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Improved Syntheses of Cyclopentadienyl Dichloro Nitrosyl Complexes of Molybdenum and Tungsten. Utility of Phosphorus Pentachloride as a Chlorinating Agent[1,2]

Neil H. Dryden and Peter Legzdins*

Department of Chemistry, The University of British Columbia,
Vancouver, British Columbia, Canada V6T 1Z1

Raymond J. Batchelor and Frederick W. B. Einstein*

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

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Summary: Treatment of $\mathrm{Cp'M(NO)(CO)_2}$ (Cp′ = Cp (η^5-$\mathrm{C_5H_5}$) or Cp* (η^5-$\mathrm{C_5Me_5}$); M = Mo or W) with an equimolar amount of $\mathrm{PCl_5}$ in $\mathrm{Et_2O}$ at 20 °C results in the efficient, high-yield (80–95%) syntheses of the corresponding $[\mathrm{Cp'M(NO)Cl_2}]_2$ complexes. The product complexes have been fully characterized by conventional analytical and spectroscopic methods, including a single-crystal X-ray crystallographic analysis of $[\mathrm{Cp^*Mo(NO)Cl_2}]_2$, which reveals a dimeric molecular configuration, the piano-stool monomers being linked through bridging chlorine atoms.

The principal impetus of our recent research efforts has involved the study of the characteristic chemistry of various types of organometallic nitrosyl complexes of the group 6 metals. In this regard, the diiodo nitrosyl complexes $[\mathrm{Cp'M(NO)I_2}]_n$ (Cp′ = η^5-$\mathrm{C_5H_5}$ or η^5-$\mathrm{C_5Me_5}$; M = Mo or W; n = 1 or 2) have served as the initial precursors for our syntheses of alkyl[3] and diene[4] derivatives containing the Cp′M(NO) fragments. A subsequent electrochemical examination of the reduction behavior of the dihalomolybdenum compounds, $[\mathrm{Cp'Mo(NO)X_2}]_2$ (X = Cl, Br, I), revealed that the chloro species should be the superior starting materials for the preparation of these derivative complexes.[5] This conclusion was based on the facts that both types of syntheses evidently proceed by initial single-electron transfer and that the chloro complexes form the most thermally stable radical anions upon electron addition. Application of these ideas has led to the successful synthesis of $\mathrm{Cp^*Mo(NO)(CH_2SiMe_3)_2}$[6] and has also helped to explain the formation of $[\mathrm{Cp^*Mo(NO)I}]_2$ as the major product when the diiodo precursor is treated with the (trimethylsilyl)methyl Grignard reagent.[5] The utility of the dichloro precursors has also been realized during the syntheses of diene-containing complexes via metatheses with magnesium–diene reagents. Attempts to form a butadiene complex from $[\mathrm{CpMo(NO)I_2}]_2$ in this fashion result in the eventual formation of the desired product, but the 6-day reaction time (eq 1)[4] is inconvenient for routine synthetic use. In contrast, the reactions of the $[\mathrm{CpMo(NO)Cl_2}]_2$ and $[\mathrm{Cp^*Mo(NO)Cl_2}]_2$ compounds with the same magnesium–diene reagent result in formation of the desired diene complexes in 40% isolated yields, but within hours instead of days (eq 1).[7,8]

$$[\mathrm{Cp'Mo(NO)I_2}]_2 + 2(\mathrm{C_4H_6})\mathrm{Mg(THF)_2} \xrightarrow{\mathrm{THF}} 2\mathrm{Cp'Mo(NO)}(\eta^4\text{-}\mathrm{C_4H_6}) + 2\mathrm{MgX_2} \quad (1)$$

$$X = \mathrm{I},\ 6\ \text{days} \qquad X = \mathrm{Cl},\ 3\text{–}6\ \mathrm{h}$$

At the inception of this work, only one of the required chloro complexes, namely $[\mathrm{CpMo(NO)Cl_2}]_2$, had been reported in the chemical literature. Consequently, we set out to develop an efficient synthetic route to all the $[\mathrm{Cp'M(NO)Cl_2}]_2$ (M = Mo, W) compounds. The convenient preparations of these species, by using $\mathrm{PCl_5}$ as the chlorinating agent, and their characterizations, including the solid-state molecular structure determination of $[\mathrm{Cp^*Mo(NO)Cl_2}]_2$, are presented in this paper. The syntheses of the $[\mathrm{Cp^*M(NO)Cl_2}]_2$ (M = Mo, W) compounds by the traditional route appeared in the literature[10] as this manuscript was being prepared.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anhydrous and anaerobic conditions using conventional drybox and vacuum-line Schlenk techniques under an atmosphere of dinitrogen unless specified otherwise.[11,12] General procedures routinely employed in these laborabories have been described in detail elsewhere.[13] The organometallic complexes $\mathrm{CpM(NO)(CO)_2}$ (M = Mo, W)[14] and $\mathrm{CpM^*(NO)(CO)_2}$ (M = Mo, W)[15] were prepared by established procedures. Phosphorus pentachloride (99%, Aldrich) was used as received.

IR spectra were recorded on a Nicolet 5DX FT-IR instrument, internally calibrated with a He/Ne laser. ^{1}H and ^{13}C NMR spectra were obtained on Varian Associates XL-300 or Bruker WP-80 or AM-200E spectrometers. Low-resolution mass spectra (EI, 70 eV) were recorded on a Kratos MS50 spectrometer by using the direct-insertion method with the assistance of Dr. G. K. Eigendorf. All elemental analyses were performed by Mr. P. Borda at the University of British Columbia.

Reactions of the $\mathrm{Cp'M(NO)(CO)_2}$ Complexes with $\mathrm{PCl_5}$. All these reactions were performed in a similar manner, the procedure for effecting the reaction of $\mathrm{Cp^*W(NO)(CO)_2}$ with $\mathrm{PCl_5}$

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[1] Organometallic Nitrosyl Chemistry. 45. For part 44, see: Dryden, N. H.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics*, in press.

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[8] It is interesting to note that the opposite halide dependence has been observed during metatheses reactions of $\mathrm{Cp_2MX_2}$ (M = Mo, W; X = Cl, Br, I) with Grignard reagents and lithium alkyls, the isolated yields of products varying as I > Br > Cl.[9]

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[15] The $\mathrm{Cp^*Mo(NO)(CO)_2}$ complex was prepared by utilizing a procedure analogous to that published for the synthesis of the congeneric tungsten complex: Dryden, N. H.; Legzdins, P.; Einstein, F. W. B.; Jones, R. H. *Can. J. Chem.* 1988, *66*, 2100.

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Table I. IR, Analytical, and ^1H and $^{13}C\{^1H\}$ NMR Data for the Dichloro Nitrosyl Complexes

complex	IR (CH_2Cl_2) ν_{NO}, cm^{-1}	NMR ($CDCl_3$)		anal. found (calcd)		
		^1H, δ	$^{13}C\{^1H\}$, δ	C	H	N
$[CpW(NO)Cl_2]_2$	1653	6.35[a]	107.62[b]	17.01 (17.16)	1.50 (1.44)	3.80 (4.00)
$[CpMo(NO)Cl_2]_2$	1690	6.29[a]	*c*	22.96 (22.93)	1.87 (1.92)	5.26 (5.34)
$[Cp^*W(NO)Cl_2]_2$	1624	2.11[d]	118.36[e] 10.55[f]	29.00 (28.60)	3.68 (3.60)	3.06 (3.33)
$[Cp^*Mo(NO)Cl_2]_2$	1659	1.95[d]	120.51[e] 10.60[f]	36.17 (36.17)	4.60 (4.55)	4.30 (4.22)

[a] C_5H_5. [b] C_5H_5. [c] The compound was not sufficiently soluble to permit the observation of this signal. [d] $C_5(CH_3)_5$. [e] $C_5(CH_3)_5$. [f] $C_5(CH_3)_5$.

being described below as a representative example.

***Caution*:** *Large amounts of CO gas are evolved during the progress of this reaction. Care must be taken to avoid the buildup of excess pressure in the system during the initial stages of the reaction and to vent the liberated CO to an efficient fume hood.*

An orange solution of $Cp^*W(NO)(CO)_2$ (18.0 g, 44.5 mmol) in Et_2O (120 mL) was prepared in the reaction flask, and the system was cooled for 15 min in a saturated $CaCl_2$(aq)/dry ice bath (−20 °C). A sample of PCl_5 (8.80 g, 42.0 mmol) was weighed into a glass vial in the drybox, was sealed with an airtight polyethylene stopper, and was removed from the box. The solid PCl_5 was quickly transferred from the vial into the cooled, rapidly stirred solution of $Cp^*W(NO)(CO)_2$ under a countercurrent of N_2. The reaction flask was kept open to the bubbler on the N_2 manifold, and the cooling bath was removed. As the reaction mixture warmed to room temperature, the solution changed color from orange to green, vigorous gas evolution occurred, and a brown solid was deposited. When all observable gas evolution had ceased, the mixture was warmed to ca. 35 °C with a warm water bath, and the reaction vessel was periodically evacuated to remove any liberated CO. When no more CO could be evacuated from the system, the reaction was considered to be complete. The brown precipitate was isolated from the pale green supernatant solution by filtration on a medium-porosity glass frit, and the collected solid was washed with Et_2O (3 × 40 mL) to remove traces of the PCl_3 byproduct and excess $Cp^*W(NO)(CO)_2$. The solid was then dried under vacuum (20 °C, 10^{-2} Torr) for 12 h to obtain $[Cp^*W(NO)Cl_2]_2$ (14.65 g, 83% yield based on PCl_5) as a brown powder.

Both tungsten complexes were isolated in 80–95% yields as brown powders, while the Cp– and Cp*–molybdenum complexes were isolated in 90–95% yields as orange powders. The characterization data for all complexes are collected in Tables I and II.

The $[Cp^*Mo(NO)Cl_2]_2$ complex could be crystallized from CH_2Cl_2 with a 95% recovery of solid by Soxhlet extraction of the orange powder over a period of 8 h. The extraction solution was then allowed to cool slowly to room temperature, a procedure which resulted in the deposition of large, well-formed red blocks of the organometallic complex. A single crystal suitable for X-ray crystallographic analysis was selected from the material obtained in this manner.

Perplexingly, an attempt to crystallize $[Cp^*W(NO)Cl_2]_2$ from a saturated CH_2Cl_2 solution by cooling to −25 °C resulted in the decomposition of the organometallic complex. This decomposition was manifested by the conversion of the initially green solution to a deep blue solution, and by the deposition of a blue, oily residue on the sides of the flask. No attempt to isolate a tractable material from this solution was made.

X-ray Crystallographic Analysis of $[Cp^*Mo(NO)Cl_2]_2$. The selected crystal (vide supra) was mounted on a Pyrex filament with epoxy resin and was transferred to an Enraf-Nonius CAD-4F diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Intensity data were collected at 200 K with an extensively in-house-modified low-temperature attachment based on a commercial Enraf-Nonius system. The data were corrected for Lorentz and polarization effects, and an analytical absorption correction was applied.[16] Pertinent crystallographic and experimental parameters for the complex are summarized in Table III.

Table II. Low-Resolution Mass Spectral Data for the Dihalo Nitrosyl Complexes

compd	m/z[a]	intensity[b]	assgnt[c]
$[CpMo(NO)Cl_2]_2$	453	0.1	$[2P - 2Cl]^+$
	423	0.1	$[2P - 2Cl - NO]^+$
	263	26.0	$[P]^+$
	233	100.0	$[P - NO]^+$
$[CpW(NO)Cl_2]_2$	351	27.3	$[P]^+$
	321	100.0	$[P - NO]^+$
$[Cp^*Mo(NO)Cl_2]_2$	563	0.1	$[2P - 2Cl - NO]^+$
	333	27.1	$[P]^+$
	303	80.1	$[P - NO]^+$
	267	100.0	$[P - NO - Cl]^+$
$[Cp^*W(NO)Cl_2]_2$	738	0.3	$[2P - 2Cl - NO]^+$
	421	12	$[P]^+$
	405	23	$[P - CH_4]^+$
	391	35	$[P - NO]^+$
	134	100.0	$[Cp^* - H]^+$
$Cp^*W(NO)I_2$	952	0.8	$[2P - 2I]^+$
	922	0.7	$[2P - 2I - NO]^+$
	603	100.0	$[P]^+$
	573	75.9	$[P - NO]^+$

[a] All spectra were recorded at a probe temperature of 120 °C, and m/z are reported for the most abundant mass of the isotopic cluster. [b] Relative percentage of the ion current of the most abundant mass of the isotopic cluster. [c] P relates to the respective monomeric $Cp'M(NO)X_2$ species.

Table III. Crystallographic and Experimental Data for $[Cp^*Mo(NO)Cl_2]_2$

formula	$Mo_2Cl_4O_2N_2C_{20}H_{30}$	λ, Å	0.71069
		cryst size, mm	0.13 × 0.29 × 0.32
temp, K	200	transm	0.687–0.828[b]
cryst syst	monoclinic	scan mode	ω–2Θ
space group	$P2_1/c$ (No. 14)	scan width,[c] deg	0.9 + 0.35 tan θ
		scan speed,[d] deg min^{-1}	0.8–5.5
a, Å	8.917 (2)[a]		
b, Å	8.449 (2)	min–max 2θ, deg	5–52
c, Å	18.118 (4)	no. of unique data	2503
β, deg	110.17 (2)		
V, Å^3	1281.2	no. of obsd data	1967[e]
Z	2	params	145
fw	664.16	R[f]	0.021
ρ_c, g cm^{-3}	1.722	R_{wf}[g]	0.025
μ(Mo Kα), cm^{-1}	13.96	max peak, e Å^{-3}	0.47 (17)
		GOF[h]	1.06

[a] The unit cell was determined from 25 well-centered reflections 21.9° < Θ < 23.0°. [b] The intensities were corrected analytically for the effects of absorption. Standard reflections (2) were measured every hour of aquistion time and showed no significant variations. [c] The background intensities were estimated by extension of the predetermined scan angle by 25% on either side. [d] The scan speed for each reflection was determined from the intensity of a preliminary scan. [e] $F_o \geq 5.0\sigma(F_o)$. The reflection (−1,0,2) suffered from extinction and was omitted during the structure refinement. [f] $R_f = \sum(|F_o| - |F_c|)/\sum|F_o|$, for 1966 observed data. [g] $R_{wf} = [\sum(w(|F_o| - |F_c|)^2)/\sum(wF_o^2)]^{1/2}$, for 1966 observed data; $w = [2.51929t_0(x) + 3.25116t_1(x) + 1.07507t_2(x)]^{-1}$, where $x = |F_o|/F_{max}$ and t_n are the polynomial functions of the Chebyshev series. [h] $GOF = [\sum w(|F_o| - |F_c|)^2/(\text{degrees of freedom})]^{1/2}$.

The structure was solved by conventional heavy-atom methods and was refined by full-matrix least-squares, minimizing the function $\sum w(|F_o| - |F_c|)^2$ and applying the weighting scheme such

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Table IV. Final Fractional Coordinates (×10^4) and Isotropic or Equivalent Isotropic Temperature Factors (Å^2 × 10^4) for the Non-Hydrogen Atoms of [Cp*Mo(NO)Cl$_2$]$_2$ at 200 K

atom	x/a	y/b	z/c	U(iso)
Mo(1)	1936.7 (3)	240.3 (3)	957.5 (1)	228
Cl(1)^a	−1119 (2)	266 (4)	485 (1)	311
Cl(10)^b	−964 (5)	−347 (7)	530 (3)	311
Cl(2)^c	1481 (2)	2031 (2)	1891.0 (9)	374
Cl(20)^d	3824 (4)	2072 (3)	775 (1)	374
O(1)^c	4195 (5)	2606 (6)	763 (2)	489 (11)
O(10)^d	1533 (10)	2555 (11)	2105 (5)	489 (11)
N(1)^c	3184 (6)	1750 (5)	796 (2)	369 (9)
N(10)^d	1576 (10)	1694 (11)	1559 (6)	369 (9)
C(1)	4104 (3)	−1487 (3)	1271 (2)	296
C(2)	3919 (3)	−879 (3)	1967 (2)	246
C(3)	2490 (3)	−1524 (3)	2028 (2)	317
C(4)	1782 (4)	−2490 (4)	1366 (2)	371
C(5)	2773 (4)	−2475 (4)	901 (2)	362
C(10)	5546 (5)	−1268 (5)	1039 (2)	489
C(20)	5132 (4)	99 (4)	2578 (2)	398
C(30)	1946 (5)	−1336 (5)	2720 (3)	538
C(40)	307 (5)	−3488 (5)	1218 (4)	618
C(50)	2525 (7)	−3486 (5)	193 (3)	615

^{a}Occupancy = 0.689 (7). ^{b}Occupancy = 0.311 (7). ^{c}Occupancy = 0.656 (3). ^{d}Occupancy = 0.344 (3).

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for [Cp*Mo(NO)Cl$_2$]$_2$ at 200 K^a

Mo(1)–Cl(1)	2.559 (2)	Mo(1)–Cl(1)′	2.495 (2)
Mo(1)–Cl(2)	2.406 (2)	Mo(1)–N(1)	1.781 (5)
Mo(1)–C(1)	2.330 (3)	Mo(1)–C(2)	2.266 (2)
Mo(1)–C(3)	2.360 (3)	Mo(1)–C(4)	2.441 (3)
Mo(1)–C(5)	2.426 (3)	Mo(1)–Cp	2.035
O(1)–N(1)	1.174 (7)		
Cl(1)–Mo(1)–Cl(1)	76.00 (6)	Cl(2)–Mo(1)–Cl(1)	79.14 (7)
Cl(2)–Mo(1)–Cl(1)′	141.68 (9)	N(1)–Mo(1)–Cl(1)	126.3 (2)
N(1)–Mo(1)–Cl(1)′	85.7 (1)	N(1)–Mo(1)–Cl(2)	86.1 (1)
Cp–Mo(1)–Cl(1)	116.1	Cp–Mo(1)–Cl(1)′	106.7
Cp–Mo(1)–Cl(2)	110.3	Cp–Mo(1)–N(1)	117.5
Mo(1)–Cl(1)–Mo(1)	104.00 (6)	O(1)–N(1)–Mo(1)	169.7 (4)

^{a}Prime = $-x$, $-y$, $-z$. Cp = center of gravity of the ring.

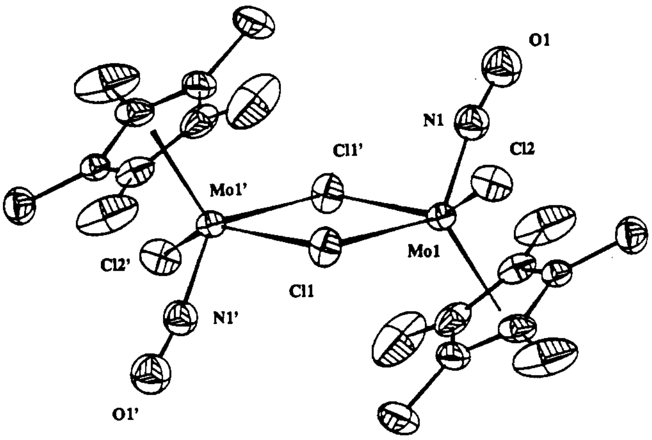

Figure 1. The SNOOPI plot of the solid-state molecular structure of [Cp*Mo(NO)Cl$_2$]$_2$, with the hydrogen atoms having been omitted for clarity.

that $\langle w(|F_o| - |F_c|)^2\rangle$ was nearly constant as a function of both $|F_o|$ and $(\sin\theta)/\lambda$. The position of the molybdenum atom was determined from the Patterson map, and subsequent Fourier synthesis revealed most of the remaining non-hydrogen atoms. The NO and terminal Cl ligands were found to be mutually disordered between their respective coordination sites. This disorder extended to a slight positional disorder of the other ligands. Hence, the bridging Cl ligand was modeled by two sites, but the Cp* ligand was modeled by a single orientation and anisotropic thermal parameters for the carbon atoms. A single occupancy parameter was refined for the N, O, and terminal-Cl sites such that the total for each atom was 1. An independent occupancy was similarly refined for the bridging Cl atom sites. The hydrogen atoms were placed in calculated positions, and a single isotropic thermal parameter was refined for the H atoms of each methyl group. These H atoms were repositioned after further refinement of the whole structure. In the final cycles, coordinate shifts for the hydrogen atoms were linked with those of their respective methyl carbon atoms. Anisotropic thermal parameters were refined for the Mo and Cl atom sites, and the two sites for each Cl atom were constrained to have equivalent motion. The maximum ratio of calculated shift to esd was 0.01 for the final full-matrix least-squares refinement of 145 parameters for 1966 observations ($F_0 \geq 5.0\sigma(F_0)$). The largest peak in the final difference map was of height 0.47 (17) e Å^{-3}. During the final cycles of the refinement, the weighting scheme employed was $w = 1/[2.51929t_0(x) + 3.25116t_1(x) + 1.07507t_2(x)]$ where $x = |F_o|/F_{max}$ and t_n (n = 0–2) are the polynomial functions of the Chebyshev series.[17]

The final residuals R, R_{wf}, and goodness of fit (GOF) for the refinement of [Cp*Mo(NO)Cl$_2$]$_2$ are listed in Table III. Complex neutral-atom scattering factors were taken from ref 18. The computations were performed on a MICROVAX II computer using the NRC VAX crystal structure package[19] and the CRYSTALS suite of programs.[20] Final positional and isotropic or equivalent isotropic thermal parameters for the complex at 200 K are given in Table IV. Bond lengths (Å) and bond angles (deg) are listed in Table V. Anisotropic thermal parameters, the remaining molecular dimensions (including hydrogen-atom coordinates), and tables of calculated and observed structure factors for the complex are provided as supplementary material. A view of the solid-state molecular structure of [Cp*Mo(NO)Cl$_2$]$_2$ is presented in Figure 1.[21]

Results

Preparation of the [Cp′M(NO)Cl$_2$]$_2$ Complexes. The generally accepted route to the dihalo nitrosyl complexes is via reaction of their dicarbonyl precursors with the appropriate elemental halogen, i.e.

$$Cp'M(NO)(CO)_2 + X_2 \rightarrow \tfrac{1}{2}[Cp'M(NO)X_2]_2 + 2CO \quad (2)$$

$$Cp' = Cp;\ M = W;\ X = I^{22}$$

$$Cp' = Cp^*;\ M = W;\ X = I^{15}$$

$$Cp' = Cp^*;\ M = Mo;\ X = I^{23}$$

$$Cp' = Cp;\ M = Mo;\ X = Cl, Br, I^{24}$$

$$Cp' = Cp^*;\ M = Mo, W;\ X = Cl, Br, I^{10}$$

This methodology has been successfully employed for the production of the various complexes indicated in reactions 2. However, this route is undesirable for the large-scale preparation of the dichloro complexes, since chlorine is a

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difficult reagent to handle stoichiometrically. Consequently, we have investigated alternative chlorinating agents with a view to developing more convenient routes to the desired dichloro complexes.

We have found that the most successful preparation of the dichloro nitrosyl complexes results from the reaction of PCl_5 with their dicarbonyl nitrosyl precursors, i.e., eq 3 in which Cp′ = Cp or Cp*; M = Mo or W. Conversions

$$Cp'M(NO)(CO)_2 + PCl_5 \xrightarrow[-2CO]{Et_2O} \tfrac{1}{2}[Cp'M(NO)Cl_2]_2 + PCl_3 \quad (3)$$

3 represent an excellent synthetic route to the dichloro complexes, being characterized by consistently high yields (80–95%). The reaction scale has been varied in our hands from 1 to 200 mmol with equal success, a factor which is particularly crucial for the preparation of these species, since they have become primary starting materials in this research group, supplanting the diiodo analogues used previously. The product complexes of reactions 3 are moderately air-stable powders, orange in the case of the molybdenum complexes and brown in the case of the tungsten complexes. They are slightly soluble in common polar organic solvents and afford emerald-green to turquoise solutions, the tungsten complexes being noticeably more soluble than their molybdenum analogues. This solubility difference is the reason suspected for the slightly lower yields of the tungsten complexes vis-à-vis the molybdenum species, since more of the tungsten produces are dissolved and lost during the filtration and washing of the product complexes (see the Experimental Section).

The IR and NMR spectroscopic properties exhibited by the $[Cp'M(NO)Cl_2]_2$ species (Table I) are similar to those previously reported for their iodo analogues. A characteristic shift in the ν_{NO} of approximately 30 cm^{-1} to lower energy occurs in going from the Cp to the Cp* complexes due to the greater electron-donating capacity of the Cp* ligand.[25] Furthermore, a 35-cm^{-1} difference between the Mo and W complexes is evident, the lower ν_{NO} values for the W species constituting a common observation for group 6 nitrosyl complexes.[26] Finally, the ^1H and $^{13}C\{^1H\}$ NMR chemical shifts of the signals due to the Cp and Cp* ligands are as expected for these complexes.

Discussion

Syntheses of the $[Cp'M(NO)Cl_2]_2$ Complexes. The convenience and efficiency of the preparations of the desired dichloro nitrosyl complexes via reactions 3 can be attributed to a number of salient features of the transformations. First of all, PCl_5 is a solid, a fact which allows careful control of the reactant stoichiometry simply by weighing the reagents. Secondly, since both the PCl_5 reactant and the $[Cp'M(NO)Cl_2]_2$ products are quite insoluble in Et_2O, there is never a large concentration of either present in solution. The feature presumably minimizes the possibility for further reaction of the organometallic products with PCl_5. Thirdly, the phosphorus trichloride byproduct is unreactive with the organometallic product complexes under the reaction conditions employed, and it is very soluble in Et_2O so that its removal is easily accomplished. Since it has been established that $[CpMo(NO)Cl_2]_2$ readily forms 1:1 adducts with electron-rich trialkyl phosphines,[27] the lack of such adduct formation with PCl_3 must be due to the poor electron-donor properties of the latter. In the recent report of the direct chlorination of the $Cp^*M(NO)(CO)_2$ (M = Mo, W) complexes, the syntheses required the preparation of standard solutions of Cl_2 in CCl_4 and their subsequent titration to establish the concentration of Cl_2.[10] These operations were apparently necessary to control the stoichiometries of the reactants. Similar precautions were used by other investigators during the previously reported chlorination of $CpMo(NO)(CO)_2$.[24] In our view, the syntheses of the dichloro nitrosyl complexes using phosphorus pentachloride as the chlorinating agent are superior to direct chlorination with elemental chlorine. Conversion 3 give equivalent or higher product yields than those obtained with Cl_2, and they provide the added conveniences of avoiding the need to handle very reactive chlorine gas and of eliminating the tedious steps needed to control the amount of chlorine added.

In the report of the optimized halogenations of $CpMo(NO)(CO)_2$ (eq 2),[24] it is noted that other nitrosyl-containing products are sometimes formed during the preparations using elemental bromine and chlorine, but no byproducts are detectable during the halogenation using iodine. The authors of this report attribute this problem to the purity of the $CpMo(NO)(CO)_2$ starting material employed, but the nitrosyl-containing byproducts could just as easily have resulted from further reactions of the $[CpMo(NO)X_2]_2$ products with the halogen reagents. Furthermore, the trend in isolated yields of the $[CpMo(NO)X_2]_2$ products, i.e. I > Br > Cl, is opposite to the trend in reactivity of the halogens used. Finally, it may be noted that a cyclic voltammetric study of the $[Cp'Mo(NO)X_2]_2$ product complexes has shown that they undergo chemically irreversible oxidation processes fairly readily,[28] an observation fully in accord with the view that they may be prone to undergo further reactions with halogens.

One final point merits mention. Phosphorus pentachloride has rarely been utilized as a chlorinating agent for organometallic complexes. To the best of our knowledge, this reactivity has been exploited only once previously, namely during the transformations summarized in eq 4.[29]

$$Cp^*M(CO)_3Me + PCl_5 \xrightarrow{CH_2Cl_2} Cp^*MCl_4 \quad (4)$$

$$M = Mo, W$$

Mass Spectroscopic and Solid-State X-ray Crystallographic Investigation of the Molecular Structures of the $[Cp'M(NO)(Cl)_2]_2$ Complexes. Although reports of the $[Cp'Mo(NO)X_2]_2$ compounds have been in the literature since 1967,[30] the recently reported solid-state molecular structure of the 16-electron $Cp^*W(NO)I_2$[15] (vide infra) is the first to have been determined for this general family of dihalo nitrosyl complexes. The single-crystal X-ray crystallographic analysis of $[Cp^*Mo(NO)Cl_2]_2$ has thus been performed as part of the present studies. The most important feature of this structure is that the complex is an 18-electron symmetric dimer which possesses a center of inversion (Figure 1). The general metrical parameters of the Cp*–Mo and Mo–NO groups are not exceptional and compare with those of other Cp*Mo(NO)-containing complexes that have been structurally characterized previously.[31] The Mo–Cl–Mo bridging units

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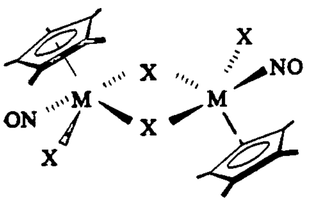
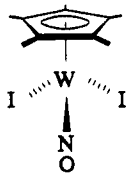
are slightly asymmetric as indicated by the Mo–Cl$_{\text{bridging}}$ bond lengths (2.559 (2) and 2.495 (2) Å); however, both of these bonds are significantly longer than the Mo–Cl$_{\text{terminal}}$ bond length (2.406 (2) Å). These markedly longer Mo–Cl$_{\text{bridging}}$ bonds are manifestations of the fact that the interactions between the monomers to form the dimer are relatively weak. This feature will become important during the discussion of the mass spectra exhibited by the [Cp′M(NO)Cl$_2$]$_2$ complexes (vide infra). The solid-state molecular structure of [Cp*Mo(NO)Cl$_2$]$_2$ is similar to that recently reported for [Cp*Mo(NO)Br$_2$]$_2$, which also exists as a halide-bridged dimer in the solid state.[10] To reiterate, both of these latter structures contrast with the other structurally characterized member of the family, namely Cp*W(NO)I$_2$, which is a three-legged piano-stool monomer in the solid state.[15]

In order to satisfy the 18-valence-electron rule, the family of complexes [Cp′M(NO)X$_2$]$_2$ has generally been formulated as having halide-bridged molecular structures of the type shown in A (the cyclopentadienyl ring shown representing either Cp or Cp*). However, the only physical evidence generally proffered for this formulation has been the observation of signals due to [CpM(NO)X]$_2^+$ dimetallic ions in the mass spectra of these complexes.[27,32] These dimetallic daughter ions are believed to arise via the loss of two halogen atoms from a parent dimer as in A. However, prior to this work, no structural studies had been reported to confirm these predictions. The solid-state molecular structure of Cp*W(NO)I$_2$ is that of a 16-electron monomer as shown in B, and a molecular-weight determination of the compound in CH$_2$Cl$_2$ indicates that it retains this structure in solutions.[15] This fact is of interest when the mass spectrum exhibited by Cp*W(NO)I$_2$ is compared to the mass spectra of the dichloro complexes (Table II). Essentially, all these compounds exhibit qualitatively similar mass spectra, even though Cp*W(NO)I$_2$ is unquestionably monomeric and [Cp*Mo(NO)Cl$_2$]$_2$ is dimeric. The observation of signals due to ions such as [Cp*W(NO)I]$_2^+$ in the mass spectrum of the iodo complex suggests that ion–molecule reactions of Cp*W(NO)I$_2$ and derived species in the mass spectrometer may well be the sources of these dimetallic ions. In other words, the presence of signals due to these ions in the mass spectra in no way confirms the degree of association of the parent complexes in the solid state. Similar bimetallic ion–molecule products have been observed in the mass spectra of the related monomeric complex, CpMo(NO)(SPh)$_2$.[33] The longer Mo–Cl$_{\text{bridging}}$ bonds extant in [Cp*Mo(NO)Cl$_2$]$_2$ indicate that the associations of all the dihalo complexes in the solid state, if present, are relatively weak. Therefore, under the conditions of the mass spectroscopic analysis, these bonds could be easily broken to form Cp′M(NO)X$_2$ as the principal species in the gas phase. This would explain the qualitative resemblance of the mass spectra of all the dichloro complexes to the mass spectrum of Cp*W(NO)I$_2$. Furthermore, the dominant features of the mass spectra of the dichloro complexes are consistent with this rationale, being due to the [Cp′M(NO)Cl$_2$]$^+$ species and ionic fragments derived from them.



A



B

At present, it seems that the only qualitative indication of the degree of association of the dihalo nitrosyl complexes is their color. The monomeric Cp*W(NO)I$_2$ has a distinctive green color,[15] while the dimeric [Cp*Mo(NO)Cl$_2$]$_2$ forms red crystals or orange powders. All the dichloro complexes prepared during this work are orange to brown powders, thereby indicating that they also possess dimeric structures in the solid state similar to that determined for [Cp*Mo(NO)Cl$_2$]$_2$. However, since all the dichloro complexes are geen to turquoise in solution, it is probable that they possess monomeric structures in solution similar to that found for Cp*W(NO)I$_2$ in the solid state. Unfortunately, none of the [Cp′M(NO)Cl$_2$]$_2$ complexes is sufficiently soluble to allow solution molecular-weight determinations in noncoordinating solvents to be effected. Nevertheless, their reactivity and electrochemical properties are most consistent with the view that they exist as (possibly solvated) monomers in solution.

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Supplementary Material Available: Tables of anisotropic thermal parameters and the remaining molecular dimensions (including hydrogen atom coordinates and bond distances and angles) (3 pages); a listing of calculated and observed structure factors for [Cp*Mo(NO)Cl$_2$]$_2$ (17 pages). Ordering information is given on any current masthead page.

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