

β -CD, or the diminished value of k_- from β -CD in the presence of surfactants. For Py, the stabilization by hydrophobic interaction with the β -CD-surfactant complex can be considerably larger than that of the β -CD-surfactant complex with N which is less hydrophobic than Py. Therefore, the degree of "fitting" of the cavity of CD with N is more important in order to form a complex.

Surfactant in the N- β -CD system caused a disruption of excimer formation. For instance, Hamai^{4a} observed excimer emission in the system containing 5.8×10^{-5} M N and 1×10^{-3} M $<[\beta\text{-CD}] < 1 \times 10^{-2}$ M. However, the excimer emission was undetected with the condition: $[\text{N}] = 1-2 \times 10^{-4}$ M and 6×10^{-4} M $\leq [\beta\text{-CH}] \leq 1.37 \times 10^{-2}$ M in the presence of 20 mM of C_4^- ,

C_6^- , and $\text{C}_8\text{SO}_4^- \text{Na}^+$. This can also be attributed to the space-filling effect of surfactants in the CD cavity, preventing the further aggregation of N-CD complexes.

Consequently, different features were observed for the effects of surfactants with guest-CD systems depending on the size and hydrophobicity of the guest molecules.

Acknowledgment. The authors thank the National Science Foundation for support of this work via Grant No. CHE82-01226. We are grateful to Dr. I. Nakamura for his assistance in experiments and for stimulating discussions.

Registry No. Py, 129-00-0; N, 91-20-3; β -CD, 7585-39-9.

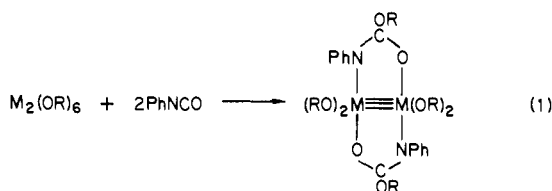
Mechanistic Insight into the Reaction of Phenyl Isocyanate with Ditungsten Hexa-*tert*-butoxide: Isolation and Characterization of Early Intermediates

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Abstract: By working at low temperature (-80 to -45 °C) the purple crystalline compound $\text{W}_2(\text{OCMe}_3)_6(\mu\text{-PhNCO})$ (**1**), which is known to be a precursor in the preparation of $\text{W}_2(\text{OCMe}_3)_4[\mu\text{-PhNC}(\text{OCMe}_3)\text{O}]_2$ (**2**) from $\text{W}_2(\text{OCMe}_3)_6$ and PhNCO, has been isolated and its structure determined. The molecule consists of a $(\text{RO})_3\text{W}=\text{W}(\text{OR})_3$ ($\text{R} = \textit{tert}$ -butyl) moiety ($\text{W}-\text{W} = 2.488$ (1) Å) bridged by the PhNCO molecule and the structure is quite similar to that of $\text{W}_2(\text{OR})_6(\mu\text{-tolylNCNtolyl})$ recently reported by us. Compound **1** will react with additional PhNCO at temperatures above -15 °C to give **2**. It has also been found that **1** reacts with PMe_3 to give $\text{W}_2(\text{OR})_5(\text{PMe}_3)[\mu\text{-PhNC}(\text{OR})\text{O}]$ (**3**), which has also been structurally characterized. The molecule contains a $(\text{RO})_3\text{W}=\text{W}(\text{OR})_2\text{PMe}_3$ moiety bridged by the bidentate $\text{PhNC}(\text{OR})\text{O}^-$ ligand. Crystallographic data for the two compounds are as follows. **1**: $P2_1/c$; $a = 11.054$ (6) Å, $b = 17.821$ (7) Å, $c = 19.401$ (8) Å, $\beta = 100.52$ (2)°; $V = 3758$ (2) Å³, $Z = 4$. **3**: $P\bar{1}$; $a = 10.2916$ (6) Å, $b = 21.1376$ (7) Å, $c = 22.0929$ (6) Å, $\alpha = 117.04$ (1)°, $\beta = 90.33$ (4)°, $\gamma = 93.73$ (4)°; $V = 4268.2$ (3) Å³, $Z = 4$. Mechanistic pathways for the formation of **2** are discussed critically in the light of the new structural information.

Dimolybdenum and ditungsten hexaalkoxides are known to react readily with phenyl isocyanate. Chisholm and co-workers found that $\text{Mo}_2(\text{O-}i\text{-Pr})_6$ reacts in the presence of pyridine to give $\text{cis-Mo}_2(\text{O-}i\text{-Pr})_4[\mu\text{-PhNC}(\text{O-}i\text{-Pr})\text{O}]_2$ and in our laboratory we found that $\text{W}_2(\text{OCMe}_3)_6$ reacts to give $\textit{trans-W}_2(\text{OCMe}_3)_4[\mu\text{-PhNC}(\text{OCMe}_3)\text{O}]_2$. Both of these reactions as well as the full characterization of both products by spectroscopic data and X-ray crystallography have recently been reported in a joint publication.¹ Although the stereochemistry of the two products differs, the type of reaction is otherwise the same in each case, as shown schematically in eq 1. The key transformation, which takes place



twice, is the migratory insertion of PhNCO into an M-OR bond to form the anion of a carbamate ester which takes up a bidentate bridging posture with respect to the triply bonded M_2 core.

In the case of the $\text{W}_2(\text{OCMe}_3)_6$ reaction the observation that at least one intermediate was stable in solution at low temperature

encouraged us to attempt to determine, at least in part, how the overall transformation represented by eq 1 takes place. We have been able to gain direct insight into at least one and perhaps two of the first steps and we report those results here.

Experimental Section

Ditungsten hexa-*tert*-butoxide, $\text{W}_2(\text{OCMe}_3)_6$, was prepared² by Na/Hg reduction of WCl_6 in THF at -10 °C in the presence of LiOCMe_3 , followed by recrystallization from hexane at -10 °C. All reactions were done under an argon atmosphere.

Preparation of $\text{W}_2(\text{OCMe}_3)_6(\mu\text{-C}_6\text{H}_5\text{NCO})$. A weighed amount of $\text{W}_2(\text{OCMe}_3)_6$ (400 mg, 0.5 mmol) was dissolved in a 20 mL of toluene. The solution was cooled to -79 °C. At this temperature 0.2 mL (1.6 mmol) of phenyl isocyanate was added to the solution by using a syringe. The solution began to turn from red to purple. After 1 h, the reaction mixture (totally purple) was allowed to warm up to -45 °C where it was stirred for 2 h. The solution was then filtered into a precooled (-45 °C) storage tube. Crystals of **1** were obtained by removing the solvent slowly under vacuum (5×10^{-3} torr; -45 °C for 8 h) in 80-90% yield based on tungsten.

Preparation of $\text{W}_2(\text{OCMe}_3)_5(\text{PMe}_3)[\mu\text{-(C}_6\text{H}_5\text{)NC(O)OCMe}_3]$ (3**).** A weighed amount (ca. 100 mg, 0.11 mmol) of $\text{W}_2(\text{OCMe}_3)_6(\mu\text{-C}_6\text{H}_5\text{NCO})$ (**1**) was dissolved in 10 mL of toluene at -79 °C. Trimethylphosphine, 0.1 mL (1.6 mmol), was added at this temperature. No color change was observed. After 2 h of stirring at -79 °C there was still no color change, and the solution was allowed to warm up over a period of 2 h to room temperature where it was then stirred for 2 h. The color

(1) Chisholm, M. H.; Cotton, F. A.; Folting, K.; Huffman, J. C.; Ratermann, A. R.; Shamsoum, E. S. *Inorg. Chem.* **1984**, *23*, 4423.

(2) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

Table I

| formula | W ₂ (OCMe ₃) ₆ ^c (μ-OCNC ₆ H ₅) (1) | W ₂ O ₇ ·NPC ₃₄ H ₆₈ (3) |
|--|--|--|
| formula wt | 925.52 | 1001.60 |
| space group | P2 ₁ /c | P1 |
| a, Å | 11.054 (6) | 10.2916 (6) |
| b, Å | 17.821 (7) | 21.1376 (7) |
| c, Å | 19.401 (8) | 22.0929 (6) |
| α, deg | | 117.04 (1) |
| β, deg | 100.52 (2) | 90.33 (4) |
| γ, deg | | 93.73 (4) |
| V, Å ³ | 3758 (2) | 4268.2 (3) |
| Z | 4 | 4 |
| d _{calcd} , g/cm ³ | 1.636 | 1.661 |
| cryst size, mm | 0.3 × 0.25 × 0.3 | 0.2 × 0.25 × 0.35 |
| μ(Mo Kα), cm ⁻¹ | 62.89 | 55.782 |
| data collectn instrument | CAD-4 | CAD-4 |
| radiatn (monochromated in incident beam) | Mo Kα | Mo Kα |
| orientation reflns, no., range (2θ) | 5° ≤ 2θ ≤ 14° | 25, 16° ≤ 2θ ≤ 31° |
| temp. °C | -108 | 25 ± 1 |
| scan method | ω-2θ | ω-2θ |
| data collectn range, 2θ, deg | 0 ≤ 2θ ≤ 45 | 4-45 |
| no. unique data, total with F _o ² > 3σ(F _o ²) | 5857, 3808 | 7439, 3115 |
| no. of params refined | 360 | 391 |
| trans. factors, max, min | 100%, 70% | 100%, 68% |
| R ^a | 0.0614 | 0.076 |
| R _w ^b | 0.0734 | 0.086 |
| quality-of-fit indicator ^c | 1.726 | 1.838 |
| largest shift/esd, final cycle | 0.18 | 0.01 |
| largest peak, e/Å ³ | 1.2 | 2.5 |

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obsd}} - N_{\text{parameters}})]^{1/2}$.

of the solution had begun changing from purple to brown-yellow when the temperature reached 0–5 °C. The solution was then filtered into a storage tube, and yellow-brown crystals were obtained after 2–3 days of cooling at -10 °C. These crystals are extremely air and moisture sensitive and also appear to be temperature sensitive.

X-ray Crystallographic Procedures. The structures of single crystals containing **1** and **3** were determined by applying the general procedure that we have already described elsewhere.³ The crystal parameters and basic information pertaining to data collection and structure refinement for both compounds are summarized in Table I.

Compound 1. A purple needle was mounted in a Lindemann glass capillary and all geometric and intensity data were collected from this crystal on a CAD-4 diffractometer at -104 °C. Unit cell dimensions and the crystal orientation were derived from setting angles of 25 reflections in the range 5° < 2θ < 14° by least-squares refinement. During 45.4 h of exposure time three standard reflections that were checked every hour showed no loss of intensity. Semiempirical absorption corrections were made based on the results of azimuthal scans of nine reflections with Eulerian angle χ near 90°. Systematic absences unambiguously indicated the space group P2₁/c. The positions of the tungsten atoms were obtained by a combination of Patterson and direct methods and the remaining atoms were located and refined in an alternating series of least-squares cycles and difference maps. Of the 41 atoms refined, 39 behaved well with anisotropic thermal vibration parameters. Two atoms, O(5) and C(51), which are in the same *tert*-butoxy group, were poorly resolved and the peaks chosen and treated isotropically are associated with additional low-density peaks (0.75–0.97 e/Å³). We did not see any well-defined disorder scheme and therefore left matters in this way. There were also two weak residual peaks (ca. 1.1 e/Å³) near each tungsten atom in the final difference map. In the final cycle no parameter shifted by more than 0.2σ.

Compound 3. This extremely air-sensitive and perhaps X-ray and heat-sensitive compound proved very difficult to deal with. Initial attempts to obtain data on crystals wedged in capillaries and protected with epoxy cement or mineral oil failed because of rapid decay. Finally, a crystal immersed in degassed stopcock grease wedged in a Lindemann glass capillary survived long enough (67% isotropic loss of intensity over

Table II. Positional Parameters and Their Estimated Standard Deviations for W₂(OCMe₃)₆(μ-PhNCO)

| atom | x | y | z | B(A2) ^a |
|-------|-------------|--------------|--------------|----------------------|
| W1 | 0.10221 (7) | -0.02280 (4) | -0.22013 (4) | 1.66 (1) |
| W2 | 0.28943 (7) | -0.06606 (4) | -0.26289 (4) | 1.64 (1) |
| O(1) | 0.428 (1) | -0.0136 (7) | -0.2132 (7) | 2.6 (3) |
| O(2) | 0.208 (1) | -0.1244 (6) | -0.3417 (6) | 2.0 (3) |
| O(3) | 0.338 (1) | -0.1519 (6) | -0.2101 (6) | 2.1 (3) |
| O(4) | -0.044 (1) | -0.0341 (7) | -0.2841 (6) | 2.4 (3) |
| O(5) | 0.065 (1) | -0.1011 (7) | -0.1648 (6) | 1.9 (2) ^b |
| O(6) | 0.182 (1) | 0.0390 (6) | -0.1445 (6) | 2.2 (3) |
| O(10) | 0.110 (1) | 0.0827 (6) | -0.2834 (7) | 2.5 (3) |
| N(1) | 0.271 (2) | 0.0272 (9) | -0.3340 (7) | 2.6 (4) |
| C(1) | 0.183 (2) | 0.039 (1) | 0.2965 (9) | 1.6 (3) ^b |
| C(4) | 0.311 (2) | 0.072 (1) | -0.384 (1) | 2.7 (4) |
| C(5) | 0.233 (2) | 0.137 (1) | -0.409 (1) | 3.7 (5) |
| C(6) | 0.271 (2) | 0.181 (1) | -0.463 (1) | 4.2 (6) |
| C(7) | 0.377 (2) | 0.160 (1) | -0.491 (1) | 3.9 (6) |
| C(8) | 0.446 (2) | 0.099 (1) | -0.464 (1) | 4.1 (5) |
| C(9) | 0.413 (2) | 0.052 (1) | -0.410 (1) | 2.9 (4) |
| C(11) | 0.495 (2) | 0.051 (1) | -0.183 (1) | 2.8 (5) |
| C(12) | 0.623 (2) | 0.054 (1) | -0.207 (1) | 4.8 (6) |
| C(13) | 0.420 (2) | 0.122 (1) | -0.205 (1) | 3.6 (5) |
| C(14) | 0.510 (2) | 0.042 (1) | -0.102 (1) | 4.2 (6) |
| C(21) | 0.259 (2) | -0.171 (1) | -0.390 (1) | 2.9 (5) |
| C(22) | 0.199 (2) | -0.250 (1) | -0.386 (1) | 4.7 (6) |
| C(23) | 0.221 (2) | -0.136 (1) | -0.463 (1) | 3.9 (6) |
| C(24) | 0.399 (2) | -0.179 (1) | -0.368 (1) | 4.2 (5) |
| C(31) | 0.412 (2) | -0.192 (1) | -0.154 (1) | 3.0 (5) |
| C(32) | 0.394 (2) | -0.158 (1) | -0.087 (1) | 4.1 (6) |
| C(33) | 0.374 (2) | -0.275 (1) | -0.160 (1) | 3.6 (5) |
| C(34) | 0.549 (2) | -0.183 (1) | -0.166 (1) | 3.8 (5) |
| C(41) | -0.125 (2) | -0.020 (1) | -0.350 (1) | 3.4 (5) |
| C(42) | -0.172 (2) | 0.063 (1) | -0.351 (1) | 3.8 (5) |
| C(43) | -0.056 (2) | -0.035 (1) | -0.410 (1) | 4.9 (6) |
| C(44) | -0.234 (2) | -0.071 (1) | -0.352 (1) | 5.0 (6) |
| C(51) | 0.002 (2) | -0.172 (1) | -0.162 (1) | 2.7 (4) |
| C(52) | 0.014 (2) | -0.219 (1) | -0.228 (1) | 3.7 (5) |
| C(53) | -0.135 (2) | -0.148 (1) | -0.168 (1) | 4.1 (5) |
| C(54) | 0.047 (2) | -0.210 (1) | -0.094 (1) | 4.1 (5) |
| C(61) | 0.117 (2) | 0.076 (1) | -0.093 (1) | 3.3 (5) |
| C(62) | -0.021 (2) | 0.077 (1) | -0.118 (1) | 3.5 (5) |
| C(63) | 0.165 (2) | 0.157 (1) | -0.088 (1) | 6.7 (6) |
| C(64) | 0.153 (2) | 0.032 (2) | -0.027 (1) | 6.5 (8) |

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$. ^b Refined isotropically.

100.0 h of exposure to the X-ray beam) to provide a useful data set. As all further attempts to obtain greater (or even comparable) survival of crystals failed, this data set was corrected for decay and used. Twenty five reflections in the range 16° < 2θ < 31° were used to determine crystal orientation and unit cell dimensions and azimuthal scans of nine reflections with χ near 90° were used to make absorption corrections. The crystals were found to be triclinic and space group P1 was assumed. The positions of four independent tungsten atoms were found by direct methods and the other atoms were located and refined by alternating difference maps and cycles of least-squares refinement. The four tungsten and two phosphorus atoms were refined anisotropically, while the remaining 90 atoms were refined isotropically; in the final cycle no parameter changed by more than 0.01σ.

The combined effects of decomposition and poor crystal quality reduced the number of high angle data and hence the overall quality of the structure. However, no particular atom was especially badly behaved and the only significant residual peaks after the refinement had converged were in the immediate vicinity of the tungsten atoms. The dimensions of the two crystallographically independent molecules agree well.

Tables of structure factors for both compounds are available as supplementary material.

Tables II and III list the atomic coordinates for **1** and **3**, respectively, while Tables IV and V give important bond distances and angles for the two structures. Complete tables of anisotropic thermal parameters and structure factor data are available as supplementary material. Figures 1–4 show the structures and atom numbering schemes.

Other Physical Measurements. ¹H NMR spectra of a slightly impure sample of **1** were obtained at -50, -10, and 20 °C on a VARIAN XL-200 PFT spectrometer in toluene-*d*₈. The spectrum remained the same at all three temperatures. The observed chemical shifts (in parts per million relative to internal Me₄Si) are as follows: -50 °C. 1.486 (s),

Table III. Positional Parameters and Their Estimated Standard Deviations for $W_2(OCMe_3)_6[\mu-N(C_6H_5)C(O)OCMe_3]PMe_3$

| atom | x | y | z | B(A ²) ^a | atom | x | y | z | B(A ²) ^a |
|-------|------------|------------|------------|---------------------------------|-------|------------|-----------|-----------|---------------------------------|
| W1 | 0.8508 (2) | 0.1312 (1) | 0.2300 (1) | 2.42 (6) | C(33) | 0.498 (7) | 0.813 (3) | 0.691 (3) | 7 (2) ^b |
| W2 | 0.8537 (2) | 0.2299 (1) | 0.2071 (1) | 2.55 (6) | C(34) | 0.293 (6) | 0.761 (3) | 0.597 (3) | 7 (2) ^b |
| W3 | 0.3334 (2) | 0.6501 (1) | 0.2671 (1) | 2.84 (6) | C(36) | 0.129 (6) | 0.580 (2) | 0.138 (2) | 5 (1) ^b |
| W4 | 0.3548 (2) | 0.7695 (1) | 0.2850 (1) | 2.84 (6) | C(37) | 0.081 (6) | 0.499 (3) | 0.110 (3) | 6 (2) ^b |
| P(1) | 0.069 (2) | 0.0920 (7) | 0.1781 (7) | 5.2 (5) | C(38) | 0.212 (6) | 0.591 (3) | 0.085 (3) | 7 (2) ^b |
| P(2) | 0.536 (2) | 0.6650 (7) | 0.3389 (7) | 4.9 (5) | C(39) | -0.012 (7) | 0.374 (3) | 0.836 (3) | 8 (2) ^b |
| O(1) | -0.008 (3) | 0.283 (1) | 0.296 (1) | 4.3 (8) ^b | C(41) | 0.279 (6) | 0.024 (2) | 0.858 (2) | 5 (1) ^b |
| O(2) | 0.089 (3) | 0.295 (1) | 0.396 (1) | 3.3 (8) ^b | C(42) | 0.427 (6) | 0.023 (3) | 0.858 (3) | 7 (2) ^b |
| O(3) | 0.279 (3) | 0.866 (1) | 0.705 (1) | 3.7 (8) ^b | C(43) | 0.221 (6) | 0.032 (3) | 0.800 (3) | 6 (2) ^b |
| O(4) | 0.235 (3) | 0.948 (1) | 0.850 (1) | 3.9 (8) ^b | C(44) | 0.229 (6) | 0.077 (2) | 0.933 (2) | 5 (1) ^b |
| O(5) | 0.279 (3) | 0.712 (1) | 0.726 (1) | 2.9 (7) ^b | C(46) | 0.174 (6) | 0.589 (2) | 0.355 (2) | 5 (1) ^b |
| O(6) | 0.011 (3) | 0.232 (1) | 0.156 (1) | 3.1 (7) ^b | C(47) | 0.197 (7) | 0.612 (3) | 0.431 (3) | 8 (2) ^b |
| O(7) | 0.264 (3) | 0.786 (1) | 0.866 (1) | 2.5 (7) ^b | C(48) | 0.226 (5) | 0.521 (2) | 0.303 (2) | 4 (1) ^b |
| O(11) | 0.492 (3) | 0.735 (1) | 0.200 (1) | 2.6 (7) ^b | C(49) | 0.019 (8) | 0.596 (3) | 0.345 (3) | 10 (2) ^b |
| O(12) | 0.414 (3) | 0.352 (1) | 0.886 (1) | 4.6 (9) ^b | C(51) | 0.318 (5) | 0.648 (2) | 0.715 (2) | 4 (1) ^b |
| O(31) | 0.198 (3) | 0.596 (2) | 0.194 (1) | 4.6 (9) ^b | C(52) | 0.332 (6) | 0.614 (3) | 0.635 (3) | 7 (2) ^b |
| O(41) | 0.239 (3) | 0.651 (1) | 0.344 (1) | 4.0 (8) ^b | C(53) | 0.439 (7) | 0.669 (3) | 0.754 (3) | 8 (2) ^b |
| O(51) | 0.247 (3) | 0.763 (1) | 0.215 (1) | 3.7 (8) ^b | C(54) | 0.226 (5) | 0.602 (2) | 0.734 (2) | 5 (1) ^b |
| O(61) | 0.475 (3) | 0.190 (1) | 0.656 (1) | 4.3 (8) ^b | C(56) | 0.204 (6) | 0.814 (2) | 0.199 (2) | 5 (1) ^b |
| O(71) | 0.235 (4) | 0.830 (2) | 0.355 (1) | 5.4 (9) ^b | C(57) | 0.078 (6) | 0.861 (3) | 0.231 (3) | 7 (2) ^b |
| N(1) | 0.017 (4) | 0.815 (2) | 0.685 (2) | 4 (1) ^b | C(58) | 0.325 (7) | 0.879 (3) | 0.209 (3) | 8 (2) ^b |
| N(2) | 0.515 (4) | 0.380 (2) | 0.811 (2) | 4 (1) ^b | C(59) | 0.167 (6) | 0.774 (3) | 0.117 (3) | 8 (2) ^b |
| C(1) | 0.019 (5) | 0.251 (2) | 0.328 (2) | 3 (1) ^b | C(61) | 0.067 (6) | 0.276 (2) | 0.129 (2) | 5 (1) ^b |
| C(2) | 0.035 (5) | 0.151 (2) | 0.348 (2) | 4 (1) ^b | C(62) | 0.110 (7) | 0.346 (3) | 0.185 (3) | 9 (2) ^b |
| C(3) | 0.955 (5) | 0.098 (2) | 0.353 (2) | 3 (1) ^b | C(63) | 0.962 (8) | 0.280 (4) | 0.082 (4) | 12 (3) ^b |
| C(4) | -0.018 (6) | 0.937 (3) | 0.614 (2) | 6 (2) ^b | C(64) | 0.184 (8) | 0.243 (4) | 0.088 (4) | 12 (3) ^b |
| C(5) | 0.146 (6) | 0.071 (3) | 0.413 (3) | 7 (2) ^b | C(66) | 0.417 (5) | 0.108 (2) | 0.627 (2) | 4 (1) ^b |
| C(6) | 0.221 (5) | 0.126 (2) | 0.403 (2) | 4 (1) ^b | C(67) | 0.475 (8) | 0.939 (3) | 0.400 (3) | 10 (2) ^b |
| C(7) | 0.166 (6) | 0.169 (2) | 0.376 (2) | 5 (1) ^b | C(68) | 0.351 (7) | 0.109 (3) | 0.687 (3) | 8 (2) ^b |
| C(11) | 0.050 (6) | 0.059 (2) | 0.082 (2) | 5 (1) ^b | C(69) | 0.323 (7) | 0.114 (3) | 0.568 (3) | 9 (2) ^b |
| C(12) | 0.141 (5) | 0.019 (2) | 0.181 (2) | 4 (1) ^b | C(71) | 0.355 (6) | 0.829 (2) | 0.922 (2) | 5 (1) ^b |
| C(13) | 0.222 (7) | 0.166 (3) | 0.206 (3) | 9 (2) ^b | C(72) | 0.459 (6) | 0.864 (3) | 0.893 (2) | 6 (2) ^b |
| C(16) | 0.302 (6) | 0.305 (3) | 0.682 (2) | 6 (2) ^b | C(73) | 0.271 (6) | 0.901 (2) | 0.970 (2) | 5 (1) ^b |
| C(17) | 0.471 (6) | 0.274 (3) | 0.569 (2) | 6 (2) ^b | C(74) | 0.405 (5) | 0.796 (2) | 0.958 (2) | 4 (1) ^b |
| C(18) | 0.425 (7) | 0.415 (3) | 0.660 (3) | 8 (2) ^b | C(76) | 0.137 (6) | 0.833 (2) | 0.406 (2) | 5 (1) ^b |
| C(21) | 0.148 (5) | 0.367 (2) | 0.413 (2) | 4 (1) ^b | C(77) | 0.017 (6) | 0.787 (3) | 0.358 (3) | 7 (2) ^b |
| C(22) | 0.210 (6) | 0.375 (3) | 0.483 (3) | 7 (2) ^b | C(78) | 0.100 (6) | 0.913 (3) | 0.435 (3) | 7 (2) ^b |
| C(23) | 0.036 (5) | 0.417 (2) | 0.425 (2) | 5 (1) ^b | C(79) | 0.220 (6) | 0.817 (3) | 0.458 (2) | 5 (1) ^b |
| C(24) | 0.245 (6) | 0.368 (3) | 0.361 (2) | 6 (2) ^b | C(91) | 0.477 (5) | 0.328 (2) | 0.826 (2) | 3 (1) ^b |
| C(26) | 0.362 (6) | 0.310 (3) | 0.912 (3) | 6 (2) ^b | C(92) | 0.523 (5) | 0.547 (2) | 0.162 (2) | 4 (1) ^b |
| C(27) | 0.258 (6) | 0.246 (2) | 0.862 (2) | 5 (1) ^b | C(93) | 0.337 (7) | 0.459 (3) | 0.847 (3) | 8 (2) ^b |
| C(28) | 0.472 (7) | 0.283 (3) | 0.939 (3) | 8 (2) ^b | C(94) | 0.292 (6) | 0.525 (3) | 0.872 (3) | 7 (2) ^b |
| C(29) | 0.293 (6) | 0.365 (2) | 0.975 (2) | 5 (1) ^b | C(95) | 0.385 (6) | 0.584 (2) | 0.880 (2) | 5 (1) ^b |
| C(31) | 0.370 (5) | 0.830 (2) | 0.651 (2) | 4 (1) ^b | C(96) | 0.517 (6) | 0.571 (2) | 0.868 (2) | 5 (1) ^b |
| C(32) | 0.405 (6) | 0.886 (2) | 0.627 (2) | 5 (1) ^b | C(97) | 0.441 (6) | 0.494 (2) | 0.157 (2) | 5 (1) ^b |

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$. ^b Refined isotropically.

1.569 (s), 1.699 (s), 1.737 (s) with ratio 2:2:1:1; -10 °C, 1.455 (s), 1.535 (s), 1.687 (s), 1.703 (s) with ratio 2:2:1:1; +20 °C, 1.436 (s), 1.515 (s), 1.681 (s), 1.701 (s) with ratio 2:2:1:1. There is also an impurity peak at 1.036 (s) which we attribute to $LiOCMe_3$.

Infrared spectra of **1** were recorded on a Perkin-Elmer 783 Infrared spectrophotometer in KBr pellets. The following principal peaks were found: 2980 (s), 2955 (w), 1680 (m), 1590 (m), 1475 (m), 1375 (w), 1355 (m), 1310 (m), 1230 (m), 1165 (s), 1020 (w), 1000 (m), 960 (s), 932 (m), 917 (w), 860 (w), 770 (w), 750 (m), 690 (w) cm^{-1} .

Results

Structures. The molecular structure of compound **1** is shown in its entirety in Figure 1. Important bond lengths and angles are listed in Table IV. The entire molecule is the crystallographic asymmetric unit and has no imposed symmetry. Indeed, it has no approximate symmetry either. Given its general constitution, the only symmetry it could have would be provided by a mirror plane containing the CNCO chain of the isocyanate ligand and two metal atoms, but there are considerable deviations from that. For one thing the two ends of the molecule are not eclipsed; there is a twist about the W-W axis. Further, the pairs of W-W-O angles that would be related by such a mirror plane are decidedly unequal. Thus, we have $W(1)-W(2)-O(1) = 108.7 (3)^\circ$ while $W(1)-W(2)-O(2) = 97.7 (3)^\circ$ and $W(2)-W(1)-O(4) = 114.8 (3)^\circ$ while $W(2)-W(1)-O(6) = 98.1 (3)^\circ$. The structure of the important central region of the molecule is highlighted in Figure 2.

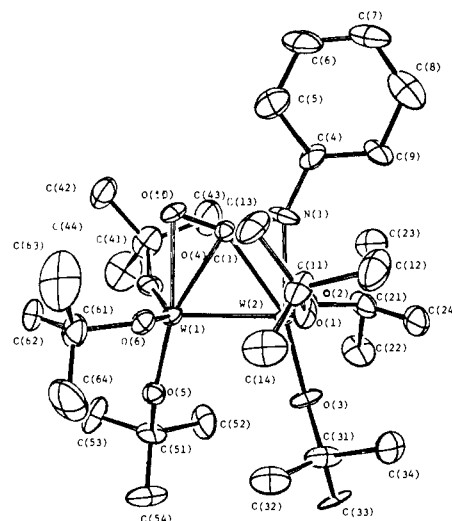


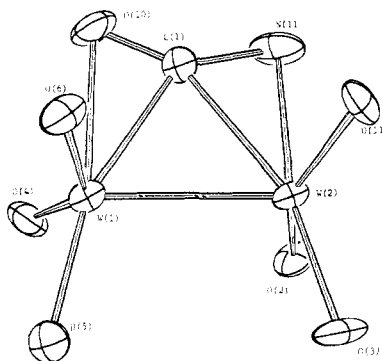
Figure 1. ORTEP drawing of the entire $W_2(OCMe_3)_6(\mu-PhNCO)$ molecule, giving the atomic labeling scheme. All atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

The structure of **1** does bear striking resemblance to those of the several $W_2(OCMe_3)_6(\mu-RNCNR)$ molecules whose structures

Table IV. Selected Bond Distances and Angles for the $W_2(OCMe_3)_6(\mu\text{-PhNCO})$ Molecule

| Bond Distances, Å | | | |
|-------------------|-----------|------------|-----------|
| W(1)-W(2) | 2.488 (1) | O(6)-C(61) | 1.48 (2) |
| W(1)-O(4) | 1.861 (9) | W(2)-O(1) | 1.898 (9) |
| W(1)-O(5) | 1.851 (9) | W(2)-O(2) | 1.932 (9) |
| W(1)-O(6) | 1.914 (9) | W(2)-O(3) | 1.864 (9) |
| W(1)-O(10) | 2.255 (9) | W(2)-N(1) | 2.15 (1) |
| W(1)-C(1) | 2.17 (1) | W(2)-C(1) | 2.24 (1) |
| O(1)-C(11) | 1.44 (2) | O(10)-C(1) | 1.19 (2) |
| O(2)-C(21) | 1.44 (2) | N(1)-C(1) | 1.33 (2) |
| O(3)-C(31) | 1.43 (2) | O(10)-N(1) | 2.40 (2) |
| O(5)-C(51) | 1.45 (2) | N(1)-C(4) | 1.39 (2) |

| Bond Angles, deg | | | |
|------------------|-----------|-----------------|-----------|
| W(1)-W(2)-O(1) | 108.7 (3) | N(1)-W(2)-C(1) | 35.1 (5) |
| W(1)-W(2)-O(2) | 97.7 (3) | W(1)-C(1)-W(2) | 68.6 (4) |
| W(1)-W(2)-O(3) | 104.1 (3) | O(10)-C(1)-N(1) | 145.0 (1) |
| W(1)-W(2)-N(1) | 89.2 (4) | O(4)-W(1)-O(5) | 92.8 (4) |
| W(1)-W(2)-C(1) | 54.3 (4) | O(4)-W(1)-O(6) | 142.6 (4) |
| W(2)-W(1)-O(4) | 114.8 (3) | O(4)-W(1)-O(10) | 80.9 (4) |
| W(2)-W(1)-O(5) | 104.2 (3) | O(4)-W(1)-C(1) | 91.0 (5) |
| W(2)-W(1)-O(6) | 98.1 (3) | O(5)-W(1)-O(6) | 96.2 (4) |
| W(2)-W(1)-O(10) | 87.8 (3) | O(5)-W(1)-O(10) | 168.0 (4) |
| W(2)-W(1)-C(1) | 57.1 (4) | O(5)-W(1)-C(1) | 160.5 (5) |
| O(1)-W(2)-O(2) | 152.1 (4) | O(6)-W(1)-O(10) | 83.1 (4) |
| O(1)-W(2)-O(3) | 90.1 (4) | O(6)-W(1)-C(1) | 92.4 (5) |
| O(1)-W(2)-N(1) | 85.4 (5) | O(10)-W(1)-C(1) | 31.0 (4) |
| O(1)-W(2)-C(1) | 93.8 (5) | W(1)-O(4)-C(41) | 153.0 (1) |
| O(2)-W(2)-O(3) | 92.3 (4) | W(1)-O(5)-C(51) | 146.5 (9) |
| O(2)-W(2)-N(1) | 86.1 (4) | W(1)-O(6)-C(61) | 124.0 (9) |
| O(2)-W(2)-C(1) | 94.3 (4) | W(2)-O(1)-C(11) | 155.6 (9) |
| O(3)-W(2)-N(1) | 166.7 (4) | W(2)-O(2)-C(21) | 130.0 (9) |
| O(3)-W(2)-C(1) | 158.1 (5) | W(2)-O(3)-C(31) | 153.5 (9) |

**Figure 2.** View of the central part of the $W_2(OCMe_3)_6(\mu\text{-PhNCO})$ molecule emphasizing the way in which the ligand atoms bonded directly to the tungsten atoms are arranged.

we have determined.^{4,5} The placement of the $\mu\text{-RNCO}$ and $\mu\text{-RNCNR}$ ligands relative to the $W_2(OCMe_3)_6$ moieties is essentially the same and the corresponding internuclear distances do not differ significantly. Thus for $W_2(OCMe_3)_6[\mu\text{-}(p\text{-tolyl})\text{-NCN}(p\text{-tolyl})]$ (**4**) we have $W-W = 2.482(1)$ Å and in **1** we have $W-W = 2.488(1)$ Å. In **4** the $W-C$ distances (where C is the central atom of the carbodiimide ligand) are 2.20 (2) and 2.21 (2) Å, while in **1** they differ somewhat, viz., 2.17 (1) and 2.24 (1) Å, because of the unsymmetrical nature of the PhNCO ligand, but have about the same average value. In **4** the $W-N$ bond lengths are 2.12 (1) and 2.14 (1) Å, while that in **1** is 2.15 (1) Å.

From the great similarity in the structures of **1** and **4** it is clear that whatever description of the bonding is valid for **4** should also pertain, with only slight quantitative differences, to **1**. It has previously been suggested⁴ that **4** can be considered to contain

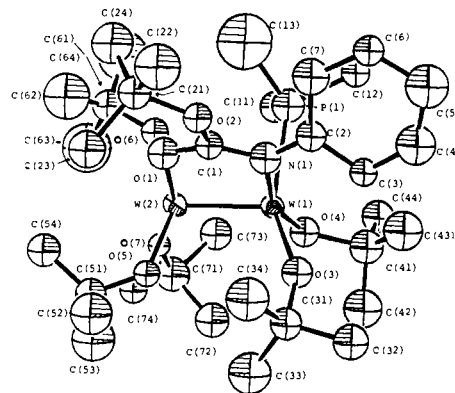
(4) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics* **1985**, *4*, 461.

(5) In addition to the $(p\text{-tolyl})\text{NCN}(p\text{-tolyl})$, compound described in ref 4, the similar molecules containing $(c\text{-C}_6\text{H}_{11})\text{NCN}(c\text{-C}_6\text{H}_{11})$ and $(i\text{-C}_3\text{H}_7)\text{NCN}(i\text{-C}_3\text{H}_7)$ have also been prepared and fully characterized (Cotton, F. A.; Shamshoum, E. S. *Polyhedron*, in press).

Table V. Important Bond Distances and Angles for the $W_2(OCMe_3)_3PMe_3[\mu\text{-PhNC}(OCMe_3)O]$ Molecules

| molecule a | | molecule b | |
|-------------------|-----------|-------------|-----------|
| Bond Distances, Å | | | |
| W(1)-W(2) | 2.358 (2) | W(3)-W(4) | 2.364 (2) |
| W(1)-P(1) | 2.54 (1) | W(3)-P(2) | 2.53 (1) |
| W(1)-O(3) | 1.94 (3) | W(3)-O(31) | 1.98 (3) |
| W(1)-O(4) | 1.95 (2) | W(3)-O(41) | 1.96 (2) |
| W(1)-N(1) | 2.11 (3) | W(3)-N(2) | 2.24 (3) |
| W(2)-O(1) | 2.21 (3) | W(4)-O(11) | 2.23 (2) |
| W(2)-O(5) | 2.04 (2) | W(4)-O(51) | 1.85 (3) |
| W(2)-O(6) | 1.99 (2) | W(4)-O(61) | 2.07 (3) |
| W(2)-O(7) | 1.90 (2) | W(4)-O(71) | 1.99 (3) |
| O(1)-C(1) | 1.22 (4) | O(11)-C(91) | 1.27 (4) |
| N(1)-C(1) | 1.32 (4) | O(11)-N(2) | 2.33 (4) |
| O(1)-N(1) | 2.30 (4) | N(2)-C(91) | 1.31 (4) |
| O(2)-C(1) | 1.51 (4) | O(12)-C(91) | 1.36 (4) |
| P(1)-C(11) | 1.92 (4) | P(2)-C(16) | 1.87 (5) |
| P(1)-C(12) | 1.78 (4) | P(2)-C(17) | 1.85 (4) |
| P(1)-C(13) | 2.02 (5) | P(2)-C(18) | 1.77 (5) |
| O(3)-C(31) | 1.47 (4) | O(31)-C(36) | 1.32 (4) |
| O(4)-C(41) | 1.56 (4) | O(41)-C(46) | 1.56 (4) |
| O(5)-C(51) | 1.36 (4) | O(51)-C(56) | 1.37 (5) |
| O(6)-C(61) | 1.41 (4) | O(61)-C(66) | 1.62 (4) |
| O(7)-C(71) | 1.45 (4) | O(71)-C(76) | 1.51 (5) |
| N(1)-C(2) | 1.36 (5) | N(2)-C(92) | 1.45 (5) |
| O(2)-C(21) | 1.49 (4) | O(12)-C(26) | 1.34 (5) |

| Bond Angles, deg | | | |
|------------------|-----------|-------------------|-----------|
| W(2)-W(1)-P(1) | 94.6 (3) | W(4)-W(3)-P(2) | 93.3 (3) |
| W(2)-W(1)-O(3) | 112.9 (7) | W(4)-W(3)-O(31) | 108.9 (8) |
| W(2)-W(1)-O(4) | 105.5 (7) | W(4)-W(3)-O(41) | 106.1 (7) |
| W(2)-W(1)-N(1) | 92.7 (9) | W(4)-W(3)-N(2) | 91.1 (8) |
| W(1)-W(2)-O(1) | 85.7 (7) | W(3)-W(4)-O(11) | 87.8 (6) |
| W(1)-W(2)-O(5) | 99.9 (7) | W(3)-W(4)-O(51) | 100.5 (7) |
| W(1)-W(2)-O(6) | 109.8 (7) | W(3)-W(4)-O(61) | 103.3 (7) |
| W(1)-W(2)-O(7) | 112.2 (6) | W(3)-W(4)-O(71) | 111.9 (8) |
| P(1)-W(1)-O(3) | 149.0 (8) | P(2)-W(3)-O(31) | 155.3 (8) |
| P(1)-W(1)-O(4) | 88.7 (8) | P(2)-W(3)-O(41) | 84.9 (8) |
| P(1)-W(1)-N(1) | 77.6 (9) | P(2)-W(3)-N(2) | 79.0 (8) |
| O(3)-W(1)-O(4) | 97.0 (1) | O(31)-W(3)-O(41) | 99.0 (1) |
| O(3)-W(1)-N(1) | 87.0 (1) | O(31)-W(3)-N(2) | 90.0 (1) |
| O(4)-W(1)-N(1) | 158.0 (1) | O(41)-W(3)-N(2) | 157.0 (1) |
| O(1)-W(2)-O(5) | 84.0 (9) | O(11)-W(4)-O(51) | 79.0 (1) |
| O(1)-W(2)-O(6) | 82.6 (9) | O(11)-W(4)-O(61) | 82.8 (9) |
| O(1)-W(2)-O(7) | 162.0 (1) | O(11)-W(4)-O(71) | 160.0 (1) |
| O(5)-W(2)-O(6) | 146.2 (9) | O(51)-W(4)-O(61) | 149.0 (1) |
| O(5)-W(2)-O(7) | 90.0 (1) | O(51)-W(4)-O(71) | 92.0 (1) |
| O(6)-W(2)-O(7) | 93.6 (9) | O(61)-W(4)-O(71) | 97.0 (1) |
| O(1)-C(1)-N(1) | 129.0 (4) | O(11)-C(91)-N(2) | 129.0 (4) |
| O(1)-C(1)-O(2) | 116.0 (3) | O(11)-C(91)-O(12) | 117.0 (4) |
| O(2)-C(1)-N(1) | 114.0 (3) | O(12)-C(91)-N(2) | 113.0 (4) |

**Figure 3.** Molecule a in the crystal of $W_2(OCMe_3)_3PMe_3[\mu\text{-PhNC}(OCMe)O]$ (**3**) showing the numbering scheme.

a $W=W$ double bond with the μ ligand attached through two $W-N$ single bonds and a three-center, two-electron bridge bond encompassing the $W-C-W$ group. That some sort of picture, with one $W-N$ bond replaced by a $W-O$ bond, seems appropriate here in compound **1**.

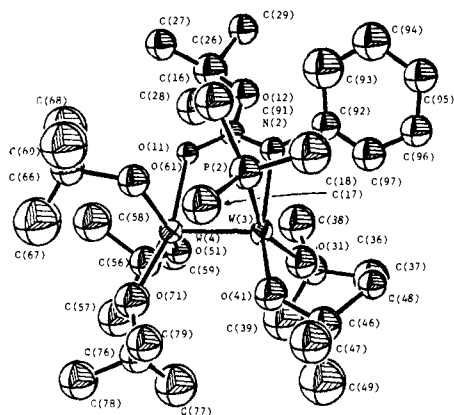
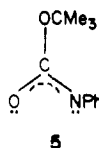


Figure 4. Molecule b in the crystal of $W_2(OCMe_3)_5PMe_3[\mu-PhNC(OCMe_3)O]$ (**3**) showing the numbering scheme.

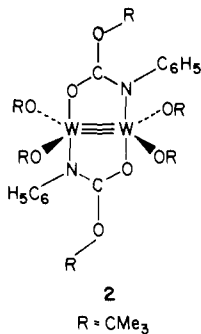
For compound **3** there are two independent molecules (a and b) in the asymmetric unit and these are depicted in Figures 3 and 4. Each of the two crystallographically distinct molecules occurs in enantiomeric pairs related by crystallographic inversion centers. Figure 3 shows a molecule that happens to be the approximate mirror image of the b molecule shown in Figure 4. There are no chemically significant differences between the a and b molecules, as emphasized by the parallel columns of corresponding molecular dimensions in Table V.

As explained in the Experimental Section, the unavoidably poor quality of the intensity data coupled with the large number of atoms in the asymmetric unit leads to results that are considerably less accurate than one ordinarily expects in contemporary crystallography of this type. It is very likely that even those differences between corresponding bond lengths and angles that are as high as 4σ , or occasionally 5σ , are probably not to be taken seriously. There can be no doubt about the overall molecular structure in a qualitative sense, nor are the most important dimensions such as W–W and W–P bond lengths in any significant doubt.

Compound **3** contains one bridging carbamate ester anion, **5**,



formed by migratory insertion of the PhNCO molecule into a W–OCMe₃ bond. This is the same type of ligand that is formed (and retained) twice when $W_2(OCMe_3)_6$ reacts with 2 mol of PhNCO to form **2**. The dimensions of this ligand in the molecules of **3** agree within experimental error with those previously found in **2**.



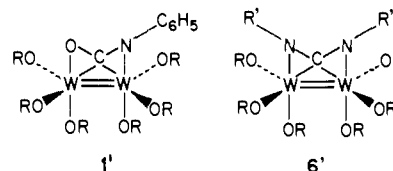
2
R = CMe₃

Discussion

The purpose of this study was to see if something definite could be learned about the steps by which $W_2(OCMe_3)_4[\mu-PhNC(OCMe_3)O]_2$ (**2**) is formed by reaction of 1 mol of $W_2(OR)_6$ with 2 mol of PhNCO, eq 1, with R = CMe₃ and M = W. The possibility of obtaining some such information was suggested to us by our earlier observation that when 2 mol of PhNCO were

added to 1 mol of $W_2(OCMe_3)_6$ at low temperature there was a fairly prompt color change from red to purple, but that further reaction leading to the final product **2** did not occur until the temperature was raised above $-15^\circ C$. We therefore attempted to isolate the purple intermediate by crystallization at low temperature and, happily, we were able to do this and, further, to determine its identity and structure by X-ray crystallography.

The purple intermediate is, apparently, the molecule that makes up crystalline compound **1**. It is an approximately side-on adduct of PhNCO with $W_2(OCMe_3)_6$ and is very similar to the side-on adducts, **6**, formed between various carbodiimides^{4,5} and $W_2(OCMe_3)_6$, as shown by the schematic drawings **1'** and **6'**. The

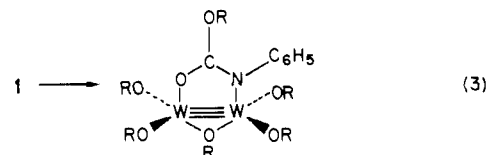


interaction between the RNCO or RNCNR molecule and the tungsten atoms is an extensive one and appears to be best understood, in a formal sense, as resulting from an opening of one of the W–W π bonds followed by interaction with a biradical form of the new ligand, viz., RNCO or RNCNR, so that a total of three electron pairs become engaged in attaching RNCO or RNCNR to the ditungsten core.⁴

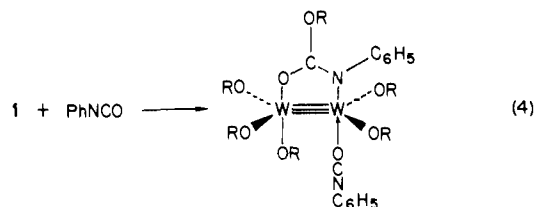
Species of types **1'** and **6'** are as different in reactivity as they are similar in structure. As already reported⁴ and confirmed by additional work,⁵ an adduct of type **6'** at least with the R' groups so far used, namely, *p*-tolyl, cyclohexyl, and isopropyl, is a dead end. These adducts are quite stable molecules that have not been made to undergo any further useful reaction. In the case of a molecule of the **1'** type, specifically compound **1**, where R' = Ph and R = CMe₃, further reactions will occur readily unless the temperature is kept low ($<-15^\circ C$). In the presence of at least one further mole of PhNCO we get reaction 2 proceeding essentially to completion.



There are a number of possible pathways for process 2 and visually at least we have no indication that any distinct stages occur. In other words, all steps in the process form a rapid cascade and we can only speculate as to what sequence may actually occur. An obvious question in attempting to suggest a reasonable sequence is whether the next step is a unimolecular migratory insertion, (3), where the postulate of a bridging OR group is purely spec-



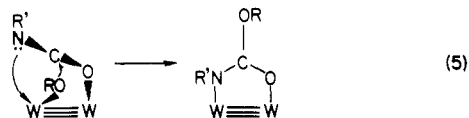
ulative, or whether a second PhNCO molecule must attack **1** and induce the migratory insertion, as indicated in (4).



We have obtained some evidence favoring step 4, the nucleophile-induced migratory insertion, by treating **1** with the nucleophile PMe_3 . When **1** is treated with PMe_3 in toluene at low temperature it fails to react, just as it fails to react with excess PhNCO. Again, however, on warming up, there is a reaction to give a yellow-brown solution from which yellow-brown crystals of a very delicate compound, **3**, were obtained. This compound is found to be the type of product shown in process 4, namely,

one in which both the μ -PhNC(O CMe_3)O ligand and the PMe_3 ligand are coordinated.

We thus feel reasonably secure in proposing that the overall process represented in eq 1 begins with the formation of 1 followed by eq 4. Beyond this we are again reduced to sheer speculation, but it does not seem unlikely that a simple unimolecular rearrangement, as represented schematically by (5), might be the way



in which the process is completed. It is possible, though perhaps unlikely, that further mechanistic information may be obtained about these reactions and some additional experiments are to be

carried out. We believe, however, that our present understanding is reasonably sound and that a report giving the results now in hand may be of value to others investigating the chemistry of metal-metal multiple bonds.

Acknowledgment. We thank the National Science Foundation for support and Dr. Larry Falvello for his valuable advice in crystallography.

Registry No. 1, 96791-13-8; 2, 93110-45-3; 3, 96760-84-8; $\text{W}_2(\text{OCMe}_3)_6$, 57125-20-9; PhNCO, 103-71-9; PMe_3 , 594-09-2.

Supplementary Material Available: Table of observed and calculated structure factors, anisotropic thermal parameters, and bond lengths and angles and a more detailed account of the crystallographic work (52 pages). Ordering information is given on any current masthead page.

Unusual Configuration and Low Iron-Uptake Ability of Isomugineic Acid Produced from Chlorotic Gramineous Plants

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Abstract: The two-dimensional $^{13}\text{C}/^1\text{H}$ NMR and CD data showed that isomugineic acid is the isomer of mugineic acid, (2*S*,2'*S*,3'*S*,3''*S*)-*N*-[3-carboxyl-3-[(3-carboxy-3-hydroxypropyl)amino]-2-hydroxypropyl]azetidino-2-carboxylic acid, with respect to the configuration at the 3'-carbon position. The ESR *g* tensors and reduction potential of the isomugineic acid-Fe(III) complex were clearly different from those of the corresponding mugineic acid and 2'-deoxymugineic acid complexes, but they were remarkably close to those of the 2'-deoxy-3'-decarboxylmugineic acid-Fe(III) complex. The present results revealed that the 3'-carboxyl group of isomugineic acid does not participate in the metal binding and that the ^{59}Fe -uptake activity of isomugineic acid is significantly lower than that of normal mugineic acid.

The biochemistry of iron transport is becoming an extremely popular subject. Although microorganisms are often in danger of iron starvation, the mechanism of siderophore-mediated iron uptake has now been elucidated and indeed many different siderophores have been identified from microorganisms.^{2,3} The general feature of all siderophores is that they are capable of forming a "molecular cage" at the center of which ferric ion is held as part of a six-coordinate, octahedral complex. On the other hand, certain plants also excrete phytosiderophores such as mugineic acid in order to absorb and utilize iron in soil.⁴ It is well-known that iron-sufficient (green) plants often become chlorotic. Heavy metals and arsenate induce iron stress and cause iron chlorosis which turns the young leaves to yellow or white.⁵ As a result, the plants cease to grow and eventually they wither up. For the purpose of effective incorporation of iron in soil, gramineous plants such as barley, wheat, and oats have been found to excrete novel amino acids from their roots.⁴ Mugineic acid, (2*S*,2'*S*,3'*S*,3''*S*)-*N*-[3-carboxyl-3-[(3-carboxy-3-hydroxypropyl)amino]-2-hydroxypropyl]azetidino-2-carboxylic acid, is a typical phytosiderophore isolated from the water-cultured barley of *Hordeum vulgare* L. var. Minorimugi, and in fact this chelator

significantly stimulates ^{59}Fe uptake in the rice root.⁶

Herein, we found that the ligand configuration and metal complexation of isomugineic acid (1) obtained from growth-depressed barley are clearly different from those of normal mugineic acid (2). Of special interest is the fact that isomugineic acid showed lower biological activity for iron uptake than mugineic acid. The structure of mugineic acids is given in Table I.

Experimental Sections

The isolation of mugineic acid from chlorotic barley was performed according to the procedure reported previously for the isolation of mugineic acid.^{4,7} When barley plants expanded their second and third leaves, they were transported to iron-deficient solution and then the culture was continued for 1 week or more. After strong development of the yellowing of the leaves, the root washings were collected by the soaking of the root in deionized water once a day for 2 weeks. The root washings were first chromatographed on an Amberlite IR-120 B(H^+ form). For the separation of isomugineic acid and mugineic acid, the technique of gradient elution with ammonia-formate buffer (pH 2.5-3.1) on a Dowex 50W \times 4 resin was suitable. Isomugineic acid was eluted with the buffer of pH 2.6-2.7 and mugineic acid with the buffer of pH 2.8-2.9. After the gel filtration (Sephadex G-10) of the former fractions containing the iron-chelating activity which was determined by the *o*-phenanthroline method, amorphous powder of isomugineic acid was obtained. The gel filtration of the latter fractions yielded mugineic acid as crystals.

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