8.0 mmol), except that the reaction was effected in refluxing toluene (30 mL) under a constant N$_2$ purge for 24 h. The solvent was removed from the final dark red solution under reduced pressure to obtain an orange-red solid, which was triturated with hexanes (10 mL) and washed with Et$_2$O

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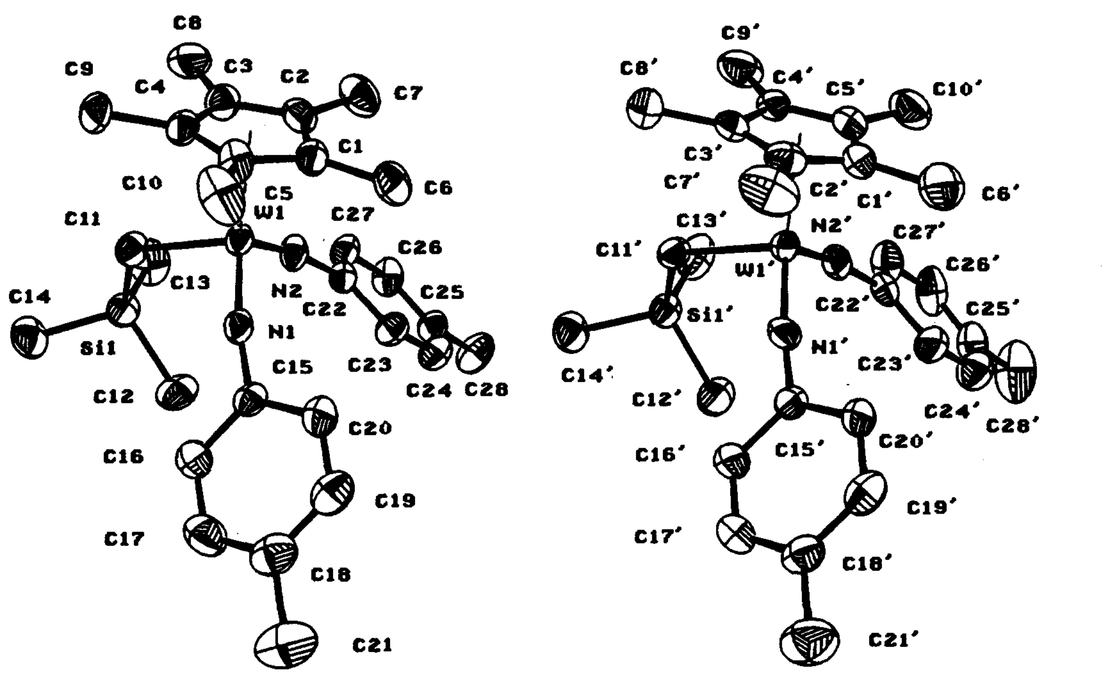

Figure 1. Views of the two crystallographically independent molecules of Cp*W(NC_6H_4-*p*-Me)$_2$(CH_2SiMe_3) (2). For the non-hydrogen atoms, 50% probability ellipsoids are shown.

(5 mL, −20 °C). The orange-red solid was extracted with 2:1 CH_2Cl_2/hexanes (30 mL) and filtered on a column of Celite (3 × 3 cm) supported on a sintered-glass frit. The red filtrate was concentrated in vacuo and placed in a freezer (−35 °C) to induce crystallization. After 1 week, 0.27 g (48% yield) of red crystals of Cp*W(NC_6H_4-*p*-Me)[N(C_6H_4-*p*-Me)C(O)N(C_6H_4-*p*-Me)](CH_2SiMe_3) (3) was isolated by removal of the mother liquor via cannula.

Anal. Calcd for $C_{36}H_{47}N_3OSiW$: C, 57.67; H, 6.32; N, 5.60. Found: C, 57.66; H, 6.29; N, 5.75. IR (KBr pellet): $\nu_{C=O}$ 1663 (s) cm^{-1}; ν_{Si-Me} 1242 (m) cm^{-1}; also 1609 (m), 1504 (s), 1448 (m), 1344 (m), 1300 (vs), 1135 (m), 850 (m), 825 (m), 814 (m), 798 (m) cm^{-1}. IR (CH_2Cl_2): $\nu_{C=O}$ 1653 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 8.07 (d, $^2J_{HH}$ = 8.7 Hz), 7.51 (d, $^2J_{HH}$ = 8.4 Hz), 7.20 (d, $^2J_{HH}$ = 8.1 Hz), 7.08 (d, $^2J_{HH}$ = 8.1 Hz), 6.98 (d, $^2J_{HH}$ = 8.7 Hz), 6.87 (d, $^2J_{HH}$ = 8.4 Hz) (6 × 2 H = 12 H, 3 × $C_6H_4CH_3$), 2.33 (s), 2.28 (s), 2.04 (s) (3 × 3 H = 9 H, 3 × $C_6H_4CH_3$), 1.85 (s, 15 H, $C_5(CH_3)_5$), 1.57 (d, 1 H, $J_{H_a-H_b}$ = 11.4 Hz, CH_aH_b), 0.28 (d, 1 H, $J_{H_a-H_b}$ = 11.4 Hz, CH_aH_b), −0.16 (s, 9 H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 164.80 ($C(O)(NC_6H_4CH_3)_2$), 153.71, 144.11, 142.52 (3 × $N-C_{ipso}$), 137.46, 131.46, 129.03, 128.95, 127.62, 123.51 (C_{meta} and C_{ortho}), 116.99 ($C_5(CH_3)_5$), 40.36 (CH_2SiMe_3, $^1J_{WC}$ = 60.5 Hz), 21.14, 20.84, 20.77 (3 × $C_6H_4CH_3$), 11.47 ($C_5(CH_3)_5$), 3.28 ($Si(CH_3)_3$). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 749 (P^+), 616 (P − [*p*-MeC_6H_4NCO]$^+$).

X-ray Crystallographic Analysis of Cp*W(NC_6H_4-*p*-Me)$_2$(CH_2SiMe_3) (2). An irregular orange crystal of the complex was mounted in a thin-walled glass capillary under N_2 and transferred to a Rigaku AFC6S diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda_{K\alpha}$ = 0.710 69 Å). Final unit-cell parameters for the complex were obtained by a least-squares analysis of setting angles for 25 carefully centered reflections ($11.51 \leq 2\theta \leq 22.82°$). The intensities of three standard reflections were measured every 200 reflections during the data collections. The intensities of the standard reflections showed linear 27.2% decreases with time, and so a linear correction factor was applied to the data to account for this phenomenon. The data were corrected for Lorentz and polarization effects and for absorption using the azimuthal scan method.[19] Pertinent crystallographic and experimental parameters are summarized in Table I.

Interpretation of the Patterson function yielded the coordinates of the heaviest atoms in the structure, and the full structure of the compound was then derived by conventional electron density methods and refined by full-matrix least-squares methods on *F*, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o)^2$. The asymmetric unit contains two independent molecules of 2. Hydrogen atoms were fixed in calculated positions with C–H = 0.98 Å. Final refinements were carried out with non-hydrogen atoms being permitted anisotropic thermal motion. Complex neutral atom scattering factors (for all atoms) and anomalous scattering corrections for the non-hydrogen atoms were taken from ref 20. Final positional and equivalent isotropic thermal parameters for the complex are given in Table II, and selected bond lengths (Å) and bond angles (deg) are listed in Tables III and IV, respectively. A view of the solid-state molecular structure of complex 2 is displayed in Figure 1.

X-ray Crystallographic Analysis of Cp*W(NC_6H_4-*p*-Me)[N(C_6H_4-*p*-Me)C(O)N(C_6H_4-*p*-Me)](CH_2SiMe_3) (3). A crystal of the complex was mounted in a thin-walled glass capillary under N_2 and transferred to an Enraf-Nonius CAD4-F diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda_{K\alpha_1}$ = 0.709 30, $\lambda_{K\alpha_2}$ = 0.713 59 Å). Final unit-cell parameters were obtained by least-squares analysis of 2(sin θ)/λ values for 25 well-centered reflections with $13 \leq \theta \leq 16°$. The intensities of three standard reflections were measured every 1 h of X-ray exposure time during the data collection and showed no appreciable variations in intensity with time. The data were corrected for Lorentz and polarization effects and for absorption using the Gaussian integration method.[21-23] Pertinent crystallographic and experimental parameters are summarized in Table I.

Interpretation of the Patterson function yielded the coordinates of the W and Si atoms, and the full structure was then derived by conventional electron density methods and refined by full-

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[19] TEXSAN/TEXRAY structure analysis package, which includes versions of the following: MITHRIL, integrated direct methods, by C. J. Gilmore; DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least-squares, and ORFFE, functions and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

[20] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

[21] The computer programs used include locally written programs for data processing and locally modified versions of the following: ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier syntheses, by A. Zalkin; ORTEP II, illustrations, by C. K. Johnson.

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Table I. Crystallographic and Experimental Data[a] for the Complexes Cp*W(NC$_6$H$_4$-*p*-Me)$_2$(CH$_2$SiMe$_3$) (2) and $\overline{\text{Cp*W(NC}_6\text{H}_4\text{-}p\text{-Me)[N(C}_6\text{H}_4\text{-}p\text{-Me)C(O)N}}$(C$_6H_4$-*p*-Me)]-(CH$_2$SiMe$_3$) (3)

	2	3
color	orange	red
formula	$C_{28}H_{40}N_2SiW$	$C_{36}H_{47}N_3OSiW$
fw	616.57	749.72
cryst syst	triclinic	monoclinic
space group	*P*1	$P2_1$
a, Å	15.095 (3)	14.5279 (11)
b, Å	18.583 (4)	10.447 (7)
c, Å	10.828 (2)	11.6482 (13)
α, deg	95.01 (2)	90
β, deg	107.01 (2)	105.170 (6)
γ, deg	89.02 (2)	90
V, Å^3	2893 (2)	1706.3 (11)
Z	4	2
d_{calcd}, Mg/m^3	1.415	1.46
F(000)	1240	760
μ(Mo Kα), cm^{-1}	41.33	35.2
T, K	294	294
crystal dimens, mm^3	0.10 × 0.30 × 0.35	0.10 × 0.20 × 0.33
transmissn factors	0.60–1.00	0.49–0.72
scan type	ω–2θ	ω–2θ
scan range, deg	1.05 + 0.35 tan θ	0.65 + 0.35 tan θ
scan speed, deg/min	1.3–16	1.3–10
2θ limits, deg	$0 \le 2\theta \le 50.1$	$0 \le 2\theta \le 55$
data collected	$+h,\pm k,\pm l$	$+h,+k,\pm l$
no. of unique rflns	10171	4118
no. of reflns with $I \ge 3\sigma(I)$	5463	2479
no. of variables	577	178
R_F[b]	0.033	0.058
R_{wF}[c,d]	0.031	0.081
goodness of fit[e]	1.71	2.3
max Δ/σ (final cycle)	0.19	1.3
residual density, e/Å^3	–0.74 to +0.70	–2.3 to +1.7

[a] Conditions: Rigaku AFC6S diffractometer for 2 and Enraf-Nonius CAD4-F diffractometer for 3, Mo Kα radiation, graphite monochromator. [b] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$. [d] $w = 4F_o^2/\sigma^2(F_o^2)$ for 2 and $w = [\sigma^2(F)]^{-1}$ for 3. [e] GOF = $[\sum w(|F_o| - |F_c|)^2/(\text{no. of degrees of freedom})]^{1/2}$. [f] U_{22} of C22; mean Δ/σ = 0.05.

matrix least-squares methods on *F*, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F)]^{-1}$. Refinement of the tungsten and silicon atoms with anisotropic thermal motion and oxygen, nitrogen, and carbon atoms with isotropic thermal parameters gave $R = 0.049$, with some unreasonable interatomic dimensions in the Cp* group and in the two phenyl rings attached to the urea ligand. These features persisted after further refinement, with all non-hydrogen atoms being permitted anisotropic thermal motion. Refinement of the enantiomorphic model (since the space group is chiral) gave the same results. As neither the peaks of residual electron density determined by a difference Fourier synthesis nor the shapes of the thermal ellipsoids of the atoms involved suggested a model for disorder, the three problematic aromatic rings were treated as rigid bodies in further calculations. The nitrogen and ipso carbon of the remaining imido ligand were described by isotropic temperature factors, and all other non-hydrogen atoms were permitted anisotropic thermal motion. Hydrogen atoms were placed in idealized positions, which were recalculated before each cycle. Convergence was reached at $R = 0.058$ and $R_w = 0.081$. Complex neutral atom scattering factors were taken from ref 20. Final positional and equivalent isotropic thermal parameters ($U_{eq} = {}^1/_3$ (trace diagonalized *U*)) for the complex are given in Table V, and selected bond lengths (Å) and bond angles (deg) are listed in Table VI. Views of the solid-state molecular structure of the complex are displayed in Figure 2.

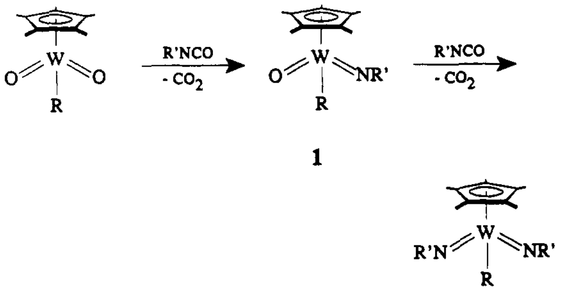
Table II. Final Positional and Equivalent Isotropic Thermal Parameters (Å^2) with Esd's in Parentheses for the Non-Hydrogen Atoms of Complex 2

atom	*x*	*y*	*z*	B_{eq}[a]
W(1)	0.21267 (2)	0.33808 (2)	0.52810 (3)	3.71 (2)
Si (1)	0.3299 (2)	0.2393 (1)	0.7806 (2)	4.9 (1)
N(1)	0.1594 (4)	0.2600 (4)	0.4401 (6)	4.6 (3)
N(2)	0.1572 (4)	0.3626 (4)	0.6480 (6)	4.5 (3)
C(1)	0.1669 (5)	0.4229 (5)	0.3745 (9)	4.6 (4)
C(2)	0.2130 (6)	0.4650 (5)	0.493 (1)	5.1 (4)
C(3)	0.3058 (6)	0.4452 (5)	0.5303 (9)	5.0 (4)
C(4)	0.3203 (6)	0.3948 (5)	0.429 (1)	4.9 (4)
C(5)	0.2371 (6)	0.3824 (5)	0.3341 (8)	4.6 (4)
C(6)	0.0657 (6)	0.4290 (5)	0.2979 (9)	6.2 (5)
C(7)	0.1659 (7)	0.5197 (5)	0.562 (1)	7.0 (5)
C(8)	0.3798 (7)	0.4778 (6)	0.645 (1)	7.9 (6)
C(9)	0.4141 (6)	0.3679 (5)	0.422 (1)	7.7 (6)
C(10)	0.2209 (7)	0.3373 (6)	0.208 (1)	8.1 (6)
C(11)	0.3369 (5)	0.2888 (5)	0.6432 (8)	4.7 (4)
C(12)	0.2181 (6)	0.1896 (5)	0.749 (1)	6.9 (5)
C(13)	0.3462 (7)	0.3037 (6)	0.927 (1)	8.6 (6)
C(14)	0.4243 (7)	0.1712 (5)	0.811 (1)	7.3 (5)
C(15)	0.1037 (5)	0.2022 (5)	0.3662 (8)	4.0 (4)
C(16)	0.1314 (6)	0.1309 (6)	0.379 (1)	5.9 (5)
C(17)	0.0763 (8)	0.0751 (5)	0.304 (1)	6.6 (5)
C(18)	–0.0056 (7)	0.0868 (6)	0.212 (1)	6.1 (5)
C(19)	–0.0330 (6)	0.1567 (7)	0.199 (1)	6.0 (5)
C(20)	0.0195 (6)	0.2135 (5)	0.273 (1)	5.6 (4)
C(21)	–0.0631 (7)	0.0241 (6)	0.127 (1)	8.5 (6)
C(22)	0.0918 (5)	0.3708 (4)	0.7153 (8)	3.8 (4)
C(23)	0.0019 (5)	0.3434 (5)	0.6602 (8)	4.8 (4)
C(24)	–0.0615 (5)	0.3491 (5)	0.7291 (9)	5.2 (4)
C(25)	–0.0407 (6)	0.3824 (5)	0.853 (1)	4.9 (4)
C(26)	0.0467 (6)	0.4109 (5)	0.9048 (8)	5.5 (4)
C(27)	0.1116 (5)	0.4066 (5)	0.8374 (9)	5.1 (4)
C(28)	–0.1105 (6)	0.3863 (6)	0.930 (1)	7.5 (5)
W(1′)	0.70285 (2)	0.16920 (2)	0.49378 (3)	3.87 (2)
Si(1′)	0.7100 (2)	0.2556 (1)	0.2289 (2)	4.8 (1)
N(1′)	0.6815 (4)	0.2499 (3)	0.5810 (6)	4.6 (3)
N(2′)	0.5994 (4)	0.1431 (4)	0.3740 (6)	4.8 (3)
C(1′)	0.7271 (6)	0.0875 (5)	0.654 (1)	5.5 (5)
C(2′)	0.8112 (7)	0.1257 (5)	0.6900 (8)	5.0 (4)
C(3′)	0.8540 (6)	0.1110 (5)	0.593 (1)	4.7 (4)
C(4′)	0.7980 (6)	0.0595 (5)	0.4970 (8)	4.5 (4)
C(5′)	0.7211 (6)	0.0430 (5)	0.536 (1)	5.0 (4)
C(6′)	0.6599 (8)	0.0821 (6)	0.733 (1)	8.9 (7)
C(7′)	0.8467 (8)	0.1737 (6)	0.812 (1)	8.5 (6)
C(8′)	0.9483 (6)	0.1375 (6)	0.596 (1)	8.5 (6)
C(9′)	0.8210 (8)	0.0271 (5)	0.379 (1)	7.9 (6)
C(10′)	0.6452 (7)	–0.0101 (5)	0.469 (1)	7.5 (5)
C(11′)	0.7787 (5)	0.2159 (4)	0.3788 (8)	4.3 (4)
C(12′)	0.6062 (6)	0.3078 (5)	0.245 (1)	6.6 (5)
C(13′)	0.6736 (7)	0.1799 (6)	0.0995 (9)	7.6 (6)
C(14′)	0.7853 (6)	0.3180 (5)	0.175 (1)	6.7 (5)
C(15′)	0.6605 (5)	0.3079 (5)	0.6543 (7)	3.7 (3)
C(16′)	0.6807 (6)	0.3781 (5)	0.6370 (8)	5.0 (4)
C(17′)	0.6635 (6)	0.4354 (5)	0.713 (1)	5.8 (5)
C(18′)	0.6253 (6)	0.4270 (5)	0.8138 (9)	5.3 (4)
C(19′)	0.6047 (6)	0.3575 (6)	0.8298 (9)	5.9 (5)
C(20′)	0.6215 (6)	0.2982 (5)	0.7535 (8)	5.1 (4)
C(21′)	0.6102 (7)	0.4904 (6)	0.904 (1)	8.5 (6)
C(22′)	0.5055 (6)	0.1333 (4)	0.3038 (8)	4.4 (4)
C(23′)	0.4384 (6)	0.1648 (5)	0.355 (1)	5.8 (5)
C(24′)	0.3452 (7)	0.1575 (6)	0.286 (1)	6.7 (5)
C(25′)	0.3182 (7)	0.1206 (6)	0.168 (1)	6.7 (6)
C(26′)	0.3814 (8)	0.0865 (6)	0.116 (1)	7.4 (6)
C(27′)	0.4774 (7)	0.0928 (6)	0.183 (1)	6.6 (5)
C(28′)	0.2144 (8)	0.1131 (9)	0.089 (1)	12.1 (8)

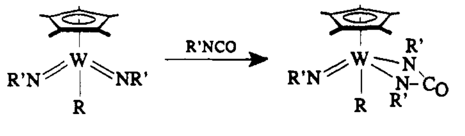
[a] $B_{eq} = {}^8/_3\pi^2\sum\sum U_{ij}a_i a_j(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Results and Discussion

Synthesis and Characterization of Complexes 1–3. Treatment of Cp*W(O)$_2$(CH$_2$SiMe$_3$) with excess *p*-tolyl isocyanate under appropriate experimental conditions leads to the formation of Cp*W(O)(NC$_6$H$_4$-*p*-Me)-(CH$_2$SiMe$_3$) (1), Cp*W(NC$_6$H$_4$-*p*-Me)$_2$(CH$_2$SiMe$_3$) (2), and $\overline{\text{Cp*W(NC}_6\text{H}_4\text{-}p\text{-Me)[N(C}_6\text{H}_4\text{-}p\text{-Me)C(O)N}}$(C$_6H_4$-*p*-Me)]-(CH$_2$SiMe$_3$) (3) (eqs 1 and 2). Each of the complexes 1–3 is derived in a sequential manner from its precursor by incorporation of an additional *p*-tolyl isocyanate fragment or molecule. Effected on a preparative scale, the syntheses



(1)



(2)

2 3

R = CH_2SiMe_3; R' = *p*-tolyl

of 1 and 2 are best conducted in hexanes at elevated temperatures in a heavy-walled glass bomb.[24] The desired organometallic imido (1) and bis(imido) (2) complexes are isolable from aliphatic solvents as an analytically pure yellow powder and orange crystals, respectively. The isolation of 2 is complicated by residual small amounts of 1 which are nearly inseparable from the desired 2.[25] Interestingly, complex 2 does not react further with *p*-tolyl isocyanate in hexanes at elevated temperatures. Although the conversions 1 → 2 (in hexanes) and 1 → 3 and 2 → 3 (in toluene) may be effected by treatment of the appropriate reactant with *p*-tolyl isocyanate, the synthesis giving the highest overall yield of 3 involves reacting $Cp^*W(O)_2(CH_2SiMe_3)$ and *excess* *p*-tolyl isocyanate in refluxing toluene. Under these reaction conditions intermediate complexes 1 and 2 are completely consumed. Compound 3 is much less soluble in common organic solvents than either of its precursors and is isolated as red crystals by crystallization from CH_2Cl_2/hexanes. All three imido complexes 1–3 are air-stable and diamagnetic.

The reaction of $p\text{-}MeC_6H_4N{=}C{=}O$ with $Cp^*W(O)_2(CH_2SiMe_3)$ in C_6D_6 has also been monitored by ^1H NMR spectroscopy. Regardless of the ratio of the reactants used, i.e. 1:1, 2:1, or 3:1, the major product detectable is the ultimate imido species, i.e. complex 3. Under the conditions of the NMR experiments no evidence for the presence of 1 in the reaction mixtures was found, although minor resonances attributable to complex 2 were observable. At present, we do not understand why complex 2, while unreactive toward $p\text{-}MeC_6H_4N{=}C{=}O$ in aliphatic solvents, is so much more reactive toward $p\text{-}MeC_6H_4N{=}C{=}O$ in aromatic solvents.

The physical and spectroscopic properties of the isolable organometallic imido complexes 1–3 (summarized in the Experimental Section) are consistent with their possessing three-legged (1 and 2) and four-legged (3) piano-stool molecular structures. Notable spectroscopic features of these compounds include the following.

(1) The IR spectrum of complex 3 exhibits a strong $\nu_{C=O}$ absorption at 1660 cm^{-1}, and the carbonyl carbon of the ditolyl urea ligand resonates at 164.80 ppm in the $^{13}C\{^1H\}$ NMR spectrum of 3.

(2) The ^1H NMR spectrum of 3 in C_6D_6 exhibits signals reflecting three *p*-tolyl group environments.

(3) The methylene proton signals in the ^1H NMR spectra of the three compounds are particularly diagnostic, being singlets when equivalent (as in the dioxo starting material and 2) and two doublets when diastereotopic (as in 1 and 3).

Table III. Bond Lengths (Å) with Esd's in Parentheses for Complex 2[a]

W(1)–N(1)	1.736 (7)	W(1')–N(1')	1.777 (7)
W(1)–N(2)	1.765 (6)	W(1')–N(2')	1.757 (7)
W(1)–C(1)	2.339 (8)	W(1')–C(1')	2.350 (8)
W(1)–C(2)	2.422 (9)	W(1')–C(2')	2.462 (8)
W(1)–C(3)	2.451 (9)	W(1')–C(3')	2.492 (8)
W(1)–C(4)	2.488 (7)	W(1')–C(4')	2.471 (8)
W(1)–C(5)	2.448 (7)	W(1')–C(5')	2.424 (8)
W(1)–C(11)	2.164 (8)	W(1')–C(11')	2.160 (7)
W(1)–Cp	2.110 (4)	W(1')–Cp'	2.124 (4)
Si(1)–C(11)	1.846 (8)	Si(1')–C(11')	1.859 (8)
N(1)–C(15)	1.41 (1)	N(1')–C(15')	1.370 (9)
N(2)–C(22)	1.388 (8)	N(2')–C(22')	1.41 (1)

[a] Here and elsewhere Cp and Cp' are the unweighted centroids of the pentamethylcyclopentadienyl ligands.

Table IV. Bond Angles (deg) with Esd's in Parentheses for Complex 2

N(1)–W(1)–N(2)	107.8 (3)	N(1')–W(1')–N(2')	108.0 (3)
N(1)–W(1)–C(11)	97.7 (3)	N(1')–W(1')–C(11')	98.4 (3)
N(1)–W(1)–Cp	120.2 (2)	N(1')–W(1')–Cp'	120.3 (2)
N(2)–W(1)–C(11)	100.5 (3)	N(2')–W(1')–C(11')	100.8 (3)
N(2)–W(1)–Cp	117.3 (3)	N(2')–W(1')–Cp	116.6 (3)
C(11)–W(1)–Cp	109.8 (3)	C(11')–W(1')–Cp'	109.3 (2)
C(11)–Si(1)–C(12)	113.5 (4)	C(11')–Si(1')–C(12')	114.8 (4)
C(11)–Si(1)–C(13)	109.3 (5)	C(11')–Si(1')–C(13')	107.3 (4)
C(11)–Si(1)–C(14)	108.1 (4)	C(11')–Si(1')–C(14')	109.8 (4)
C(12)–Si(1)–C(13)	109.0 (5)	C(12')–Si(1')–C(13')	110.0 (5)
C(12)–Si(1)–C(14)	107.4 (5)	C(12')–Si(1')–C(14')	107.5 (4)
C(13)–Si(1)–C(14)	109.5 (5)	C(13')–Si(1')–C(14')	107.2 (4)
W(1)–N(1)–C(15)	171.5 (5)	W(1')–N(1')–C(15')	174.3 (5)
W(1)–N(2)–C(22)	162.9 (6)	W(1')–N(2')–C(22')	163.4 (6)
W(1)–C(11)–Si(1)	118.6 (4)	W(1')–C(11')–Si(1')	117.3 (4)
N(1)–C(15)–C(16)	121.5 (8)	N(1')–C(15')–C(16')	121.7 (7)
N(1)–C(15)–C(20)	121.9 (8)	N(1')–C(15')–C(20')	121.0 (8)
N(2)–C(22)–C(23)	120.6 (8)	N(2')–C(22')–C(23')	119.0 (8)
N(2)–C(22)–C(27)	122.1 (7)	N(2')–C(22')–C(27')	121.9 (8)

Solid-State Molecular Structures of Complexes 2 and 3. Single-crystal X-ray crystallographic analyses of 2 and 3 have been performed to confirm their molecular structures (Figures 1 and 2). Intramolecular metrical parameters of the molecules are collected in Tables III and IV for 2 and Table VI for 3. A crystallographic analysis of complex 1 was deemed to be unnecessary, given that we have previously determined the solid-state molecular structure of CpW(O)(N-*o*-tolyl)(*o*-tolyl),[12] the prototype of this class of imido oxo compounds.

The intramolecular dimensions of the solid-state molecular structure of $Cp^*W(NC_6H_4\text{-}p\text{-}Me)_2(CH_2SiMe_3)$ generally resemble those exhibited by the analogous alkyl dioxo complex $CpW(O)_2(CH_2SiMe_3)$.[28] The tungsten–nitrogen linkages in 2 average 1.76 Å, a distance intermediate between that expected for a linear W≡N—C grouping (1.71 Å)[3] and that for a bent W=N—C link (1.84

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[24] $Cp^*W(O)_2(CH_2SiMe_3)$ and *p*-tolyl isocyanate do not react in hexanes under normal reflux conditions.

[25] It should be noted that a few analogues of complex 2 have been prepared by synthetic methodologies completely different from that used for the synthesis of 2, namely, $CpCr(N\text{-}t\text{-}Bu)_2R$ (R = Me, CH_2CMe_3, CH_2SiMe_3, CH_2CMe_2Ph)[26] and $Cp^*W(NPh)_2Me$.[27]

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[29] Legzdins, P.; Veltheer, J. E. Unpublished observations.

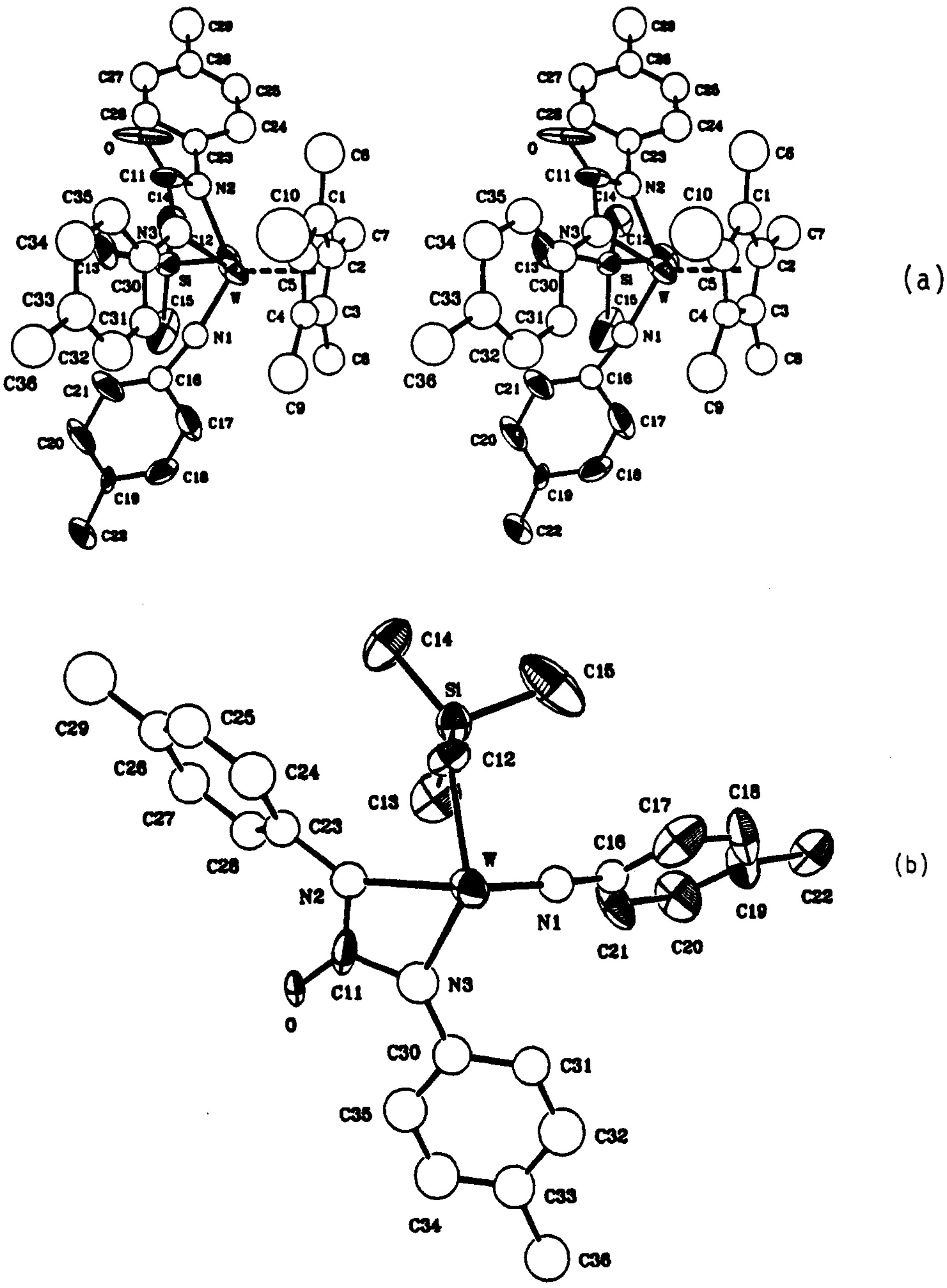

Figure 2. (a) Stereoview of the molecular structure of $Cp^*W(NC_6H_4\text{-}p\text{-}Me)[N(C_6H_4\text{-}p\text{-}Me)C(O)N(C_6H_4\text{-}p\text{-}Me)](CH_2SiMe_3)$ (3). Atoms treated anisotropically are drawn with shaded ellipsoids; those refined isotropically are drawn as open circles; H atoms are omitted for clarity. (b) View of the molecule along the (Cp* centroid)–W vector, with the Cp* ligand and H atoms being omitted for clarity.

Å).[30] Furthermore, the W–N–C angles involving the imido ligands average 168°, a dimension closer to the linear 180° rather than to the bent 120°. The imido ligands in 2 may therefore be providing some extra electron density from nitrogen to tungsten, thereby permitting the metal center in the complex (in a formal oxidation state of +6) to attain the favored 18-valence-electron configuration.[31] Consistently, $Cp^*W(NC_6H_4\text{-}p\text{-}Me)_2(CH_2SiMe_3)$ does not form isolable 1:1 adducts with Lewis bases.[29] Interestingly, complex 2 undergoes further reaction with *p*-tolyl isocyanate to form the imido metallacycle 3 (reaction 2).

The crystal structure study of 3 has revealed that the molecule contains one imido group and a ditolylurea ligand. The W–N1(imido) distance of 1.778 (13) Å is much shorter than the two W–N single bonds (i.e. 2.218 (13) and 2.117 (12) Å) to the ditolylurea ligand. Again, the W–N-(imido) bond length lies between 1.71 and 1.84 Å (vide supra), and the W–N–C bond angle of 171 (4)° is much closer to 180° than to 120°. Hence, in 3 (as in 2) the bond order of the tungsten–imido linkage is probably closer to 3 than to 2, thereby making the imido ligand a formal

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(30) Cotton, F. A.; Shamshoum, E. S. *J. Am. Chem. Soc.* **1984**, *106*, 3222.

(31) Imido groups acting as linear four-electron donors are relatively common.[32] Recent structural results, however, challenge the notion that linearity of an imido ligand necessarily implies donation of the electron pair on nitrogen to the metal.[5a,13a,33] Hence, our simple descriptions of the metal–imido ligand bonding in complexes 2 and 3 presented above must await the results of detailed molecular orbital calculations for confirmation.

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(33) Parkin, G.; van Asselt, A.; Leahy, D. J.; Whinnery, L.; Hua, N. G.; Quan, R. W.; Henling, L. M.; Schaefer, W. P.; Santarsiero, B. D.; Bercaw, J. E. *Inorg. Chem.* **1992**, *31*, 82.

Table V. Final Positional (Fractional; Si, O, N, and C × 10^4; W × 10^5) and Isotropic or Equivalent Isotropic Thermal Parameters ($U \times 10^3$ Å^2) with Esd's in Parentheses for the Non-Hydrogen Atoms of Complex 3

	x	y	z	U_{eq}/U_{iso}
W	77328 (5)	62940	16199 (7)	46
Si	7378 (5)	3738 (7)	3532 (6)	45
O	8143 (13)	3864 (25)	−767 (14)	84
C11	8007 (15)	4470 (23)	32 (23)	45
C12	8107 (14)	5146 (23)	3307 (19)	40
C13	6688 (17)	2939 (28)	2126 (26)	64
C14	8165 (19)	2560 (28)	4470 (27)	72
C15	6469 (30)	4274 (38)	4362 (31)	107
C17	5426 (16)	7140 (29)	2669 (26)	66
C18	4498 (19)	7253 (26)	2797 (26)	63
C19	3751 (12)	6575 (34)	2149 (19)	40
C20	3987 (15)	5768 (29)	1354 (24)	67
C21	4906 (15)	5661 (31)	1181 (21)	65
C22	2762 (14)	6731 (31)	2414 (23)	54
N1	6538 (9)	6406 (37)	1732 (11)	38 (3)
N2	8409 (8)	4520 (12)	1185 (12)	39 (4)
N3	7388 (9)	5515 (15)	−119 (10)	53 (5)
C1	9218 (7)	7306 (12)	1529 (8)	59 (7)
C2	9114 (7)	7508 (11)	2668 (8)	48 (6)
C3	8274 (7)	8189 (11)	2566 (8)	51 (6)
C4	7860 (7)	8406 (12)	1364 (9)	39 (5)
C5	8442 (8)	7861 (14)	723 (8)	52 (7)
C6	10042 (10)	6597 (19)	1217 (13)	85 (9)
C7	9803 (10)	7061 (19)	3829 (10)	71 (8)
C8	7876 (11)	8621 (18)	3595 (10)	59 (8)
C9	6925 (9)	9120 (18)	840 (13)	77 (8)
C10	8263 (12)	7870 (22)	−631 (8)	133 (19)
C16	5620 (10)	6282 (53)	1827 (13)	34 (4)
C23	9058 (6)	3461 (11)	1682 (8)	39 (5)
C24	9903 (8)	3705 (11)	3543 (11)	61 (7)
C25	10516 (7)	2704 (13)	3013 (10)	54 (6)
C26	10284 (7)	1459 (12)	2622 (9)	46 (4)
C27	9440 (8)	1215 (10)	1762 (10)	51 (5)
C28	8826 (7)	2216 (11)	1292 (9)	46 (6)
C29	10964 (10)	350 (14)	3143 (13)	80 (9)
C30	6648 (7)	5889 (10)	−1189 (8)	46 (6)
C31	5931 (8)	6733 (13)	−1098 (8)	43 (5)
C32	5232 (8)	7087 (13)	−2110 (9)	67 (7)
C33	5250 (7)	6597 (12)	−3214 (8)	56 (6)
C34	5967 (9)	5753 (15)	−3305 (8)	63 (8)
C35	6666 (9)	5399 (13)	−2293 (9)	60 (7)
C36	4480 (10)	6987 (18)	−4328 (10)	65 (7)

Table VI. Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses for Complex 3

W–N(1)	1.778 (13)	Si–C(12)	1.87 (2)
W–N(2)	2.218 (13)	O–C(11)	1.18 (3)
W–N(3)	2.117 (12)	N(1)–C(16)	1.37 (2)
W–C(12)	2.24 (2)	N(2)–C(11)	1.32 (3)
W–Cp	2.023 (5)	N(3)–C(11)	1.40 (3)
N(1)–W–N(2)	124.8 (13)	W–N(2)–C(23)	144.6 (9)
N(1)–W–N(3)	96.0 (7)	C(11)–N(2)–C(23)	116.1 (14)
N(1)–W–C(12)	89.3 (9)	W–N(3)–C(11)	101.4 (12)
N(1)–W–Cp	121.7 (12)	W–N(3)–C(30)	130.3 (9)
N(2)–W–N(3)	57.9 (5)	C(11)–N(3)–C(13)	128.2 (14)
N(2)–W–C(12)	74.5 (7)	O–C(11)–N(2)	135 (2)
N(2)–W–Cp	113.4 (4)	O–C(11)–N(3)	124 (2)
N(3)–W–C(12)	125.1 (7)	N(2)–C(11)–N(3)	101.4 (18)
N(3)–W–Cp	112.3 (4)	W–C(12)–Si	121.8 (10)
C(12)–W–Cp	110.6 (6)	N(1)–C(16)–C(17)	112 (3)
W–N(1)–C(16)	171 (4)	N(1)–C(16)–C(21)	131 (3)
W–N(2)–C(11)	99.2 (12)		

four-electron donor to the metal center.[31]

The four-membered ditolylurea chelate ring is slightly folded (the maximum torsion angle being 3.8 (15)°), and the tolyl rings are rotated out of the urea plane by 46 and 12°. The other molecular dimensions of 3 (Table VI) are generally not far from expected values. Complex 3 is another example of a still-rare class of organometallic urea complexes. To our knowledge, it is only the second molecule of this type to be formed by trapping of a metal–imido linkage with an isocyanate molecule. The other example is (η^6-*p*-cymene)$\overline{\mathrm{OsN}(t\text{-Bu})\mathrm{C(O)N}}$(*t*-Bu), which has been characterized by Bergman's group.[5g]

Concluding Considerations. As implied by eqs 1 and 2, the isolated complex 1 can be converted to either 2 or 3 and complex 2 can be converted to 3 under appropriate experimental conditions. Interestingly, the reaction of 1 with *p*-MeC$_6$H$_4$N=C=O gives 2 and not the oxo analogue of 3, namely Cp*$\overline{\mathrm{W(O)[N(C_6H_4\text{-}}p\mathrm{\text{-}Me)C(O)N}}$(C$_6H_4$-*p*-Me)](CH$_2$SiMe$_3$), which remains unknown. Reaction 2 also implies that complex 2 is still sufficiently nucleophilic at nitrogen to react with *p*-MeC$_6$H$_4$N=C=O to give complex 3. Finally, the inertness of complex 3 to *p*-MeC$_6$H$_4$N=C=O can be explained on steric grounds. From the molecular structure of 3 (Figure 2), it is clear that formation of a bis(ditolylurea) complex would lead to extreme steric congestion at the metal center. However, it is also possible that the inertness of 3 is a manifestation of the stronger metal–nitrogen bond to the lone imido ligand.

The conversions of W=O bonds to W=NR linkages effected during this work are reminiscent of the related W=O to W=S transformations performed by Faller and his group.[34] While the individual synthetic steps that yield complexes 1–3 are not unique, the overall transformation of a dioxo complex to an imido urea complex in three discrete chemical reactions has not been previously documented. In addition, the trapping of a metal–nitrogen multiple bond with an isocyanate molecule (reaction 2) is still a relatively rare chemical process. The characteristic chemical properties of the product complexes 1–3 remain to be determined. A particularly interesting prospect is the possibility that 3 may be induced to expel CO under appropriate conditions and form the imido analogue of the well-known oxo peroxo complex Cp*W(O)(O$_2$)(CH$_2$SiMe$_3$).[10] Such a complex may well serve as an imido transfer reagent since the peroxo complex is known to transfer an oxo ligand to organic substrates.[35]

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen parameters, all bond distances and angles, torsion angles, intermolecular distances involving the non-hydrogen atoms, intramolecular distances involving the hydrogen atoms, and least-squares planes and deviations therefrom for complex 2 and tables of anisotropic thermal parameters, hydrogen parameters, all bond distances and angles, and torsion angles and a packing diagram for complex 3 (25 pages). Ordering information is given on any current masthead page.

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