

On the Trail of Dichlorodinitrosyltungsten: A Tale of Two Reactions

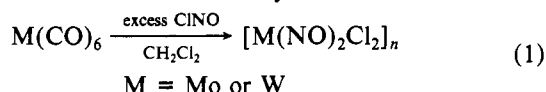
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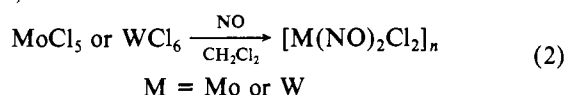
Polymeric $[\text{W}(\text{NO})_2\text{Cl}_2]_n$ may be synthesized in high yields by two preparative methods. The first method involves treatment of WCl_6 in CH_2Cl_2 with an excess of NO followed by complete purging of the ClNO byproduct from the system. It has been established that this reductive nitrosylation proceeds via the isolable intermediate complexes, dark violet *cis*- $\text{W}(\text{NO})_2\text{Cl}_4$ and bright green *fac*- $\text{W}(\text{NO})_3\text{Cl}_3$. The second method involves controlled reaction of $\text{W}(\text{CO})_6$ with 2 equiv of ClNO in CH_2Cl_2 after initiation of the conversion with traces of an oxidant. Evidence is presented that this reaction probably proceeds via a catalytic, radical chain mechanism, the initiation step being the formation of substitutionally labile $\text{W}(\text{CO})_6^+$ and the final propagation step being the reduction of $\text{W}(\text{NO})_2\text{Cl}_2^+$ by $\text{W}(\text{CO})_6$, which affords the final product and regenerates $\text{W}(\text{CO})_6^+$. If either synthesis is effected in the presence of 2 equiv of CH_3CN , the only nitrosyl-containing product formed is yellow-green $\text{W}(\text{NO})\text{Cl}_3(\text{CH}_3\text{CN})_2$, a solid complex also obtainable by reaction of $\text{W}(\text{NO})_2\text{Cl}_4$ or $\text{W}(\text{NO})_3\text{Cl}_3$ with CH_3CN . A variety of hard and soft Lewis bases, L, cleave polymeric $[\text{W}(\text{NO})_2\text{Cl}_2]_n$ to produce new, monomeric $\text{W}(\text{NO})_2\text{Cl}_2\text{L}_2$ compounds that can be isolated in good yields. The stereochemistries of these octahedral complexes can generally be established by conventional spectroscopic methods. The complexes having L = THF, Et_2O , or CH_3CN undergo metathesis with *n*- $\text{Bu}_3\text{Sn}(\text{C}_5\text{H}_5)$ to form the known $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{Cl}$ in moderate yields.

Introduction

During some of our previous investigations,^{1,2} we had occasions to prepare the polymeric complexes $[\text{M}(\text{NO})_2\text{Cl}_2]_n$ (M = Mo or W). These compounds are green, hygroscopic powders, and their molecular structures are believed to involve kinked chains having bridging chlorine atoms and terminal *cis* nitrosyl groups attached to octahedral metal centers.³ Two principal methods have been reported for the synthesis of these materials, namely (1) treatment of the respective binary carbonyls with an excess of nitrosyl chloride, i.e.^{3,4}



and (2) reductive nitrosylation of the appropriate metal chloride, i.e.⁵



In our hands,² reaction 1 proceeded essentially as described for M = Mo but appeared to be much more complex when M = W. Specifically, we first observed that traces of O_2 were necessary to initiate a reaction between $\text{W}(\text{CO})_6$ and ClNO, and we then found that use of an excess of nitrosyl chloride led to a marked decrease in both the yield and the purity of the desired product. Consequently, we next attempted to employ reaction 2 for the synthesis of $[\text{W}(\text{NO})_2\text{Cl}_2]_n$. We soon discovered that this method was extremely sensitive to variations in reaction conditions such as concentration and scaling up of the amounts of the reactants. Indeed, we found that a variety of chloro nitrosyl complexes of tungsten could be isolated from the final reaction mixtures after treatment of WCl_6 with NO under slightly different experimental conditions.

Intrigued by the apparent complexities of these two synthetic methods, we set out to determine exactly how $[\text{W}(\text{NO})_2\text{Cl}_2]_n$ could be prepared *reproducibly* by reactions 1 and 2. In so doing, we have also acquired some insight into the probable mechanisms of these reactions and have identified other complexes that are intermediates or byproducts formed during these transformations. The complete results of our investi-

gations involving reactions 1 and 2 when M = W along with some derivative chemistry of the $[\text{W}(\text{NO})_2\text{Cl}_2]_n$ product are described in this paper. For clarity of presentation, reaction 2 is considered first.

Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions unless specified otherwise. General procedures routinely employed in these laboratories have been described in detail previously.⁶ Trimethyl phosphite was distilled from sodium and was stored under N_2 at -10°C prior to use.⁷ Nitric oxide (Matheson CP grade, 99.0% minimum) was purified by passing it through a column of activated silica gel maintained at -78°C . A mass spectrum of the effluent gas exhibited only a sharp peak at m/z 30 assignable to NO^+ ; it did not display signals attributable to ions such as NO_2^+ or N_2O^+ . ^{31}P NMR spectra were recorded at 32.31 MHz on a Bruker WP-80 spectrometer with reference to external NaPF_6 in CD_3CN (δ -144, i.e. upfield from H_3PO_4), but all ^{31}P chemical shifts are reported in ppm downfield from H_3PO_4 . Elemental analyses were performed by P. Borda of this department.

Reactions of WCl_6 with NO. A. To Produce $\text{W}(\text{NO})_2\text{Cl}_4$. A 500-mL, three-necked flask was equipped with two gas inlet valves, one being connected to a Nujol bubbler and the other to a two-way stopcock connected to cylinders containing dry N_2 and NO gases. The flask was charged under N_2 with WCl_6 (5.00 g, 12.6 mmol) and CH_2Cl_2 (250 mL) to obtain a red supernatant solution over a violet-black solid. The mixture was stirred rapidly at room temperature as the N_2 atmosphere was gradually replaced by NO at a flow rate of approximately 20 mL/min at the exit bubbler. The initially rapid uptake of NO resulted after ca. 17 min in the formation of a brown solid and a light green supernatant solution whose IR spectrum displayed a ν_{NO} at 1846 cm^{-1} due to dissolved ClNO. The NO was then flushed out of the system, and the reaction mixture was refluxed under a N_2 flow (ca. 20 mL/min) for 3.5 h to remove the ClNO byproduct. This operation produced a red solution (devoid of nitrosyl absorbances in its IR spectrum) over a dark violet solid. The solid was collected by filtration on a medium-porosity frit, washed with CH_2Cl_2 until the washings were colorless ($3 \times 30\text{ mL}$), and dried in vacuo ($5 \times 10^{-3}\text{ mm}$) at ambient temperature to obtain 2.29 g (47% yield) of $\text{W}(\text{NO})_2\text{Cl}_4$ as a violet-black, microcrystalline solid: IR (Nujol mull) ν_{NO} 1934 (m), 1798 (s) cm^{-1} ; mp 140°C dec. Anal. Calcd for $\text{WN}_2\text{O}_2\text{Cl}_4$: C, 0.00; H, 0.00; N, 7.25; Cl, 36.79. Found: C, 0.00; H, 0.00; N, 7.23; Cl 36.35.

B. To Produce $\text{W}(\text{NO})_3\text{Cl}_3$. The treatment of WCl_6 with NO was effected in a manner identical with that described in part A. However, in this instance, NO was passed over the reaction mixture for ca. 30 min until it consisted of a bright green solid suspended in a bright green solution whose IR spectrum displayed a ν_{NO} at 1846 cm^{-1} characteristic of dissolved ClNO. The solid was then collected by

(1) Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1977**, *16*, 3173.

(2) Legzdins, P.; Oxley, J. C. *Inorg. Chem.* **1984**, *23*, 1053.

(3) Cotton, F. A.; Johnson, B. F. G. *Inorg. Chem.* **1964**, *3*, 1609.

(4) Johnson, B. F. G.; Al-Obadi, K. H. *Inorg. Synth.* **1970**, *12*, 264.

(5) Kohán, J.; Vastag, S.; Bencze, L. *Inorg. Chim. Acta* **1975**, *14*, L1 and references cited therein.

(6) Hames, B. W.; Legzdins, P. *Organometallics* **1982**, *1*, 116.

(7) $\text{P}(\text{OMe})_3$ isomerizes on heating to $\text{OP}(\text{Me})(\text{OMe})_2$; cf.: Marck, V. *Mech. Mol. Migr.* **1969**, *2*, 319.

filtration as described above to obtain $W(NO)_3Cl_3$ (2.90 g, 61% yield) as a bright green, microcrystalline solid: IR (Nujol mull) ν_{NO} 1927 (m), 1800 (sh), 1760 (s) cm^{-1} ; IR (CH_2Cl_2) ν_{NO} 1919 (s), 1782 (s) cm^{-1} ; mp 128 °C dec. Anal. Calcd for $WN_3O_3Cl_3$: C, 0.00; H, 0.00; N, 11.05; Cl, 27.97. Found: C, 0.20; H, 0.00; N, 10.49; Cl, 27.70.

Reaction of WCl_6 with NO and CH_3CN . A 500-mL, three-necked flask was equipped as described in part A and was charged with powdered WCl_6 (5.00 g, 12.6 mmol), CH_3CN (1.32 mL, 25.2 mmol), and CH_2Cl_2 (180 mL). As NO was passed over the rapidly stirred mixture at ambient temperature, the supernatant red solution initially became more intense in color as all the WCl_6 dissolved. Continued treatment with NO resulted in the solution paling in color and in the formation of a light green precipitate after ca. 1 h. The volume of the final mixture was reduced to 50 mL in vacuo, and the mixture was then cooled to 0 °C for 15 min. The precipitate was isolated by filtration, and the collected solid was washed with cold CH_2Cl_2 (2×10 mL at 0 °C) and then hexanes (4×20 mL) at room temperature. Final drying of the solid under reduced pressure (5×10^{-3} mm) for 18 h afforded 3.56 g (70% yield) of yellow-green $W(NO)Cl_3(CH_3CN)_2$ as an analytically pure, powdery solid: IR (Nujol mull) ν_{CN} 2290 (m), 2315 (m) cm^{-1} , ν_{NO} 1682 (s) cm^{-1} ; IR (CH_2Cl_2) ν_{NO} 1695 (s) cm^{-1} ; IR (CH_3CN) ν_{NO} 1693 (s) cm^{-1} . Anal. Calcd for $WC_4H_6N_3OCl_3$: C, 11.94; H, 1.50; N, 10.44. Found: C, 11.96; H, 1.43; N, 10.28.

Reaction of $W(CO)_6$ with ClNO. A 500-mL, three-necked flask was equipped with a gas inlet and an addition funnel and was charged with 17.6 g (50.0 mmol) of powdered $W(CO)_6$. The entire system was then thoroughly purged with prepurified dinitrogen, and CH_2Cl_2 (90 mL) was added. The addition funnel was charged with a CH_2Cl_2 solution (ca. 30 mL) of freshly prepared ClNO (6 mL, 120 mmol).⁸ Approximately 6 mL of this red solution was then added to the rapidly stirred reaction mixture. No change was evident after continued stirring for 0.5 h at room temperature. Introduction of a small aliquot (ca. 0.5 mL) of air into the reaction vessel by means of a syringe immediately initiated a vigorous reaction.⁹ The supernatant solution changed in color from red to black as copious quantities of CO were rapidly evolved. The mixture was stirred until CO evolution had ceased (ca. 5 min) whereupon it consisted of green and white solids suspended in a green solution. The addition of the ClNO solution was then continued in 0.5 mL aliquots, care being taken to ensure that CO evolution had ceased and that the reaction mixture had returned to a green coloration before a new aliquot of the reagent was introduced (ca. 3–5-min intervals). After 2 h, ca. 80 mmol of ClNO in total had been added. The addition of the ClNO solution was then completed dropwise over a period of 1 h with careful IR monitoring of the progress of the conversion. Slightly more than 2 equiv of ClNO in total was required to cause the carbonyl absorption due to $W(CO)_6$ at 1977 cm^{-1} to just disappear from the IR spectrum of the supernatant solution, which also displayed bands at ~ 2140 (m), ~ 2070 (m), ~ 2050 (m), ~ 1920 (w), ~ 1800 (s, br), and ~ 1700 (s, br) cm^{-1} . The addition funnel was then replaced by a reflux condenser, and the final green suspension was refluxed under a stream of N_2 (ca. 60 mL/min) for 1 h. After the mixture cooled to room temperature, the green precipitate was separated from the orange-green supernatant solution by filtration of the mixture through a medium-porosity frit. The solid was washed with CH_2Cl_2 (6×25 mL) and dried in vacuo (5×10^{-3} mm) for 18 h at 20 °C to obtain 14.52 g (92% yield) of $[W(NO)_2Cl_2]_n$ as an olive green powder: IR (Nujol mull) ν_{NO} 1794 (s, br), 1680 (s, br) cm^{-1} (lit.³ 1805, 1680 cm^{-1} ; lit.⁵ 1797, 1696 cm^{-1}); mp 190 °C dec. Anal. Calcd for $WN_2O_2Cl_2$: C, 0.00; H, 0.00; N, 8.90; Cl, 22.52. Found: C, 0.28; H, 0.00; N, 8.88; Cl, 21.97.

Reaction of $W(CO)_6$ with ClNO and CH_3CN . To a stirred suspension of $W(CO)_6$ (2.10 g, 5.97 mmol) in CH_2Cl_2 (30 mL) were added CH_3CN (0.79 mL, 12 mmol) and ClNO (ca. 1 mL, 20 mmol), and the resulting mixture was stirred at room temperature for 3 days, 2-mL aliquots of air being introduced into the system each day. The final mixture consisted of green and white solids beneath a red solution. An IR spectrum of this solution revealed that the characteristic absorption due to ClNO at 1846 cm^{-1} had diminished to ca. 10% of its initial intensity and that a new, strong nitrosyl band had grown

in at 1696 cm^{-1} . Solvent was removed from the final mixture in vacuo, and unreacted $W(CO)_6$ was separated from the resulting residue by sublimation at 40 °C (5×10^{-3} mm) onto a water-cooled probe. Crystallization of the remaining solid from CH_2Cl_2 -hexanes afforded 0.28 g (0.70 mmol, 12% yield) of $W(NO)Cl_3(CH_3CN)_2$, which was identified by comparison with an authentic sample (vide supra).

Reaction of $W(CO)_4(NO)Cl$ with ClNO. To a stirred yellow solution of $W(CO)_4(NO)Cl^{10}$ (0.40 g, 1.1 mmol) in CH_2Cl_2 (45 mL) was added an excess of ClNO (ca. 7 mmol). While being stirred at ambient temperature for 19 h, the initially orange solution became dark green and a bright green solid precipitated. The solid was collected by filtration and washed with CH_2Cl_2 (2×10 mL) to obtain 0.30 g (72% yield) of $W(NO)_3Cl_3$, which was identified by its characteristic physical properties (vide supra).

The addition of 1 mL of air to an identical initial reaction mixture did not increase the rate of the conversion.

Reactions of $[W(NO)_2Cl_2]_n$ with Various Lewis Bases (L). A. L = $PMePh_2$, $P(OMe)_3$, or PPh_3 . All three of these reactions were performed in a similar manner. The experimental procedure, using the case when L = $PMePh_2$ as a representative example, was as follows:

A stoichiometric amount of neat methyldiphenylphosphine (5.70 mL, 30.6 mmol) was added to a stirred suspension of $[W(NO)_2Cl_2]_n$ (4.81 g, 15.3 mmol) in benzene (50 mL), and the mixture was warmed to 50 °C for 2 h. This operation afforded a small quantity of a light green solid suspended in a dark green solution. This mixture was filtered through a 2×6 cm column of alumina (Woelm neutral, activity 1) supported on a medium-porosity frit, and the column was then washed with 100 mL of warm (50 °C) benzene. The combined filtrates were concentrated in vacuo at 20 °C to ca. 50 mL, and hexanes (25 mL) were added to induce the precipitation of dark green crystals. The crystals were isolated by filtration, washed with a 2:1 benzene-hexanes mixture (3×20 mL), and dried for 16 h at 5×10^{-3} mm and 20 °C to obtain 9.33 g (81% yield) of analytically pure $W(NO)_2Cl_2(PMePh_2)_2 \cdot \frac{1}{2}C_6H_6$: IR (CH_2Cl_2) ν_{NO} 1764 (s), 1656 (s) cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.45 (m, 23 H), 2.29 (t, 6 H, $J = 4.30$ Hz); 1H NMR ($(CD_3)_2CO$) δ 7.50 (m, 20 H, Ph), 7.30 (s, 3H, C_6H_6), 2.32 (t, 6 H, Me, $J = 4.2$ Hz); low-resolution mass spectrum (probe 150 °C) m/z 715 (unsolvated P^+); mp 167 °C. Anal. Calcd for $WC_{29}H_{29}N_2O_2Cl_2P_2$: C, 46.18; H, 3.88; N, 3.71; O, 4.24. Found: C, 46.14; H, 3.90; N, 3.65; O, 4.19.

The analogous unsolvated trimethyl phosphite and triphenylphosphine complexes were isolated as lighter green crystalline solids in yields of 69% and 81%, respectively.

Anal. Calcd for $WC_6H_{18}N_2O_2Cl_2P_2$: C, 12.80; H, 3.22; N, 4.98; O, 22.74. Found: C, 12.96; H, 3.22; N, 4.97; O, 22.44. IR (CH_2Cl_2): ν_{NO} 1776 (s), 1670 (s) cm^{-1} . 1H NMR ($CDCl_3$): δ 3.84 (t, $J = 5.62$ Hz). Low-resolution mass spectrum (probe 150 °C): m/z 563 (P^+). Mp: 150 °C.

Anal. Calcd for $WC_{36}H_{30}N_2O_2Cl_2P_2$: C, 51.49; H, 3.58; N, 3.33; Cl, 8.46. Found: C, 51.72; H, 3.63; N, 3.10; Cl, 8.37. IR (CH_2Cl_2): ν_{NO} 1763 (s), 1650 (s) cm^{-1} . IR (Nujol mull): ν_{NO} 1749 (s), 1640 (s) cm^{-1} (lit.⁵ 1748, 1638 cm^{-1}). Mp: 240 °C dec (lit.³ 236 °C).

If commercial, reagent grade trimethyl phosphite was used without purification⁷ in the above procedure, $W(NO)_2Cl_2[OP(Me)(OMe)]_2$ was also formed in low yields during the reaction. This complex was separated from $W(NO)_2Cl_2[P(OMe)_3]_2$ by chromatography of the concentrated final reaction mixture on alumina with CH_2Cl_2 as eluant and was purified by crystallization from benzene-hexanes: IR (CH_2Cl_2) ν_{NO} 1757 (s), 1644 (s) cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.87 (d, 12 H, OMe, $J = 12$ Hz), 1.70 (d, 6 H, Me, $J = 18$ Hz). Anal. Calcd for $WC_6H_{18}N_2O_8Cl_2P_2$: C, 12.80; H, 3.22; N, 4.98. Found: C, 12.59; H, 3.24; N, 4.93.

B. L = $Ph_2PCH_2PPh_2$. To a stirred suspension of powdered $[W(NO)_2Cl_2]_n$ (1.97 g, 6.26 mmol) in benzene (200 mL) was added bis(diphenylphosphino)methane (dppm, 4.81 g, 12.5 mmol), and the resulting mixture was warmed to 45 °C for 28 h to obtain a light green supernatant solution and a darker green precipitate. The final mixture was filtered through a medium-porosity frit, and the collected solid was washed with benzene until the washings were colorless (typically 4×25 mL). The combined filtrate and washings were then concentrated under reduced pressure to ca. 5 mL to induce the precipitation of a pale yellow-green solid. Collection of this solid by filtration and its recrystallization from benzene-hexanes afforded 0.88 g (13%

(8) For a description of the handling of ClNO solutions see: Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126.

(9) Initiation of the reaction could also be accomplished by dipping a spatula into the supernatant solution, exposing it to air for 2 s, and then returning it into the solution.

yield) of analytically pure $W(NO)_2Cl_2(dppm)_2$: IR (CH_2Cl_2) ν_{NO} 1762 (s), 1657 (s) cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.7–7.1 (m, 40 H, Ph), 3.68 (m, 4 H, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 24.88 (t, 2 P, $J_{31P,^1H}$ = 19 Hz, $J_{31P,^{183}W}$ = 276 Hz), –15.18 (t, 2 P); mp 155 °C dec. Anal. Calcd for $WC_{50}H_{44}N_3O_2Cl_2P_2$: C, 55.42; H, 4.09; N, 2.59. Found: C, 55.43; H, 4.17; N, 2.70.

The green, benzene-insoluble solid separated previously was then extracted with CH_2Cl_2 until the extracts were colorless (5×25 mL). The combined dark green extracts were concentrated in vacuo to a volume of ca. 5 mL, whereupon a light green precipitate formed. An IR spectrum of the supernatant solution exhibited two strong absorptions at 1752 and 1641 cm^{-1} . The precipitate was collected by filtration and was recrystallized from CH_2Cl_2 to obtain 0.43 g (10% yield) of $W(NO)_2Cl_2(dppm)-CH_2Cl_2$ as a light green crystalline solid: IR (CH_2Cl_2) ν_{NO} 1756 (s), 1651 (s) cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.8–7.2 (m, 20 H, Ph), 5.54 (s, 2 H, CH_2Cl_2), 4.30 (m, 2 H, CH_2); mp 210 °C dec. Anal. Calcd for $WC_{26}H_{24}N_2O_2Cl_4P_2$: C, 39.83; H, 3.08; N, 3.57. Found: C, 39.94; H, 3.00; N, 3.86.

The olive green, C_6H_6 - and CH_2Cl_2 -insoluble solid remaining after the operations described above was identified as unreacted $[W(NO)_2Cl_2]_n$ (0.82 g, 42%) by comparison with an authentic sample.

Attempts to improve the yields of the products isolated from this conversion by increasing the reaction time and/or temperature led only to decomposition of the desired compounds.

C. L = CH_3CN , THF, or Et_2O . Powdered $[W(NO)_2Cl_2]_n$ (12.9 g, 41.0 mmol) was added to CH_3CN (100 mL), and the stirred mixture was warmed to 50 °C to complete the dissolution of the nitrosyl reactant. The final dark green solution was filtered while warm through a short (2×5 cm) column of Celite supported on a medium-porosity frit, and the column was then washed with CH_3CN (2×10 mL) at room temperature. The volume of the combined filtrates was reduced to ca. 20 mL in vacuo, and benzene (20 mL) was then added to complete the crystallization of a pale green solid. The solid was collected on a medium-porosity frit, washed with a 1:2 CH_3CN -benzene mixture (2×15 mL), and dried at 20 °C and 5×10^{-3} mm for 18 h to obtain 9.54 g (59% yield) of microcrystalline $W(NO)_2Cl_2(CH_3CN)_2$: IR (CH_3CN) ν_{NO} 1772 (s), 1668 (s) cm^{-1} ; IR (CH_2Cl_2) ν_{NO} 1776 (s), 1674 (s) cm^{-1} ; 1H NMR (CD_3NO_2) δ 2.57 (s, 3 H), 2.50 (s, 3 H); mp 155 °C dec. Anal. Calcd for $WC_4H_6N_4O_2Cl_2$: C, 12.11; H, 1.52; N, 14.12. Found: C, 12.11; H, 1.50; N, 13.85.

The reactions between $[W(NO)_2Cl_2]_n$ and THF or Et_2O proceeded in a manner analogous to that described above. However, in these cases, no attempt was made to isolate the $W(NO)_2Cl_2L_2$ (L = THF or Et_2O) products. They were generated either in the appropriate ethereal solvent or by the reaction of $[W(NO)_2Cl_2]_n$ with 2 equiv of the ether in CH_2Cl_2 and were used in situ. Their spectroscopic properties are presented below.

$W(NO)_2Cl_2(THF)_2$: IR (THF) ν_{NO} 1761 (s), 1660 (s) cm^{-1} ; IR (CH_2Cl_2) ν_{NO} 1760 (s), 1655 (s) cm^{-1} .

$W(NO)_2Cl_2(Et_2O)_2$: IR (Et_2O) ν_{NO} 1767 (s), 1661 (s) cm^{-1} ; IR (CH_2Cl_2) ν_{NO} 1777 (s), 1679 (s) cm^{-1} .

Reactions of $W(NO)_2Cl_2L_2$ (L = THF, Et_2O , or CH_3CN) with $n-Bu_3Sn(C_5H_5)$. These conversions were effected similarly; the reaction having L = THF was representative. A stirred suspension of powdered $[W(NO)_2Cl_2]_n$ (2.42 g, 7.68 mmol) in CH_2Cl_2 (50 mL) was treated with tetrahydrofuran (THF, 1.25 mL, 15.4 mmol). Within 5 min a deep green solution of $W(NO)_2Cl_2(THF)_2$ formed. To this solution was added $n-Bu_3Sn(C_5H_5)$ ¹¹ (2.41 mL, 7.68 mmol), and the mixture was stirred at ambient temperature for 2 h. During this time the solution darkened in color, and IR monitoring revealed the gradual diminution of the nitrosyl bands due to the reactant at 1760 and 1655 cm^{-1} and the concomitant growth of two new absorptions at 1733 and 1650 cm^{-1} . The volume of the final brown solution was reduced to 10 mL in vacuo, and the concentrated solution was transferred by syringe onto a 2×7 cm column of Florisil made up in CH_2Cl_2 . Elution of the column with CH_2Cl_2 produced an initial green band, which was collected and taken to dryness under reduced pressure. Recrystallization of the resulting residue from CH_2Cl_2 -hexanes afforded $(\eta^5-C_5H_5)W(NO)_2Cl$ (1.05 g, 40% yield) as a bright green crystalline solid, which was identified by its characteristic spectroscopic properties¹⁰ [IR (CH_2Cl_2) ν_{NO} 1732 (s), 1650 (s) cm^{-1} ; 1H NMR ($CDCl_3$) δ 6.15 (s)].

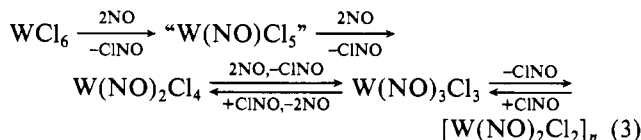
In a similar manner, treatment of $W(NO)_2Cl_2(OEt_2)_2$ and $W(NO)_2Cl_2(CH_3CN)_2$ (both generated in situ) with $n-Bu_3Sn(C_5H_5)$ in CH_2Cl_2 for 4 h and 4 days, respectively, resulted in the isolation of $(\eta^5-C_5H_5)W(NO)_2Cl$ in yields of 34% and 13%, respectively.

Caution: $n-Bu_3Sn(C_5H_5)$ is extremely toxic and must be handled with care.

The attempted use of $Na(C_5H_5)$ or $Tl(C_5H_5)$ as cyclopentadienylating agents in the above conversions resulted in decomposition and no reaction, respectively.

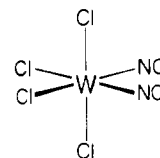
Results and Discussion

Reductive Nitrosylation of WCl_6 . As has been previously noted by other investigators,^{5,12} the treatment of WCl_6 with NO can result in the formation of a variety of chloronitrosyl complexes of tungsten. As a result of our studies, we believe that this system is best viewed as involving the sequential transformations



in which the introduction of each 2 equiv of NO results in the incorporation of a nitrosyl group into the metal's coordination sphere and the expulsion of 1 equiv of nitrosyl chloride. In addition, both the net progress of the reaction and the nature of the products ultimately recovered from the final reaction mixture are markedly dependent on the scale of the reaction, the amount of NO employed, and the final workup procedure. For instance, consistent with the report of Bencze and co-workers,⁵ we find that treatment of a solution containing 1 g of WCl_6 in CH_2Cl_2 (50 mL) at room temperature with excess NO until no further uptake of the gaseous reactant occurs and subsequent refluxing of the resulting green mixture under a current of N_2 until ClNO evolution ceases does result in the deposition of $[W(NO)_2Cl_2]_n$. This product is isolable by filtration as a slightly impure,⁵ powdery green solid in yields of 70–80%. However, scaling up of the WCl_6 solution by a factor of 5 while the same flow of NO is maintained slows the rate of reaction 3 sufficiently so that two of the intermediate chloro nitrosyl complexes may be isolated by careful control of the reaction conditions as specified in detail in the Experimental Section.

The first complex isolable is $W(NO)_2Cl_4$, which can be obtained as a dark violet solid in 47% yield. This solid is somewhat air sensitive but is stable at room temperature under N_2 indefinitely. Its Nujol mull IR spectrum exhibits two absorptions at 1934 (m) and 1798 (s) cm^{-1} , indicative of the nitrosyl groups being attached in a cis fashion to an octahedrally coordinated tungsten center, i.e.



These relatively high ν_{NO} values (cf. that of NO(g) at 1888 cm^{-1})¹³ presumably reflect the lack of electron density available at W for π back-bonding to the NO ligands. Furthermore, these nitrosyl absorbances are quite different than those displayed by $[W(NO)Cl_3]_n$ (1590 cm^{-1} as a Nujol mull)¹⁴ and ClNO (1846 cm^{-1} in CH_2Cl_2) and hence indicate that $W(N-$

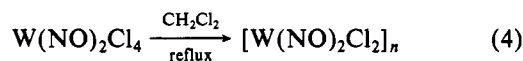
(11) Fritz, H. P.; Kreiter, C. G. *J. Organomet. Chem.* **1964**, *1*, 323.

(12) Buslaev, Yu. A.; Ovchinnikova, N. A.; Ershova, M. M.; Glushkova, M. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, *4*, 950.

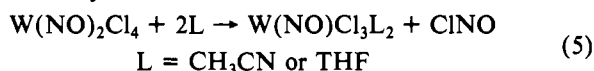
(13) Johnson, B. F. G.; McCleverty, J. A. *Prog. Inorg. Chem.* **1966**, *7*, 277.

(14) Davis, R.; Johnson, B. F. G.; Al-Obaidi, K. H. *J. Chem. Soc., Dalton Trans.* **1972**, 508.

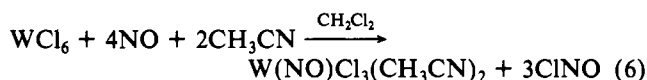
O_2Cl_4 is indeed a discrete compound and not simply a 1:1 adduct such as $\text{W}(\text{NO})\text{Cl}_3\cdot\text{ClNO}$.⁵ Since $\text{W}(\text{NO})_2\text{Cl}_4$ is virtually insoluble in nondonor solvents, there is possibly some association of the monomeric units in the solid state. Nevertheless, any association is not sufficiently strong to prevent the complex from gradually decomposing to $[\text{W}(\text{NO})_2\text{Cl}_2]_n$ as the only nitrosyl-containing product when refluxed as a suspension in CH_2Cl_2 for 3 days, i.e.



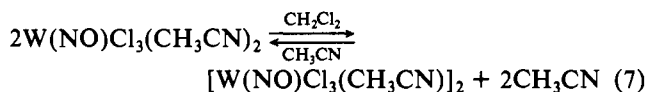
On the other hand, $\text{W}(\text{NO})_2\text{Cl}_4$ reacts readily with donor solvents such as CH_3CN or THF according to the stoichiometry



The product complex having L = CH_3CN has been recently prepared by Bencze and Kohán¹⁵ as a dark violet solid by effecting the reductive nitrosylation of WCl_6 in the presence of acetonitrile, i.e.

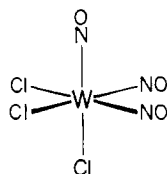


In our hands, however, both reactions 5 and 6 afford comparably good yields of analytically pure $\text{W}(\text{NO})\text{Cl}_3(\text{CH}_3\text{CN})_2$ as a powdery yellow-green solid [IR (CH_2Cl_2) ν_{NO} 1695 (s) cm^{-1}]. Solutions of this extremely air-sensitive complex in CH_3CN remain green indefinitely under N_2 at room temperature, but analogous CH_2Cl_2 solutions slowly develop a red coloration probably due to partial loss of the labile CH_3CN ligands, i.e. processes such as



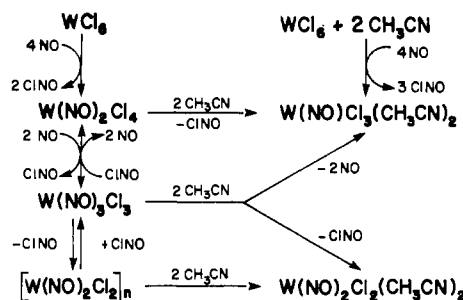
since the color change can be reversed by the addition of CH_3CN . Consistent with this inference is the fact that our $\text{W}(\text{NO})\text{Cl}_3(\text{CH}_3\text{CN})_2$ reacts cleanly with 2 equiv of PPh_3 in CH_2Cl_2 to produce the known complex, $\text{W}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2$.¹⁵ It thus appears that the previously described $\text{W}(\text{NO})\text{Cl}_3(\text{C}_6\text{H}_5\text{CN})_2$ [IR (CH_2Cl_2) ν_{NO} 1710 cm^{-1}]¹⁵ either was contaminated to some extent by a highly colored impurity or was another isomeric form.

As suggested by eq 3, treatment of WCl_6 in CH_2Cl_2 with ca. 75% more NO than is required for the formation of $\text{W}(\text{NO})_2\text{Cl}_4$ results in the precipitation of the second isolable intermediate, $\text{W}(\text{NO})_3\text{Cl}_3$, as a bright green microcrystalline solid in 61% yield. [Alternatively, $\text{W}(\text{NO})_3\text{Cl}_3$ may also be synthesized independently by the reductive nitrosylation of a suspension of $\text{W}(\text{NO})_2\text{Cl}_4$ in CH_2Cl_2 with the requisite amount of NO.] Trichlorotrinitrosyltungsten may be handled in air for short periods of time without the occurrence of noticeable decomposition. It is thermally stable under N_2 apparently indefinitely and is stable for at least 18 h under 5×10^{-3} mm pressure at ambient temperatures. Its IR spectra [(Nujol mull) ν_{NO} 1927 (m), 1800 (sh), 1760 (s) cm^{-1} ; (CH_2Cl_2) ν_{NO} 1919 (s), 1782 (s) cm^{-1}] are consistent with its molecular structure possessing the expected *fac*-octahedral stereochemistry, i.e.

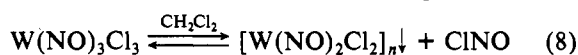


(15) Bencze, L.; Kohán, J. *Inorg. Chim. Acta* **1982**, *65*, L17.

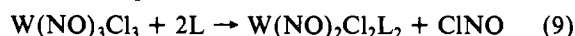
Scheme I



and rule out its being a $\text{W}(\text{NO})_2\text{Cl}_2\cdot\text{ClNO}$ adduct.⁵ The monomeric nature of this 18-electron compound is also indicated by its slight solubility in CH_2Cl_2 . However, upon dissolution in this solvent, the clear green solution initially formed readily ($t_{1/2}$ = ca. 3 min at 20 °C) becomes cloudy as reaction 8 occurs.¹⁶ This mode of decomposition of $\text{W}(\text{NO})_3\text{Cl}_3$ has been previously noted by Feltham and co-workers.¹⁷ Interestingly, IR monitoring of the progress of this decomposition indicates the transient formation of an intermediate [IR (CH_2Cl_2) ν_{NO} 1760 (w), 1660 (w) cm^{-1}], which we believe is probably solvated, monomeric $\text{W}(\text{NO})_2\text{Cl}_2$, which eventually associates to form the isolable product.



$\text{W}(\text{NO})_3\text{Cl}_3$ reacts rapidly with donor solvents such as THF or CH_3CN with concomitant NO evolution to produce red-brown solutions that contain $\text{W}(\text{NO})_2\text{Cl}_2\text{L}_2$ (L = CH_3CN or THF), $\text{W}(\text{NO})\text{Cl}_3\text{L}_2$, and ClNO in differing ratios (as measured by IR spectroscopy). These observations indicate the occurrence of the parallel reactions



IR monitoring also indicates that reaction 10 becomes less prevalent as the temperature is lowered. The product complexes having L = CH_3CN have been isolated during other portions of our work. $\text{W}(\text{NO})\text{Cl}_3(\text{CH}_3\text{CN})_2$ has been considered above (reactions 5 and 6), and the properties of $\text{W}(\text{NO})_2\text{Cl}_2(\text{CH}_3\text{CN})_2$ are presented in detail later. The interrelationships of the ternary chloro nitrosyl complexes of tungsten and their CH_3CN derivatives considered in this section are summarized in Scheme I.

Treatment of $\text{W}(\text{CO})_6$ with ClNO. It has been reported^{3,4} that when $\text{W}(\text{CO})_6$ is treated with an excess of ClNO in deaerated CH_2Cl_2 at room temperature (i.e. eq 1), a vigorous reaction ensues after a brief induction period. As the reaction proceeds, CO is evolved and a green precipitate forms. The final mixture is stirred for 2 h, and solvent and unreacted $\text{W}(\text{CO})_6$ are then removed in vacuo to afford green $[\text{W}(\text{NO})_2\text{Cl}_2]_n$ in high yield. However, we and others¹⁷ have been unable to repeat this reaction as described. Specifically, our investigations of this system have revealed two important features:

(1) Under anhydrous and anaerobic conditions no reaction between $\text{W}(\text{CO})_6$ and ClNO in CH_2Cl_2 occurs for at least 18 h at ambient temperatures. However, upon the introduction of catalytic amounts of oxidants such as air, AgBF_4 , or NOBF_4 into the system, the vigorous reaction described above is im-

(16) A bulk conversion of a suspension of 0.5 g of $\text{W}(\text{NO})_3\text{Cl}_3$ in CH_2Cl_2 (50 mL) to $[\text{W}(\text{NO})_2\text{Cl}_2]_n$ requires ca. 2 h at room temperature to go to effective completion.

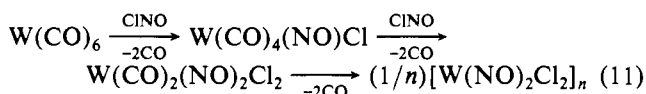
(17) Feltham, R. D.; Silverthorn, W.; McPherson, G. *Inorg. Chem.* **1969**, *8*, 344.

mediately initiated. [Lewis bases such as H₂O, CH₃CN, or THF totally inhibit this reaction (vide infra).]

(2) Use of an excess of ClNO after initiation results in the formation of a mixture of green, red, and black solids whose elemental analysis does not correspond to [W(NO)₂Cl₂]_n. Furthermore, a Nujol mull IR spectrum of these solids exhibits numerous absorption in the nitrosyl-stretching region (1950–1600 cm⁻¹) reminiscent of those displayed by W(NO)₃Cl₃ and W(NO)₂Cl₄ (vide supra). Dissolution of the solid mixture in donor solvents, L, such as CH₃CN or THF results in the vigorous evolution of NO gas and the formation of red solutions whose IR spectra confirm the presence of ClNO, W(NO)₂Cl₂L₂, and W(NO)Cl₃L₂. It thus appears, and can be verified independently, that the desired [W(NO)₂Cl₂]_n reacts with excess ClNO to produce a mixture of W(NO)₂Cl₄ and W(NO)₃Cl₃, whose behavior in donor solvents has been delineated above (cf. Scheme I).

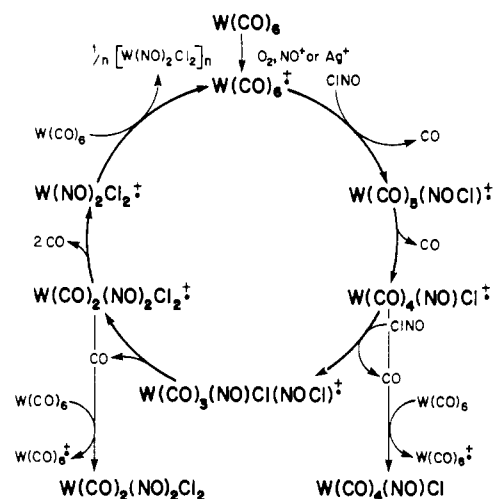
In light of these observations, the preferred procedure for the synthesis of [W(NO)₂Cl₂]_n is as follows. First, the suspension of W(CO)₆ in CH₂Cl₂ is treated with a small amount of ClNO, and the reaction is initiated with a trace amount of an oxidant. Once begun, the conversion is continued by addition of the ClNO in a slow, controlled manner until all the W(CO)₆ has just been consumed (see Experimental Section). The resulting green suspension must then be refluxed under a stream of N₂ for 1 h before the desired pure product can be collected by filtration in 92% yield. This method for the synthesis of [W(NO)₂Cl₂]_n is to be preferred over the reductive nitrosylation of WCl₆ (eq 3) since it more conveniently affords the polymeric product in better purity and yield.

This transformation of W(CO)₆ into [W(NO)₂Cl₂]_n may be accounted for by invoking the occurrence of the sequential, elementary reactions



the first two of which involve the displacement of two carbonyl ligands either by 1 equiv of ClNO or by sequential attack of NO⁺ and Cl⁻. Support for this view comes from the fact that the IR spectrum of the final supernatant reaction solution prior to reflux exhibits relatively weak carbonyl and nitrosyl absorptions at ca. 2140, 2070, 2050, and 1920 cm⁻¹, which can be attributed to the presence in low concentrations of W(CO)₄(NO)Cl¹⁰ and W(CO)₂(NO)₂Cl₂.¹ However, the sequential reactions of eq 11 cannot account either for the fact that an oxidant is needed to start the entire process or for the extremely rapid rate of the overall reaction once initiated. For instance, while it is known that W(CO)₂(NO)₂Cl₂ does indeed decarbonylate quantitatively to [W(NO)₂Cl₂]_n in CH₂Cl₂, the half-life for this process is ca. 18 h at room temperature.¹ Similarly, we have verified in a separate experiment that W(CO)₄(NO)Cl does indeed react with excess ClNO in CH₂Cl₂ in the absence of air as indicated, but again more than 19 h at ambient temperatures is required to consume completely the initial reactant. Finally, it is well-known that W(CO)₆ is inert to thermal substitution reactions with Lewis bases under ambient conditions.¹⁸ Nevertheless, once initiated, the consumption of W(CO)₆ by 2 equiv of ClNO is complete in less than 5 min at 20 °C and produces more than 10⁴ mol of [W(NO)₂Cl₂]_n for each 1 mol of oxidant added. Obviously, some mechanism other than that represented by eq 11 must be operative. We believe that the catalytic, radical chain mechanism summarized in Scheme II best accounts for our experimental observations and is in accord with literature precedents.

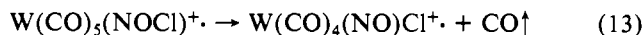
Scheme II



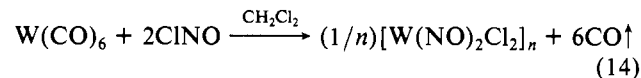
The chain initiation step involves oxidation of a small portion of the W(CO)₆ reactant to W(CO)₆⁺ by the catalytic amount of oxidant added. By analogy to related 17-electron radicals such as M(CO)_{6-n}L_n⁺ (M = Cr, Mo, or W; L = CH₃CN or pyridine), W(CO)₆⁺ should be substitutionally more labile by many orders of magnitude than its 18-electron precursor.^{18,19} Hence, it would rapidly undergo the substitution reaction



probably via an associative pathway,¹⁹ the tungsten-containing product converting in turn to the 17-electron W(CO)₄(NO)Cl⁺, i.e.



Both transformations 12 and 13 are irreversible since the rapidly evolved CO is lost from the system. The bulk of the substitutionally labile W(CO)₄(NO)Cl⁺ generated in this fashion could then undergo further rapid substitution by ClNO to form W(CO)₂(NO)₂Cl₂⁺ in a manner analogous to that shown for W(CO)₆⁺ in eq 12 and 13. Again, the thermodynamic driving force for these conversions is provided by the loss of CO. The final steps of the cycle would then involve rapid decarbonylation of the 17-electron W(CO)₂(NO)₂Cl₂⁺ and immediate reduction of the W(NO)₂Cl₂⁺ thus produced by W(CO)₆ to give the isolable [W(NO)₂Cl₂]_n and regenerate W(CO)₆⁺ for resumption of the cycle at reaction 12. The net process effected by the catalytic cycle is thus



as is observed experimentally.

According to this proposed mechanism, the traces of neutral W(CO)₄(NO)Cl and W(CO)₂(NO)₂Cl₂ detectable by IR spectroscopy in the reaction mixture (vide supra) arise from side reactions that involve reduction of the respective 17-electron cationic precursors by W(CO)₆ in solution. Such a rationale is consistent with the fact that W(CO)₄(NO)Cl undergoes an irreversible, one-electron oxidation at potentials that are some 0.5 V more positive than those required for the electrochemical oxidation of W(CO)₆ under identical experimental conditions.²⁰ In other words, replacement of two CO ligands by an NO and a Cl ligand increases the oxidation potential of a complex (i.e. makes the complex more difficult to oxidize). Hence, in accord with established criteria,¹⁹ it is

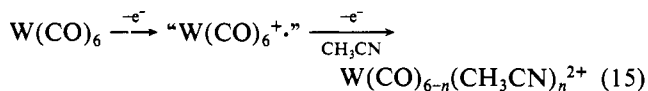
(19) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3034; **1983**, *105*, 61 and references cited therein.

(20) Legzdins, P.; Wassink, B., unpublished observations.

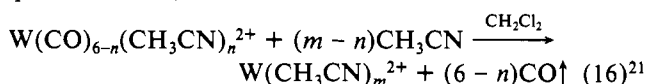
(18) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.

not unreasonable to expect that $W(CO)_2(NO)_2Cl_2^+$ and $W(NO)_2Cl_2^+$ (the precursor to the final product in Scheme II) should both be capable of functioning as oxidants toward $W(CO)_6$ as shown.

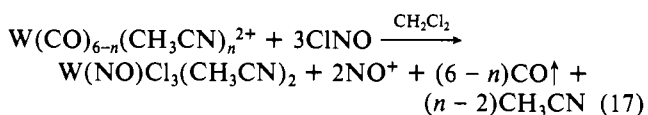
Interestingly, if the reaction between $W(CO)_6$ and excess ClNO in CH_2Cl_2 is effected in the presence of traces of air and 2 equiv of CH_3CN , the only nitrosyl-containing product (formed slowly and in low yields) is $W(NO)Cl_3(CH_3CN)_2$. It is thus evident that the cyclic mechanism of Scheme II is not followed in the presence of Lewis bases such as CH_3CN . Instead, these experimental observations may be rationalized in terms of the initial oxidation of $W(CO)_6$ occurring in the following manner:



a process that has been observed electrochemically.²¹ The dication thus formed could then engage in one of two subsequent reactions, i.e.

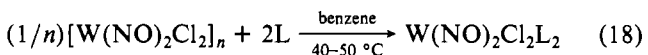


or

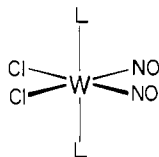


In addition to producing the final nitrosyl-containing product, reaction 17 also generates NO^+ , which could function as the oxidant for the resumption of the cycle via eq 15. Nevertheless, the low conversion of $W(CO)_6$ to $W(NO)Cl_3(CH_3CN)_2$ indicates that if indeed such a catalytic cycle (i.e. eq 15 and 17) is operative under these conditions, it has a low turnover rate either due to competition from reaction 16 as a termination step or due to the intrinsic substitutional inertness of the diamagnetic dications involved.

Some Characteristic Chemistry of $[W(NO)_2Cl_2]_n$. It is well-known that Lewis bases (L) cleave the chloride bridges in $[W(NO)_2Cl_2]_n$ and form in good yields monomeric $W(NO)_2Cl_2L_2$ complexes that possess cis nitrosyl ligands,³ i.e.



In connection with other studies,²² we have employed reaction 18 to prepare the new products having $L = PMePh_2$ or $P(OMe)_3$ as diamagnetic, green, air-stable solids. Their IR spectra display two nitrosyl absorptions in accord with the documented electron-donating abilities of the Lewis bases (i.e. $PMePh_2 > P(OMe)_3$).²³ Furthermore, their 1H NMR spectra exhibit 1:2:1 triplets due to the methyl groups. This virtual coupling establishes unambiguously²⁴ that the stereochemistry of these octahedral complexes involves the following arrangement of ligands:



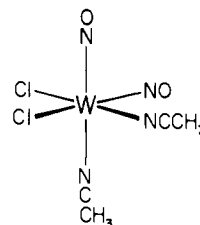
Such an arrangement has been previously demonstrated for

- (21) Christopher, J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1975**, 879.
 (22) Hunter, A. D.; Legzdins, P., unpublished observations.
 (23) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
 (24) (a) Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275. (b) Bertrand, R. D.; Ogilvie, F. B.; Verkade, J. G. *J. Am. Chem. Soc.* **1970**, *92*, 1908. (c) Ogilvie, F. B.; Jenkins, J. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1970**, *92*, 1916.

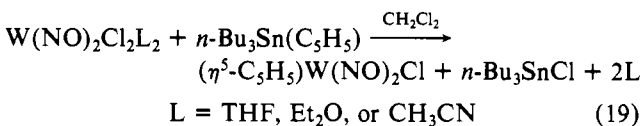
the congeneric Mo complexes.²⁵

When a potentially chelating ligand such as $Ph_2PCH_2PPh_2$ (dppm) is employed as the Lewis base in reaction 18, the conversion proceeds more slowly than with monodentate bases. Nevertheless, two different types of products may be separated by fractional crystallization from the final reaction mixture. The first is $W(NO)_2Cl_2(dppm)_2$, which is isolable as a pale green solid in 13% yield. Its spectroscopic properties indicate that it possesses the same cis NO, cis Cl, trans L arrangement of ligands around the tungsten center as the analogous $PMePh_2$ and $P(OMe)_3$ complexes. That the two trans dppm ligands are both monodentate is clearly evident from the 1H and $^{31}P\{^1H\}$ NMR spectra of the compound. The former indicates that the $PCH_2P-W-PCH_2P$ grouping constitutes an $AA'MM'X_2X'_2$ spin system,^{24b} and the latter verifies the existence of two equivalently coordinated and two equivalent uncoordinated phosphorus atoms. The second new product containing dppm that is isolable as a CH_2Cl_2 solvate in 10% yield is light green $W(NO)_2Cl_2(dppm)$. This sparingly soluble solid exhibits ν_{NO} 's at 1756 and 1651 cm^{-1} in its IR spectrum when dissolved in CH_2Cl_2 , thus confirming the presence of cis nitrosyl ligands. Steric and electronic considerations require the dppm ligand to be coordinated in a bidentate manner to cis positions in the coordination sphere. The 1H NMR spectrum of the compound does not permit the differentiation between the remaining isomeric possibilities of cis or trans Cl ligands.

Hard Lewis bases such as CH_3CN , THF, or Et_2O also react with $[W(NO)_2Cl_2]_n$ in the manner depicted in eq 18. The new $W(NO)_2Cl_2(CH_3CN)_2$ can thus be isolated from neat CH_3CN as a pale green, microcrystalline solid in 59% yield. Its IR spectra display two nitrosyl absorptions, and its 1H NMR spectrum in CD_3NO_2 consists of two sharp singlets of equal intensity. Consequently, its molecular structure must be



The analogous $W(NO)_2Cl_2(THF)_2$ and $W(NO)_2Cl_2(Et_2O)_2$ complexes may be generated appropriately in situ. All of these compounds are useful precursors for the synthesis of $(\eta^5-C_5H_5)W(NO)_2Cl$ by metathesis with $n-Bu_3Sn(C_5H_5)$, i.e.



Reaction 19 affords the organometallic nitrosyl product more directly from $W(CO)_6$, albeit in somewhat lower yield, than does the generally accepted preparative method.⁸

Conclusions

This work has established that $[W(NO)_2Cl_2]_n$ may indeed be prepared by employing reactions 1 and 2, but careful attention must be paid to experimental details. Since the reductive nitrosylation of WCl_6 in CH_2Cl_2 (eq 2) proceeds via the isolable intermediates $W(NO)_2Cl_4$ and $W(NO)_3Cl_3$ (Scheme I), the suspension of WCl_6 must first be exposed to gaseous NO at room temperature until no further uptake of the gas occurs. Subsequent refluxing of the resulting mixture under a current of N_2 to expel all of the ClNO byproduct from

- (25) (a) Visscher, M. O.; Caulton, K. G. *J. Am. Chem. Soc.* **1972**, *94*, 5923.
 (b) Hughes, W. B.; Zuech, E. A. *Inorg. Chem.* **1973**, *12*, 471.

the system then affords the sparingly soluble dichlorodinitrosyltungsten polymer. On the other hand, to synthesize this complex by the reaction of ClNO with $W(CO)_6$ in CH_2Cl_2 (eq 1), traces of an oxidant are first required to initiate the reaction, which probably proceeds via a catalytic, radical chain mechanism (Scheme II). The addition of the remaining ClNO must then be effected in a controlled manner with concomitant monitoring of the progress of the conversion by IR spectroscopy so that an excess of this reagent is avoided. Such an excess simply converts some of the desired $[W(NO)_2Cl_2]_n$ to $W(N-O)_3Cl_3$ and $W(NO)_2Cl_4$ contaminants, a conversion that may be reversed (eq 3) by refluxing the final reaction mixture for a short time under a purge of N_2 . Of the two preparative methods, reaction 1 affords $[W(NO)_2Cl_2]_n$ in the greatest yield and purity and is most convenient for the synthesis of the

polymeric complex on a large scale.

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Registry No. $W(NO)_2Cl_4$, 92473-06-8; $W(NO)_3Cl_3$, 92542-39-7; $W(NO)Cl_3(CH_3CN)_2$, 82983-81-1; $[W(NO)_2Cl_2]_n$, 42912-10-7; $W(CO)_6$, 14040-11-0; $W(CO)_4(NO)Cl$, 39899-80-4; $W(NO)_2Cl_2(PMePh)_2$, 92473-07-9; $W(NO)_2Cl_2(P(OMe)_3)_2$, 92473-08-0; $W(NO)_2Cl_2(PPh_3)_2$, 92542-40-0; $W(NO)_2Cl_2[OP(Me)(OMe)_2]_2$, 92473-09-1; $W(NO)_2Cl_2(dppm)_2$, 92473-10-4; $W(NO)_2Cl_2(dppm)$, 92473-11-5; $W(NO)_2Cl_2(CH_3CN)_2$, 92473-12-6; $W(NO)_2Cl_2(THF)_2$, 92473-13-7; $W(NO)_2Cl_2(Et_2O)_2$, 92473-14-8; $(\eta^5-C_5H_5)W(NO)_2Cl$, 53419-14-0; $n-Bu_3Sn(C_5H_5)$, 3912-86-5.

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Stereochemical Studies in the Development of Technetium Radiopharmaceuticals. 1. Fluxional Racemization of Technetium and Rhenium Penicillamine Complexes

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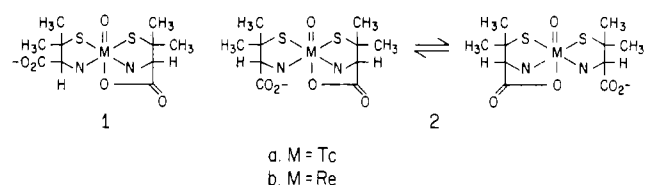
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The complexes $[(D-pen)_2MO]^-$, $[(L-pen)_2MO]^-$, and $[(D-pen)(L-pen)MO]^-$ [$M = Re, Tc$; pen = penicillaminato, $(CH_3)_2C(S^-)CH(NH_2)(CO_2^-)$] have been synthesized by $SnCl_2$ reduction of MO_4^- in the presence of optically pure or racemic penicillamine. The complexes are characterized by their chromatographic behavior, electronic spectra, fast atom bombardment mass spectra, and variable-temperature 1H NMR spectra. All complexes are six-coordinate in solution, with one tridentate penicillamine, one bidentate penicillamine, and one oxo ligand. The mixed complexes $[(D-pen)(L-pen)MO]^-$ are fluxional, racemizing by exchange of carboxylates at the site trans to the oxo ligand. Kinetics of this process were measured by complete line-shape analysis of the NMR spectra. The technetium complex racemizes with $k_1 = 940 s^{-1}$ at 25 °C and $E_a = 13.4 \pm 2.0$ kcal/mol, while the rhenium complex racemizes more slowly with $k_1 = 16.5 \pm 0.4 s^{-1}$ at 25 °C and $E_a = 18.5 \pm 1.0$ kcal/mol.

Introduction

Technetium in its +5 oxidation state has recently gained considerable attention in the development of new radiopharmaceuticals for diagnostic imaging.² Of particular interest are ^{99m}Tc complexes with tetradentate S_2N_2 chelates, which have shown promise as agents for dynamic imaging of the renal system.³ To better understand the chemistry of such complexes, we chose to investigate the penicillamine complexes of technetium, which have been reported as imaging agents for both the renal and hepatobiliary systems.⁴ Unfortunately, some reports in the medical literature have neglected to mention the enantiomeric state of the penicillamine used in

Scheme I



the pharmaceutical preparation.

Lock has recently reported the structure of a complex formed from $OTcCl_4^-$ and D-penicillamine (**1a**).⁵ In this complex one penicillamine is tridentate, coordinating through thiolate, amine, and carboxylate groups. The second penicillamine is bidentate with sulfur and nitrogen coordination. The sulfur and nitrogen atoms of the two ligands are mutually cis in this structure. The carboxylate of the second penicillamine is unable to coordinate since the oxo ligand is in the sixth position of the octahedron.

We have found that when racemic penicillamine is employed in this synthesis, a second, chromatographically separable complex is obtained in yield approximately equal to that of

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