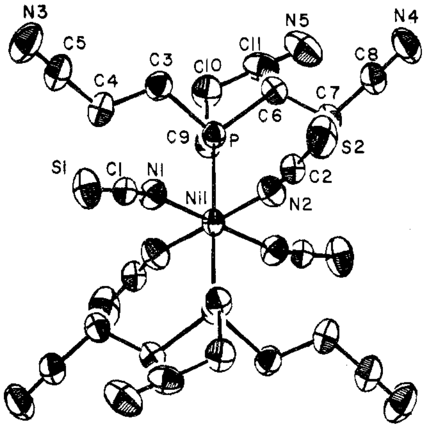

Figure 2. Molecular structure of the $\{Ni[NCS]_4[P(CH_2CH_2CN)_3]_2\}^{2-}$ ion.

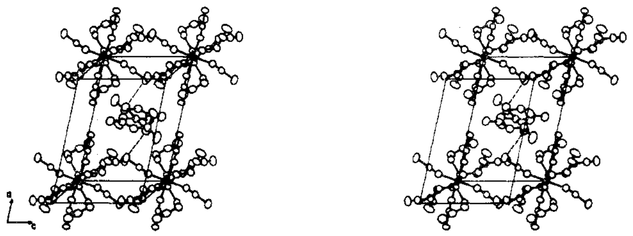

Figure 3. A stereoscopic view of the unit cell contents.

hydrogen bonding to S2 (vide infra), the reason for these distortions is obscure. There are no unusually short inter- or intramolecular contacts to the thiocyanate groups. It appears (Figure 2) that the distortions are consistent with a complex conformation of relatively low energy. It has been demonstrated that large variations in bond angles may arise in closely related conformers of transition-metal complexes.[12] In any event, the M–N–C angles are within the range of reported values (140–180°).[13]

Crystal Structure. The crystal structure (Figure 3) consists of discrete anions and cations, with a weak hydrogen bond (dotted line in Figure 3, S2⋯HO2–O2). The S–O distance is 3.41 Å and the S2–HO2–O2 angle is 166.6°. There are no other short or significant contacts ≤3.8 Å. It has been demonstrated that $M(NCS)_n$ compounds, where M is a first-row transition metal and $n = 4$–6, are stabilized by large cations of preferably equal but opposite charge.[13] It seems likely here that the anion–cation effect is mutual.

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Registry No. $[Ni(diacetone\ alcohol)_2][Ni(NCS)_4(CEP)_2]$, 68122-36-1; $Ni(NCS)_2$, 13689-92-4; acetone, 67-64-1.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (Table VI) (12 pages). Ordering information is given on any current masthead page.

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Reactions of Metal-to-Metal Multiple Bonds. 5.[1] Addition of Nitric Oxide to Hexa-*tert*-butoxyditungsten. Preparation, Properties, and Structural Characterization of Tri-*tert*-butoxy(nitrosyl)(pyridine)tungsten

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The reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and nitric oxide (2 equiv) in hydrocarbon solvents yields an insoluble pale yellow product of empirical formula $W(O\text{-}t\text{-}Bu)_3NO$ (ν(NO) 1565 cm^{-1}). Addition of the nitrogen donor ligands NH_3, NMe_3, and pyridine causes the above compound to dissolve with the formation of mononuclear compounds $W(O\text{-}t\text{-}Bu)_3(NO)(L)$. The yellow crystalline compound $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$ (ν(NO) 1555 cm^{-1}) has been obtained directly by the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and NO (2 equiv) in pyridine as the solvent. The compound crystallizes in the space group $P2_1/n$ with $Z = 4$ and unit cell dimensions a = 9.694 (2) Å, b = 15.686 (3) Å, c = 14.358(2) Å, β = 97.40 (1)°, and V = 2165.1 (7) $Å^3$. The coordination geometry of the WO_3N_2 moiety is a slightly distorted trigonal bipyramid with the axial positions occupied by the nitrogen atoms of the nitrosyl and pyridine ligands. The tungsten atom is displaced 0.34 Å toward the nitrosyl ligand from the equatorial plane of the three alkoxy oxygen atoms. There is a linear W–N–O moiety with a short W–N bond distance, 1.732 (8) Å, whereas the W–N bond distance to the coordinated pyridine is long, 2.323 (7) Å.

Introduction

Previously we have shown that the molybdenum-to-molybdenum triple bond in the dinuclear alkoxides $Mo_2(OR)_6$[3] is cleaved as in reaction 1[4] where R = Me_3C, Me_2CH, and Me_3CCH_2.

$$(RO)_3Mo{\equiv}Mo(OR)_3 + 2NO \rightarrow [Mo(OR)_3(NO)]_2 \qquad (1)$$

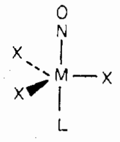
Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	0.05941 (4)	0.23082 (3)	0.08295 (2)	2.90 (1)	3.59 (2)	2.80 (1)	−0.09 (1)	0.56 (1)	0.45 (1)
O1	−0.0626 (6)	0.1482 (4)	0.0250 (4)	3.9 (3)	4.4 (3)	3.3 (3)	−0.4 (3)	−0.5 (2)	0.4 (3)
O2	0.2467 (6)	0.1974 (4)	0.1196 (4)	3.2 (3)	4.8 (3)	3.5 (3)	−0.0 (2)	0.9 (2)	0.7 (2)
O3	−0.0194 (6)	0.3097 (4)	0.1602 (4)	4.1 (3)	3.6 (3)	3.8 (3)	0.0 (3)	1.3 (2)	0.7 (2)
O4	0.0918 (8)	0.3428 (5)	−0.0806 (5)	7.0 (4)	5.7 (4)	4.5 (3)	0.6 (3)	2.1 (3)	2.6 (3)
N1	0.0779 (8)	0.2964 (5)	−0.0117 (5)	4.0 (3)	4.5 (4)	4.1 (4)	0.4 (3)	1.0 (3)	1.1 (3)
N2	0.0280 (7)	0.1486 (5)	0.2131 (5)	2.8 (3)	4.1 (3)	3.1 (3)	−0.3 (3)	0.7 (3)	0.1 (3)
C1	−0.1302 (11)	0.1312 (7)	−0.0713 (7)	5.4 (5)	4.9 (5)	3.0 (4)	−0.1 (4)	−0.8 (4)	−0.6 (4)
C2	−0.0146 (13)	0.1150 (9)	−0.1326 (8)	8.0 (7)	8.8 (7)	3.3 (5)	1.5 (6)	−0.3 (5)	−1.7 (5)
C3	−0.2176 (13)	0.2086 (7)	−0.1062 (9)	6.3 (6)	4.9 (6)	6.7 (6)	0.8 (5)	−0.7 (5)	1.2 (5)
C4	−0.2203 (13)	0.0515 (8)	−0.0594 (9)	7.1 (7)	6.0 (6)	6.5 (6)	−2.6 (5)	−2.1 (6)	0.2 (5)
C5	0.3771 (10)	0.2141 (7)	0.0837 (8)	3.2 (4)	6.5 (7)	5.4 (5)	−0.3 (4)	1.4 (4)	0.3 (5)
C6	0.4030 (12)	0.3098 (9)	0.0875 (9)	6.2 (6)	6.8 (6)	8.5 (7)	−2.7 (5)	2.5 (5)	−1.0 (6)
C7	0.3682 (11)	0.1819 (9)	−0.0177 (7)	5.2 (5)	9.0 (7)	4.1 (5)	−0.2 (6)	1.9 (4)	−1.5 (5)
C8	0.4869 (11)	0.1626 (10)	0.1500 (9)	3.1 (5)	12 (1)	6.0 (6)	1.0 (6)	0.1 (5)	1.0 (7)
C9	−0.0600 (10)	0.3984 (6)	0.1535 (7)	4.2 (4)	3.4 (4)	4.4 (4)	−0.0 (4)	1.2 (4)	0.6 (4)
C10	0.0691 (11)	0.4526 (7)	0.1492 (8)	4.9 (5)	4.2 (5)	6.6 (6)	−0.6 (4)	0.4 (5)	0.3 (5)
C11	−0.1206 (13)	0.4164 (7)	0.2459 (8)	10.7 (7)	5.1 (6)	4.9 (5)	2.4 (5)	3.7 (5)	−0.1 (4)
C12	−0.1686 (11)	0.4125 (7)	0.0670 (8)	4.7 (5)	5.9 (6)	4.6 (5)	1.2 (4)	−0.4 (4)	1.3 (4)
C13	0.1261 (9)	0.1046 (6)	0.2641 (6)	4.0 (4)	3.9 (4)	3.2 (4)	1.1 (4)	0.4 (3)	0.3 (4)
C14	0.1021 (10)	0.0589 (7)	0.3437 (7)	3.9 (5)	6.0 (6)	4.3 (5)	0.4 (4)	0.2 (4)	1.2 (4)
C15	−0.0289 (12)	0.0605 (7)	0.3711 (7)	6.5 (6)	6.4 (6)	3.4 (4)	0.4 (5)	1.0 (4)	1.6 (4)
C16	−0.1333 (11)	0.1066 (7)	0.3181 (7)	5.6 (5)	4.6 (5)	4.9 (5)	−0.4 (4)	2.5 (4)	1.0 (4)
C17	−0.1003 (10)	0.1497 (7)	0.2390 (7)	3.6 (4)	4.5 (5)	5.6 (5)	−0.3 (4)	0.9 (4)	1.8 (4)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

The structural characterization of $[Mo(O\text{-}i\text{-}Pr)_3NO]_2$ revealed two equivalent (inversion-related) distorted trigonal-bipyramidal $Mo(OR)_4NO$ units fused along a common axial-to-equatorial edge through the agency of bridging isopropoxy groups. With a Mo-to-Mo distance of 3.335 (2) Å it can be safely assumed that no direct metal-to-metal bonding exists.[5] In a formal sense reaction 1 corresponds to the replacement of the metal-to-metal triple bond by two metal-to-ligand triple bonds followed by Lewis base association.[6]

We concluded:[4] "There would not seem to be any reason why discrete mononuclear complexes of type A, where X represents a univalent ligand, L a σ donor, and M any atom or ion isoelectronic with Mo(III), should not exist as a general class."



A

We report here our preparation and characterization of the first member of this class, namely, $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$, formed in the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and NO (2 equiv) in pyridine.

Results and Discussion

Synthesis. Addition of nitric oxide (2 equiv) to hydrocarbon solutions of $W_2(O\text{-}t\text{-}Bu)_6$[7] leads to the formation of a fine yellow precipitate of empirical formula $W(O\text{-}t\text{-}Bu)_3NO$ which shows a single, sharp, and very strong IR absorption at 1565 cm^{-1} assignable to ν(NO). This compound is virtually insoluble in alkane and aromatic hydrocarbons which has hindered its further characterization. It is believed to be polymeric, $[W(O\text{-}t\text{-}Bu)_3NO]_n$, in contrast to the dimeric molybdenum analogue $[Mo(O\text{-}t\text{-}Bu)_3NO]_2$. $[W(O\text{-}t\text{-}Bu)_3NO]_n$ will dissolve in the presence of Me_3N and pyridine yielding $W(O\text{-}t\text{-}Bu)_3(NO)(L)$. The compound $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$ has also been made directly by the addition of NO (2 equiv) to a pyridine solution of $W_2(O\text{-}t\text{-}Bu)_6$ and is a yellow crystalline compound appreciably soluble in hydrocarbon solvents. For $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$ a strong, sharp IR absorption at 1555 cm^{-1} is assignable to ν(NO); a sharp band of medium intensity at 1610 cm^{-1} is assigned to a stretching vibration of the coordinated pyridine. The NMR spectra in toluene-d_8 of $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$ show the presence of only one type of *tert*-butoxy ligand, even at −60 °C. This, together with the observation of a single nitrosyl stretching frequency, is consistent with the presence in solution of a structure akin to that found in the crystal.

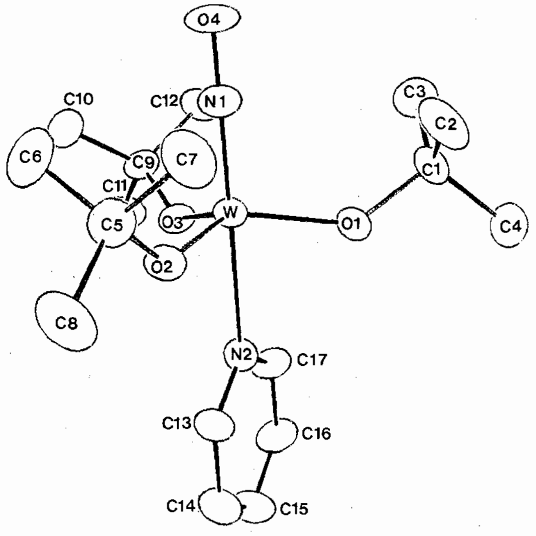


Figure 1. An ORTEP view of the $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$ molecule using 40% probability ellipsoids and showing the atom numbering scheme.

Solid-State Structure of $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$. The compound is composed of discrete mononuclear molecules in the solid state. Atomic positional and thermal parameters are given in Table I. The molecular structure is shown in Figure 1 along with the atom labeling scheme. Bond distances and angles are given in Table II. As can be seen from Figure 1, the coordination geometry is a slightly distorted trigonal bipyramid with the axial positions occupied by the nitrosyl and pyridine ligands.

The tungsten atom is displaced 0.34 Å toward the nitrosyl ligand from the equatorial plane of the three alkoxy oxygen atoms. The nitrosyl ligand is coordinated linearly, and the

Table II. Bond Distances (Å) and Angles (deg) in $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$[a]

Distances

W-O1	1.876 (6)	C1-C3	1.527 (15)
W-O2	1.898 (6)	C1-C4	1.547 (15)
W-O3	1.887 (6)	C5-C6	1.52 (2)
W-N1	1.732 (8)	C5-C7	1.533 (15)
W-N2	2.323 (7)	C5-C8	1.560 (15)
O1-C1	1.476 (11)	C9-C10	1.520 (14)
O2-C5	1.449 (11)	C9-C11	1.544 (14)
O3-C9	1.446 (11)	C9-C12	1.538 (14)
O4-N1	1.250 (10)	C13-C14	1.394 (13)
N2-C13	1.318 (11)	C14-C15	1.377 (14)
N2-C17	1.343 (11)	C15-C16	1.389 (14)
C1-C2	1.53 (2)	C16-C17	1.393 (13)

Angles

O1-W-O2	117.3 (3)	C2-C1-C3	111 (1)
O1-W-O3	115.7 (3)	C2-C1-C4	113 (1)
O1-W-N1	100.7 (3)	C3-C1-C4	112 (1)
O1-W-N2	80.4 (3)	O2-C5-C6	108.3 (9)
O2-W-O3	117.6 (3)	O2-C5-C7	109.5 (8)
O2-W-N1	100.9 (3)	O2-C5-C8	104.3 (8)
O2-W-N2	81.0 (2)	C6-C5-C7	110 (1)
O3-W-N1	99.4 (3)	C6-C5-C8	113 (1)
O3-W-N2	77.7 (3)	C7-C5-C8	111 (1)
N1-W-N2	177.0 (3)	O3-C9-C10	108.8 (8)
W-O1-C1	135.9 (6)	O3-C9-C11	104.4 (8)
W-O2-C5	134.3 (6)	O3-C9-C12	110.1 (8)
W-O3-C9	136.0 (5)	C10-C9-C11	110 (1)
W-N1-O4	179.2 (8)	C10-C9-C12	111.6 (9)
W-N2-C13	125.3 (6)	C11-C9-C12	111.8 (9)
W-N2-C17	116.0 (6)	N2-C13-C14	122.7 (9)
C13-N2-C17	118.7 (8)	C13-C14-C15	118.8 (9)
O1-C1-C2	107.4 (8)	C14-C15-C16	119.1 (9)
O1-C1-C3	108.9 (8)	C15-C16-C17	118 (1)
O1-C1-C4	103.3 (8)	N2-C17-C16	122.6 (9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

W–N1 bond is quite short, 1.732 (8) Å, indicative of some multiple-bond character whereas the tungsten-to-pyridine bond is considerably longer, W–N2 = 2.323 (7) Å. The W–O distances are in the expected range.

Bonding. The trigonal set of ligands splits the tungsten 5d orbitals into three sets: a (d_{z^2}), e ($d_{x^2-y^2}$, d_{xy}), and e (d_{xz}, d_{yz}). The second e set is but little involved in metal–ligand σ bonding and thus lies lowest in energy. In $W(O\text{-}t\text{-}Bu)_3(NO)(py)$ tungsten achieves only a 14-valence-shell-electron configuration. Ten electrons are involved in forming the five σ bonds, and the remaining four occupy the lower e orbitals which have the appropriate symmetry to interact with the empty nitrosyl π^* orbitals. The bonding is analogous to that in $[Mo(O\text{-}i\text{-}Pr)_3NO]_2$, where a bridging isopropoxide occupies the axial position trans to the nitrosyl ligand.

For a linear metal–nitrosyl moiety, metal-to-nitrosyl π^* bonding should be reflected in (i) the metal-to-nitrogen bond distance, (ii) the nitrogen-to-oxygen bond distance, and (iii) the value of the N–O stretching frequency. A lengthening of the N–O bond and a lowering of ν(NO) should correlate with an increase in metal-to-nitrosyl π^* bonding. The shortness of the metal-to-nitrogen bond may also correlate with M–N multiple-bond character, but this distance will also be influenced by the nature of the metal σ hybrid orbital used in forming the M–N bond. The latter is determined by the coordination number and geometry of the metal complex as well as by the nature of the other ligands bonded to the metal.

M–N and N–O bond distances and ν(NO) values for some compounds containing linear M–N–O moieties are given in Table III and are illustrative of the above considerations. Certainly little can be inferred from the M–N distances alone. There does, however, seem to be the expected correlation between N–O bond length and ν(NO). This correlation is limited, however, by the relatively small changes and large experimental errors which occur in N–O distances. One can conclude that the generally accepted view that ν(NO) correlates with metal-to-nitrosyl π^* bonding finds structural support in N–O bond distances.

The trihaloruthenium complexes, which contain six-coordinate metal atoms, all show very similar M–N–O parameters (see Table III). Notably the values of ν(NO) are more than 200 cm^{-1} higher, and the N–O distances are significantly shorter than those of the five-coordinate molybdenum and tungsten complexes. The metals here are all in the +2 oxidation state, if we assume the formalism $M^-(NO^+)$ for the linear M–N–O moiety. Evidently the $(t_{2g})^6$-to-NO π^* bonding is less effective in these Ru^{2+} octahedral complexes than is the $(e)^4$-to-NO π^* bonding in the Mo^{2+} and W^{2+} trigonal-bipyramidal complexes, despite the presence of only 14 valence-shell electrons in the latter. A plausible rationale for this observation may lie in the mixing of ligand-to-metal π bonding (p → d) and metal-to-NO π^* bonding. Ligand (OR or NR_2)-to-metal π bonding in the four-coordinate $Cr(NR_2)_3NO$ and five-coordinate $M(OR)_3(NO)L$ molecules will raise the energy of the filled metal d_{xz} and d_{yz} atomic orbitals from the level they would otherwise have had as a result of pure M–L σ bonding. The energy separation between filled metal d_{xz} and d_{yz} orbitals and the vacant higher energy NO π^* orbitals will be reduced and metal-to-nitrosyl π^* bonding enhanced. It is, of course, not possible to separate completely the σ- and π-donor properties of a ligand. However, the values of ν(NO) do go down as the overall donor ($\sigma + \pi$) properties of the ligand increase: compare ν(NO) 1698 cm^{-1} for $Cr(N(SiMe_3)_2)_3NO$ with ν(NO) 1640 cm^{-1} for $Cr(N\text{-}i\text{-}Pr_2)_3NO$ and ν(NO) 1643, 1640, and 1630 cm^{-1} for the compounds $[Mo(OR)_3NO]_2$ where R = CH_2CMe_3, $CHMe_2$, and CMe_3, respectively.

Experimental Section

General procedures have been described;[1] note the use of dry and

Table III. Structures of Some Complexes with Linear M–N–O Groups

compound	M–N, Å	N–O, Å	M–N–O, deg	ν(NO), cm^{-1}	ref
$W(O\text{-}t\text{-}Bu)_3(NO)(py)$	1.732 (8)	1.25 (1)	179.2 (8)	1555	*a*
$[Mo(O\text{-}i\text{-}Pr)_3NO]_2$	1.754 (7)	1.19 (1)	178 (1)	1640	*b*
$Cr(NSi_2Me_6)_3NO$	1.738 (20)	1.191 (28)	180[i]	1698[j]	*c*
$Ru(\eta^3\text{-allyl})(NO)(PPh_3)_2$	1.751 (6)	1.188 (8)	173.8 (6)	1640	*d*
$RuCl_3(NO)(PPh_3)_2$	1.737 (7)	1.142 (8)	180[i]	1876	*e*
$RuCl_3(NO)(PPh_2Me)_2$	1.744 (6)	1.132 (6)	176.4 (6)	1860[k]	*f*
$[RuBr_3(NO)(Et_2SO)]_2$	1.71 (1)	1.16 (1)	178 (1)	1874	*g*
$[Mo(CN)_5NO]^{4-}$	1.95 (3)	1.23 (4)	175 (3)	1455[l]	*h*

[a] This work. [b] Reference 4. [c] D. C. Bradley, M. B. Hursthouse, C. W. Newing, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 567 (1972). [d] M. W. Schoonover and R. Eisenberg, *J. Am. Chem. Soc.*, 99, 8371 (1977). [e] B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, **14**, 3060 (1975). [f] A. J. Schultz, R. L. Henry, and R. Eisenberg, *ibid.*, **13**, 732 (1974). [g] J. E. Fergusson, C. T. Page, and W. T. Robinson, *ibid.*, **15**, 2270 (1976). [h] D. H. Svedung and N.-G. Vännerberg, *Acta Chem. Scand.*, **22**, 1551 (1968). [i] Crystallographically imposed linearity. [j] C. W. Newing, Ph.D. Thesis, London University, 1971. [k] J. Chatt and B. L. Shaw, *J. Chem. Soc., A*, 1811 (1966). [l] R. F. Riley and L. Ho, *J. Inorg. Nucl. Chem.*, **24**, 1121 (1962).

oxygen-free atomspheres and solvents.

$W_2(O\text{-}t\text{-}Bu)_6$ was prepared from the reaction between $W_2(NMe_2)_6$ and *t*-BuOH (>6 equiv) in benzene and was recrystallized from hexane solutions.[7]

$[W(O\text{-}t\text{-}Bu)_3NO]_n$. $W_2(O\text{-}t\text{-}Bu)_6$ (0.63 g, 0.78 mmol) was dissolved in hexane (10 mL) to give a red solution. Nitric oxide (1.56 mmol) was added with the use of a calibrated manifold to the above solution frozen at liquid-nitrogen temperature which yielded upon warming to room temperature a green solution and a pale yellow precipitate. After 5 h the pale yellow precipitate was collected by filtration, washed with hexane, and dried in vacuo (10^{-4} cmHg, 25 °C); yield 0.56 g (83% based on tungsten). Anal. Calcd for $W(O\text{-}t\text{-}Bu)_3NO$: C, 33.27; H, 6.28; N, 3.23. Found: C, 33.06; H, 6.20; N, 3.40. IR data obtained from a Nujol mull between CsI plates (2000–300-cm^{-1} range): 1565 (vs), 1310 (w), 1245 (m), 1165 (s, br), 1090 (s), 1030 (w), 948 (vs, br), 928 (vs), 912 (s), 796 (m, sp), 784 (m, sp), 724 (m, br), 627 (s, sp), 595 (m), 572 (m), 485 (w), 394 (w), 381 (w), 340 (w).

$W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$. $W_2(O\text{-}t\text{-}Bu)_6$ (0.1844 g, 0.23 mmol) was dissolved in pyridine (7 mL) to form a deep red solution. This was frozen at liquid nitrogen temperature, and nitric oxide (0.46 mmol) was added using a calibrated vacuum manifold. The reaction mixture was allowed to warm to room temperature and left to stand for 12 h. The pyridine was stripped and the residue extracted with toluene (ca. 5 mL). The pale yellow solution was filtered to remove a small amount of a black, insoluble material. The filtrate was collected and cooled to −10 °C yielding pale yellow crystals (ca. 80 mg). Anal. Calcd for $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$: C, 39.86; H, 6.30; N, 5.47. Found: C, 39.65; H, 6.25; N, 5.40. IR data obtained from a Nujol mull using CsI plate in the range 2000–300 cm^{-1}: 1610 (m, sp), 1555 (vs), 1305 (w), 1240 (m), 1222 (m, sp), 1170 (m, br), 1156 (m, sp), 1076 (m, sp), 1043 (m, sp), 1027 (w), 1018 (w), 1000 (w), 965 (m), 948 (m), 937 (vs, br), 910 (m), 900 (w), 783 (m), 762 (m, sp), 722 (m, br), 694 (m, sp), 621 (s), 576 (m), 485 (w), 436 (w), 380 (w). ^{13}C NMR data obtained in toluene-d_8 at −50 °C: $\delta(OC) = 80.8$, $\delta(CH_3) = 32.9$ (δ in ppm relative to Me_4Si).

X-ray Crystallography.[8] A yellow crystal of $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$ measuring $0.23 \times 0.28 \times 0.58$ mm was mounted, embedded in epoxy cement, and sealed in a thin-walled glass capillary, with its longest dimension nearly coincident with the ϕ axis. ω scans of several intense low-angle reflections had peak widths at half-height of ca. 0.2°. Cell constants and axial photographs indicated that the crystal belonged to the monoclinic system with $a = 9.694$ (2) Å, $b = 15.686$ (3) Å, $c = 14.358$ (2) Å, $\beta = 97.40$ (1)°, and $V = 2165.1$ (7) Å^3. The observed volume was consistent with that expected for $Z = 4$. Systematic absences observed during data collection, on $0k0$ ($k = 2n + 1$) and $h0l$ ($h + l = 2n + 1$), uniquely determined the space group to be $P2_1/n$ (a nonstandard setting of $P2_1/c$, No. 14).

The data were collected at 23 ± 2 °C with a Syntex $P\bar{1}$ autodiffractometer equipped with a graphite crystal monochromator and using Mo Kα (λ 0.710730 Å) radiation. Variable scan rates from 4.8 to 24.0°/min were used for symmetric $\theta/2\theta$ scans ranging from 1.0° below to 1.0° above the calculated Mo Kα_1,Kα_2 doublet. The ratio of background to scan time was 0.5. A total of 2936 unique reflections having $0° < 2\theta(\text{Mo K}\alpha) < 45°$ were collected. The intensities of three standard reflections were monitored frequently throughout data collection and showed an approximately linear decrease of 12% over the period of data collection. The data were reduced to a set of relative $|F_o|^2$ values and then corrected for crystal decay. An empirical absorption correction based upon a series of ψ scans was applied to the data ($\mu = 56.7$ cm^{-1}); relative transmission factors ranged from 0.844 to 1.000 with an average of 0.949. The 2103 observations having $|F| > 3\sigma(|F|)$ were retained as observed and used in subsequent structure solution and refinement.

The positions of the 24 unique nonhydrogen atoms were determined by standard heavy-atom methods. The structure was refined to convergence using anisotropic thermal parameters for all 24 atoms. The final discrepancy indices were

$$R_1 = \sum \| F_o| - |F_c\| / |F_o| = 0.032$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.047$$

The estimated standard deviation of an observation of unit weight was 1.102. The top peaks in a final difference Fourier map were due to methyl group hydrogen atoms.

A table of observed and calculated structure factors is available as supplementary material.

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Registry No. $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$, 68013-63-8; $[W(O\text{-}t\text{-}Bu)_3(NO)]_n$, 68013-62-7; $W_2(O\text{-}t\text{-}Bu)_6$, 57125-20-9.

Supplementary Material Available: Observed and calculated structure factors for $W(O\text{-}t\text{-}Bu)_3(NO)(C_5H_5N)$ (9 pages). Ordering information is given on any current masthead page.

References and Notes

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