Synthesis and Structural Studies of Chromium, Molybdenum, and Tungsten Compounds containing Cyclopentadienyl-like Ligands. Part 3.† Dicarbonylnitrosyl(η-pentamethylcyclopentadienyl) Complexes

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The complexes $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$, where M = Cr, Mo, or W, have been synthesized and their i.r. and ^1H n.m.r. spectra are reported. The crystal structures of all three compounds have been determined from three-dimensional *X*-ray data measured by counter methods. The $[Cr(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ complex crystallizes in the space group $P2_1/n$ with unit-cell dimensions of $a = 12.346(5)$, $b = 7.805(4)$, $c = 14.378(5)$ Å, $\beta = 106.85(3)°$, and $Z = 4$. Full-matrix least-squares refinement has led to a final R value of 0.043 based on 1 802 unique observed reflections. The $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ (M = Mo or W) compounds are isostructural and crystallize in the space group $P\bar{1}$ with unit-cell dimensions $a = 6.992(4)$, $b = 7.828(4)$, $c = 12.955(5)$ Å, $\alpha = 84.70(3)$, $\beta = 86.71(3)$, $\gamma = 75.51(3)°$, $Z = 2$, and $a = 6.947(4)$, $b = 7.804(4)$, $c = 12.957(5)$ Å, $\alpha = 84.41(3)$, $\beta = 86.58(3)$, $\gamma = 75.48(3)°$, $Z = 2$ respectively. Full-matrix least-squares refinement has led to final R values of 0.035 and 0.073 based on 2 190 and 2 132 unique observed reflections, respectively. The three structures each have disordered $M(CO)_2(NO)$ moieties in which the CO and NO ligands are *C*- or *N*-bonded to the metal in a linear fashion. For M = Cr, four of the Cr–C(π) distances are equivalent [average 2.200(5) Å] while the remaining one is longer by 0.031(7) Å (4.4σ). For M = Mo, the equivalent Mo–C(π) distances average 2.346(3) Å while the unique distance is 0.020(6) Å (3.3σ) longer. For M = Cr, Mo, and W the methyl groups are bent away from the metal, out of the plane of the cyclopentadienyl ring.

RECENTLY, we reported the *X*-ray structures of the well known complexes $[M(\eta\text{-}C_5H_5)(CO)_2(NO)]$ (M = Cr,[1] Mo,[2] or W [2]) and the synthesis and structure of the novel dicarbonyl(η^5-9*H*-fluorenyl)nitrosylchromium.[1] A comparison of these complexes has prompted us to investigate the chemical and structural properties of a wide range of previously unknown dicarbonyl(η-cyclopentadienyl)-nitrosylmetal (M = Cr, Mo, or W) compounds. To date, the only such complex known, apart from those just mentioned, is $[Cr(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ which was obtained by the treatment of $[\{Cr(\eta\text{-}C_5Me_5)(CO)_2\}_2]$ with nitric oxide.[3]

It is important to consider the physicochemical changes which the η-pentamethylcyclopentadienyl ligand might be expected to exert upon the $M(CO)_2(NO)$ moiety. The stabilizing influence of this ligand, relative to the cyclopentadienyl homologue, is well exemplified by a number of $Zr(\eta\text{-}C_5Me_5)_2$-containing compounds.[4] In spite of this important advantage, few other $(\eta\text{-}C_5Me_5)$-containing early transition-metal complexes are known and even fewer have been characterized by *X*-ray diffraction studies.[3,5,6] In this paper, we report the syntheses, ^1H n.m.r. and i.r. spectra, and the molecular and crystal structures of $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ (M = Cr, Mo, or W).

EXPERIMENTAL

All chemicals used were of reagent grade or comparable purity and were either purchased from commercial suppliers or prepared according to reported procedures. Tetrahydrofuran was dried by refluxing over lithium tetrahydroaluminate and was distilled and thoroughly purged with prepurified nitrogen prior to use. All manipulations, unless otherwise indicated, were performed under an atmosphere of prepurified nitrogen.

The uncorrected melting points were recorded under nitrogen using a Thomas Hoover capillary melting-point apparatus. The ^1H n.m.r. spectra were obtained from a Hitachi–Perkin-Elmer R-20B spectrometer using $SiMe_4$ as an internal reference. Infrared spectra were recorded on a Beckman IR33 spectrometer and were calibrated with the absorption band of a polystyrene film at 1 601 cm^{-1}. Elemental analyses were performed by Atlantic Microlab, Inc.

Preparation of Sodium Pentamethylcyclopentadienide, $Na[C_5Me_5]$.—A stirred mixture of C_5HMe_5 [7] (10.0 g, 73.4 mmol) and $Na[NH_2]$ (5.5 g, 140 mmol) in tetrahydrofuran (thf) (200 cm^3) was allowed to react under reflux for 4 h and at 25 °C for another 15 h. Excess of $Na[NH_2]$ was removed by centrifugation and the supernatant liquid was collected. The concentration of the resulting $Na[C_5Me_5]$ solution was determined by hydrolyzing a 2.0 cm^3 sample and titrating against a standard hydrochloric acid solution

Preparation of Dicarbonylnitrosyl(η-pentamethylcyclopentadienyl) Complexes of Chromium, Molybdenum, and Tungsten, $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ (M = Cr, Mo, *or* W).—All three compounds were prepared similarly as exemplified below by the preparation of the chromium complex.

A stirred mixture of $[Cr(CO)_6]$ (2.20 g, 10.0 mmol) and $Na[C_5Me_5]$ (10.0 mmol) in thf (20 cm^3) was allowed to react for 12 h under gentle reflux. The resulting light red solution was cooled to 25 °C and a solution of Diazald (2.14 g, 10.0 mmol) in thf (20 cm^3) was added dropwise with rapid stirring. Gas was evolved and an orange solid precipitated. The reaction mixture was further stirred for 15 min and was then evaporated to dryness *in vacuo*. Sublimation (80 °C) of the dried residue onto a water-cooled probe afforded 1.3 g (4.8 mmol, 48% yield) of analytically pure $[Cr(\eta\text{-}C_5Me_5)(CO)_2(NO)]$. The molybdenum and tungsten complexes were obtained in yields of 41 and 72% respectively. The elemental analyses and the physical properties of all three compounds are displayed in Table 1.

X-Ray Data Collection and Structure Determination for $[Cr(\eta\text{-}C_5Me_5)(CO)_2(NO)]$.—*Crystal data*. $C_{12}H_{15}CrNO_3$, $M = 273.3$, Monoclinic, $a = 12.346(5)$, $b = 7.805(4)$, $c = 14.378(5)$ Å, $\beta = 106.85(3)°$, $U = 1\,325.9$ Å^3, $Z = 4$, $D_c = 1.37$ g cm^{-3}, $F(000) = 568$, $\mu(\text{Mo-}K_\alpha) = 9.9$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, space group $P2_1/n$.

Single crystals of the compound were obtained by sub-

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† Parts 1 and 2 are refs. 1 and 2 respectively.

limation at 60 °C and were mounted in a glass capillary in air. Final lattice parameters were determined from a least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 15 reflections ($\theta > 20°$) accurately centred on the diffractometer.

Data were collected on an Enraf–Nonius CAD-4 diffractometer with graphite-crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω—2θ scan technique in a manner similar to that described previously.[8] One independent quadrant of data was measured out to $2\theta \leqslant 50°$; a slow scan was performed on a total of 1 802 unique reflections. Since the data were scanned at a speed which would yield a net count of 4 000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 35 was obtained in the prescan. Based on these considerations, the data set of 1 802 reflections (used in the subsequent structural determination and refinement) was considered observed and consisted of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects but not for absorption.

TABLE 1

Elemental analyses and physical properties of $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ (M = Cr, Mo, or W)

Compound	Colour	M.p. (θ_c/°C) [a]	Analyses (%) [b] C	H	N	^{1}H n.m.r.[c] δ (p.p.m.)	I.r. (cm^{-1}) [c] ν(CO)	ν(NO)
$[Cr(\eta\text{-}C_5Me_5)(CO)_2(NO)]$	Red	84.5—85.0	52.8 (52.75)	5.55 (5.55)	5.15 (5.15)	1.81 (s)	2 000s 1 930s	1 670s
$[Mo(\eta\text{-}C_5Me_5)(CO)_2(NO)]$	Orange-red	106.0—107.0	45.45 (45.45)	4.80 (4.75)	4.50 (4.40)	1.98 (s)	2 000s 1 925s	1 642s
$[W(\eta\text{-}C_5Me_5)(CO)_2(NO)]$	Orange	133.5—134.5	35.55 (35.6)	3.75 (3.75)	3.45 (3.45)	2.10 (s)	1 994s 1 910s	1 629s

[a] Under N_2. [b] Calculated values are given in parentheses. [c] In CH_2Cl_2.

Full-matrix least-squares refinement was carried out using the Busing and Levy program ORFLS.* Bond distances and angles were calculated with the aid of ORFFE; the standard deviations were computed from the variance–covariance matrix. The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Neutral-atom scattering factors for Cr, C, O, and N were taken from Cromer and Waber;[9,†] those for H were from ref. 10.

The existence of four molecules per unit cell together with the systematic absences indicated that the molecules occupied the four-fold general position in the space group $P2_1/n$. The position of the chromium atom was located by inspection of a Patterson map. A difference-Fourier map phased on the chromium atom readily revealed the positions of the remaining non-hydrogen atoms. The carbon and nitrogen atoms of the X≡O (X = C or N) ligands were initially treated as carbon atoms. Least-squares refinement with isotropic temperature factors yielded $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.118$. At this point it was clear from the examination of the thermal parameters and the bond lengths within the $Cr(CO)_2(NO)$ unit that the carbonyl and nitrosyl ligands were disordered in such a way as to occupy each of the three equivalent positions one third of the time. A weighted scattering factor ($\frac{2}{3}f_C + \frac{1}{3}f_N$) was adopted for the disordered atoms. The anisotropic refinement of all the non-hydrogen atoms led to an R value of 0.056. The reflections (002) and $(20\bar{2})$ were removed because they apparently suffered from extinction. The methyl-hydrogen atoms were then located on a three-dimensional difference-Fourier map. This yielded a final R value of 0.043 and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(F_o)^2]^{\frac{1}{2}} = 0.049$. The largest parameter shifts in the final cycle of refinement were less than 0.02 of their standard deviations. The standard deviation of an observation of unit weight was 2.00. No systematic variation of $w(|F_o| - |F_c|)^2$ *vs.* $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 2. The thermal parameters and the observed and calculated structure factor amplitudes for this and the other two compounds are given in Supplementary Publication No. SUP 22682 (46 pp.).‡

Data Collection and Structure Solution for $[Mo(\eta\text{-}C_5Me_5)(CO)_2(NO)]$.—*Crystal data.* $C_{12}H_{15}MoNO_3$, $M = 317.2$, Triclinic, $a = 6.992(4)$, $b = 7.828(4)$, $c = 12.955(5)$ Å, $\alpha = 84.70(3)$, $\beta = 86.71(3)$, $\gamma = 75.51(3)°$, $U = 683.2$ Å^3, $Z = 2$, $D_c = 1.54$ g cm^{-3}, $F(000) = 320$, $\mu(\text{Mo-}K_\alpha) = 9.4$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, space group $P\bar{1}$. Following the data collection procedures given above, 2 190 unique observed reflections in the range $2\theta \leqslant 50°$ were obtained. No absorption correction was necessary.

A Patterson map yielded the position of the molybdenum atom and a difference Fourier afforded the positions of all the non-hydrogen atoms. The carbonyl and nitrosyl groups were found to be disordered as in the case of the chromium compound, and the problem was treated in the same fashion. Four cycles of anisotropic refinement gave $R = 0.042$, and the positions of the hydrogen atoms were then revealed on a difference map. Further refinement gave final values of $R = 0.035$ and $R' = 0.043$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. The standard deviation of an observation of unit weight was 0.88. The final values of the positional parameters are given in Table 2.

Data Collection and Structure Refinement for $[W(\eta\text{-}C_5Me_5)(CO)_2(NO)]$.—*Crystal data.* $C_{12}H_{15}NO_3W$, $M = 405.1$, Triclinic, $a = 6.947(4)$, $b = 7.804(4)$, $c = 12.957(5)$ Å, $\alpha = 84.41(3)$, $\beta = 86.58(3)$, $\gamma = 75.48(3)°$, $U = 676.3$ Å^3, $Z = 2$, $D_c = 1.99$ g cm^{-3}, $F(000) = 384$, $\mu(\text{Mo-}K_\alpha) = 90.3$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, space group $P\bar{1}$. The data were collected as described above. A total of 2 132 unique observed reflections in the range $2\theta \leqslant 50°$ were obtained and subsequently corrected for absorption.

* Other crystallographic programs used on a UNIVAC 1110 include ORFFE (distance and angles with estimated standard deviations, by W. R. Busing, K. O. Martin, and H. A. Levy), FOURIER (Fourier synthesis, D. J. Hodgson's version of Dellaca and Robinson's program), ORABS (absorption correction, by D. J. Wehe, W. R. Busing, and H. A. Levy), ORTEP (thermal ellipsoid drawings, by C. K. Johnson), and BPL (least-squares planes, by W. E. Hunter).

† The scattering for the metal atom was in each case corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman: D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

Since this compound was found to be isostructural with that of the molybdenum analogue, the atomic parameters of the latter were used to begin the analysis. Isotropic refinement of the non-hydrogen atoms led to an R index of 0.11. Conversion into anisotropic thermal parameters gave R = 0.075. The hydrogen atoms were then placed in the experimental positions of the molybdenum compound and refined for two cycles with a damping factor of 0.2. The final values were R = 0.073 and R' = 0.097. The largest parameter shifts in the final cycle of refinement were less than 0.10 of their estimated standard deviation. The standard deviation of an observation of unit weight was 4.0. The final values of the positional parameters are given in Table 2.

TABLE 2

Final fractional co-ordinates for $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ with estimated standard deviations in parentheses *

Atom	x/a	y/b	z/c
(*a*) M = Cr			
Cr	0.763 18(6)	0.178 18(9)	0.036 76(5)
O(1)	0.872 4(3)	−0.078 6(5)	0.181 6(3)
O(2)	0.696 1(3)	−0.533 3(5)	−0.133 4(3)
O(3)	0.536 0(3)	0.173 4(6)	0.073 9(3)
X(1)	0.825 4(3)	0.019 5(5)	0.123 2(3)
X(2)	0.720 4(4)	0.033 3(6)	−0.065 6(3)
X(3)	0.624 0(4)	0.172 0(6)	0.059 4(3)
C(1)	0.923 6(3)	0.314 9(6)	0.055 1(3)
C(2)	0.855 4(4)	0.333 4(5)	−0.042 2(3)
C(3)	0.756 1(4)	0.422 5(5)	−0.041 8(3)
C(4)	0.761 8(4)	0.461 7(5)	0.056 5(3)
C(5)	0.864 9(4)	0.393 3(6)	0.116 0(3)
C(6)	1.039 5(4)	0.238 5(7)	0.087 9(5)
C(7)	0.889 9(5)	0.281 8(7)	−0.130 4(4)
C(8)	0.662 8(5)	0.482 0(7)	−0.130 1(4)
C(9)	0.679 3(5)	0.567 7(7)	0.089 3(4)
C(10)	0.906 8(5)	0.411 8(8)	0.225 3(4)
H(1)[C(6)]	1.050 2	0.152 5	0.046 5
H(2)[C(6)]	1.055 0	0.197 4	0.154 8
H(3)[C(6)]	1.100 5	0.315 1	0.086 5
H(4)[C(7)]	0.828 0	0.277 4	−0.185 6
H(5)[C(7)]	0.927 0	0.178 0	−0.118 2
H(6)[C(7)]	0.946 6	0.357 3	−0.147 1
H(7)[C(8)]	0.590 1	0.484 7	−0.116 8
H(8)[C(8)]	0.658 7	0.418 9	−0.186 2
H(9)[C(8)]	0.677 1	0.594 6	−0.150 9
H(10)[C(9)]	0.663 2	0.524 9	0.146 7
H(11)[C(9)]	0.613 8	0.579 9	0.037 8
H(12)[C(9)]	0.707 8	0.681 6	0.103 6
H(13)[C(10)]	0.949 4	0.514 9	0.243 7
H(14)[C(10)]	0.954 8	0.321 6	0.252 6
H(15)[C(10)]	0.847 8	0.417 6	0.259 6
(*b*) M = Mo			
Mo	−0.001 76(6)	0.192 99(6)	0.242 65(4)
O(1)	0.173 2(8)	0.354 7(8)	0.047 7(4)
O(2)	0.372 9(7)	−0.107 4(7)	0.287 3(6)
O(3)	0.109 8(7)	0.442 5(6)	0.386 0(4)
X(1)	0.110 8(8)	0.293 6(8)	0.122 8(4)
X(2)	0.238 2(8)	0.008 5(7)	0.268 8(6)
X(3)	0.073 6(7)	0.347 4(6)	0.330 6(4)
C(1)	−0.195 7(7)	−0.006 5(7)	0.224 4(4)
C(2)	−0.272 5(7)	0.147 1(7)	0.157 5(4)
C(3)	−0.344 8(7)	0.291 3(7)	0.222 7(4)
C(4)	−0.314 0(7)	0.223 5(8)	0.326 7(4)
C(5)	−0.220 8(7)	0.037 8(7)	0.326 9(4)
C(6)	−0.117 0(10)	−0.191 7(8)	0.191 0(6)
C(7)	−0.289 8(9)	0.157 7(10)	0.043 5(5)
C(8)	−0.454 0(8)	0.475 1(8)	0.185 6(6)
C(9)	−0.378 2(9)	0.325(1)	0.419 5(6)
C(10)	−0.181(1)	−0.091(1)	0.421 4(6)
H(1)[C(6)]	−0.016 2	−0.259 6	0.236 1
H(2)[C(6)]	−0.071 8	−0.194 6	0.121 6
H(3)[C(6)]	−0.230 3	−0.249 9	0.196 4
H(4)[C(7)]	−0.400 8	0.139 2	0.023 6
H(5)[C(7)]	−0.185 1	0.067 9	0.008 0
H(6)[C(7)]	−0.285 1	0.272 9	0.010 4
H(7)[C(8)]	−0.580 1	0.484 9	0.172 2
H(8)[C(8)]	−0.393 7	0.524 8	0.127 7
H(9)[C(8)]	−0.461 2	0.558 0	0.245 6
H(10)[C(9)]	−0.508 0	0.341 9	0.438 2
H(11)[C(9)]	−0.354 9	0.445 6	0.401 9
H(12)[C(9)]	−0.319 4	0.270 8	0.481 5
H(13)[C(10)]	−0.054 7	−0.177 1	0.409 2
H(14)[C(10)]	−0.278 2	−0.156 5	0.432 3
H(15)[C(10)]	−0.177 1	−0.029 5	0.485 9

TABLE 2 (*Continued*)

Atom	x/a	y/b	z/c
(*c*) M = W			
W	−0.000 2(1)	0.192 6(1)	0.242 20(8)
O(1)	0.185(3)	0.345(4)	0.045(2)
O(2)	0.371(3)	−0.110(3)	0.289(3)
O(3)	0.112(3)	0.443(3)	0.384(2)
X(1)	0.120(3)	0.280(4)	0.121(2)
X(2)	0.233(4)	0.009(3)	0.270(2)
X(3)	0.079(3)	0.339(3)	0.329(2)
C(1)	−0.192(3)	−0.010(3)	0.224(2)
C(2)	−0.275(3)	0.152(3)	0.160(2)
C(3)	−0.338(3)	0.284(3)	0.220(2)
C(4)	−0.313(3)	0.223(3)	0.325(2)
C(5)	−0.224(3)	0.039(4)	0.328(2)
C(6)	−0.106(5)	−0.197(3)	0.193(3)
C(7)	−0.291(4)	0.158(4)	0.043(2)
C(8)	−0.457(4)	0.475(4)	0.182(3)
C(9)	−0.379(4)	0.324(5)	0.419(2)
C(10)	−0.175(6)	−0.095(5)	0.425(2)
H(1)[C(6)]	−0.016 2	−0.259 6	0.236 1
H(2)[C(6)]	−0.071 8	−0.194 6	0.121 6
H(3)[C(6)]	−0.230 3	−0.249 9	0.196 4
H(4)[C(7)]	−0.400 8	0.139 2	0.023 6
H(5)[C(7)]	−0.185 1	0.067 9	0.008 0
H(6)[C(7)]	−0.285 1	0.272 9	0.010 4
H(7)[C(8)]	−0.580 1	0.484 9	0.172 2
H(8)[C(8)]	−0.393 7	0.524 8	0.127 7
H(9)[C(8)]	−0.461 2	0.558 0	0.245 6
H(10)[C(9)]	−0.508 0	0.341 9	0.438 2
H(11)[C(9)]	−0.354 9	0.445 6	0.401 9
H(12)[C(9)]	−0.319 4	0.270 8	0.481 5
H(13)[C(10)]	−0.054 7	−0.177 1	0.409 2
H(14)[C(10)]	−0.278 2	−0.156 5	0.432 3
H(15)[C(10)]	−0.177 1	−0.029 5	0.485 9

* X = C or N.

RESULTS AND DISCUSSION

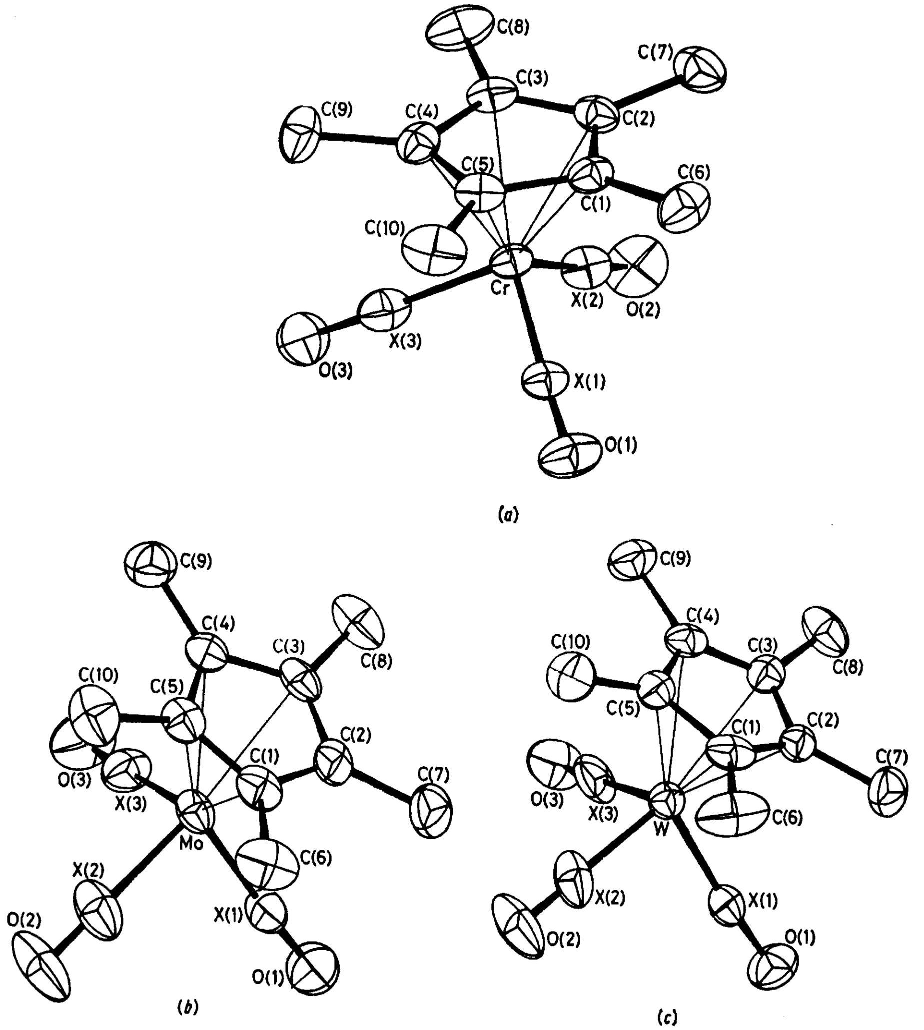
Synthesis and Physical Properties of $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ (M = Cr, Mo, *or* W).—The syntheses of $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ (M = Cr, Mo, or W), depicted in equations (1) and (2), were achieved in a manner similar to

$$Na[C_5Me_5] + [M(CO)_6] \longrightarrow Na[M(\eta\text{-}C_5Me_5)(CO)_3] + 3CO \quad (1)$$

$$Na[M(\eta\text{-}C_5Me_5)(CO)_3] + [NO][MeNO_2SC_6H_4Me\text{-}p] \xrightarrow{\text{thf}} [M(\eta\text{-}C_5Me_5)(CO)_2(NO)] + CO + Na[MeNO_2SC_6H_4Me\text{-}p] \quad (2)$$

the preparation of the analogous cyclopentadienyl compounds.[11] The expected higher nucleophilicity of the pentamethylcyclopentadienyl anion facilitated attack upon the hexacarbonyl reactants and, indeed, equation (1) was driven to completion within 12 h for all three metals. Unfortunately, equation (2) did not proceed as smoothly as in the case of the cyclopentadienyl analogues so that the desired products were obtained in only fair overall yields.

The physical properties of the $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ complexes are given in Table 1. Dichloromethane solutions of all three complexes are sufficiently stable in air to allow the recording of their i.r. and ^{1}H n.m.r. spectra. In the solid state, the compounds are stable in air for long periods of time and may be stored under nitrogen indefinitely. They exhibit sharp melting points without decomposition and are freely soluble in most organic solvents including hexanes.



(a)

(b)

(c)

FIGURE 1 Molecular structures of $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ (a) M = Cr, (b) M = Mo, and (c) M = W, with the atoms represented by their 30% probability ellipsoids for thermal motion

The CO and NO stretching frequencies of these complexes (Table 1) are 10—20 cm^{-1} lower than those of the corresponding cyclopentadienyl compounds.[11] Neglecting any steric interference of the η^5-bonded C_5Me_5 ligand with the rest of the molecule and assuming a constant M–X–O (X = C or N) geometry (see below), this observation is consistent with the greater electron-donating capability of η-C_5Me_5 relative to η-C_5H_5. Also, as in the case of the cyclopentadienyl compounds, the decrease in the CO and NO stretching frequencies, as the central metal becomes heavier, is indicative of increasing d_π–p_{π^*} bonding. The concomitant lowering in electron density about the metal atom is evidenced (Table 1) by the deshielding of the methyl protons of the η-bonded ring.

The molecular structures and atom-numbering schemes for the compounds are presented in Figure 1, and the bond distances and bond angles are given in Table 3 (additional bond lengths and angles are given in SUP 22682). Although the molecules are virtually identical in appearance, only the molybdenum and tungsten complexes have the same crystallographic environment. This is in contrast to the series $[M(\eta\text{-}C_5H_5)(CO)_2(NO)]$ where all three are isostructural.[1,2]

In $[M(\eta\text{-}C_5H_5)(CO)_2(NO)]$, the cyclopentadienyl groups are bonded in a symmetrical fashion. However, a significant asymmetry is observed for $[M(\eta\text{-}C_5Me_5)(CO)_2\text{-}(NO)]$. For M = Cr, the four equivalent Cr–C(π) lengths average 2.200(5) Å, and the remaining one, 2.231(4) Å, is 0.031(7) Å (4.4 σ) longer. With M = Mo, a different crystal system is found, but again there are four equivalent Mo–C(π) distances at 2.345(3) Å, and one 0.020(6) Å (3.3 σ) longer at 2.365(5) Å. These deviations apparently involve a tilt of the five-membered rings: in the molecules with M = Cr or Mo the rings are planar to 0.005 Å. (Figures 2 and 3 show stereoscopic views of the unit-cell packing in the chromium and molybdenum complexes respectively.) Because of the relatively high standard deviations involved, a valid comparison cannot be made for the tungsten compound. One might expect an electronic effect of this sort if the stronger electron-withdrawing nitrosyl group were *trans* to the longer M–C(π) bond, but it was not possible to define the disorder of carbonyl and nitrosyl ligands with sufficient precision to discern this. A similar *trans* effect, likely electronic in origin, was observed in the non-disordered [$Cr(\eta^5$-9*H*-$C_{13}H_9)(CO)_2(NO)$].[1]

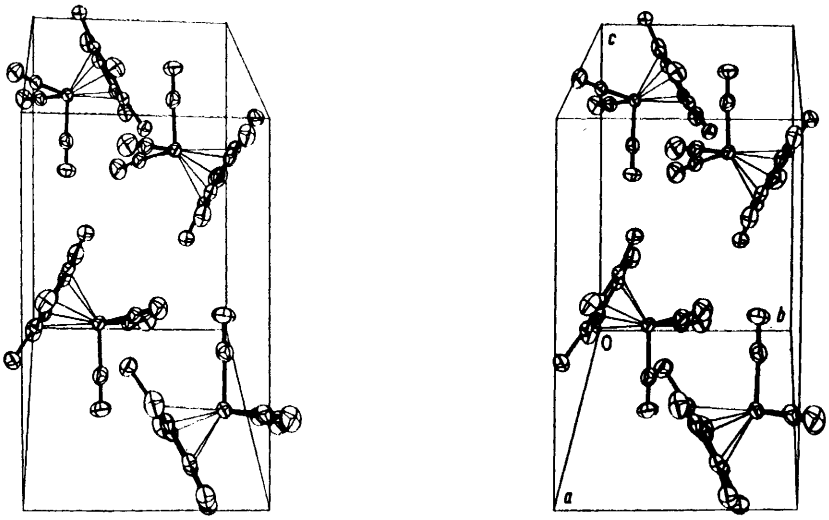


FIGURE 2 Stereoscopic view of the unit-cell packing of [$Cr(\eta$-$C_5Me_5)(CO)_2(NO)$]

The complexes containing the more electron-donating pentamethylcyclopentadienyl group show a larger average X–L–X (X = C or N) angle than do their cyclopentadienyl counterparts: for M = Cr, 94.9° *vs.* 92.6°; for M = Mo, 92.6° *vs.* 91.6°; for M = W, 92.3° *vs.* 91.4°. It appears, therefore, that the X–M–X angles are more heavily dependent on electronic effects than upon any incipient X≡O · · · methyl (ring) steric repulsion. Further support for this hypothesis is clearly demonstrated by the [$M(\eta$-$C_5Me_5)(CO)_2(NO)$] series in which the X–Cr–X angle is 2° larger than the X–Mo–X angle, even though the Cr–C(π) average distance of 2.206 Å is considerably shorter than the corresponding Mo–C(π) distance of 2.350 Å.

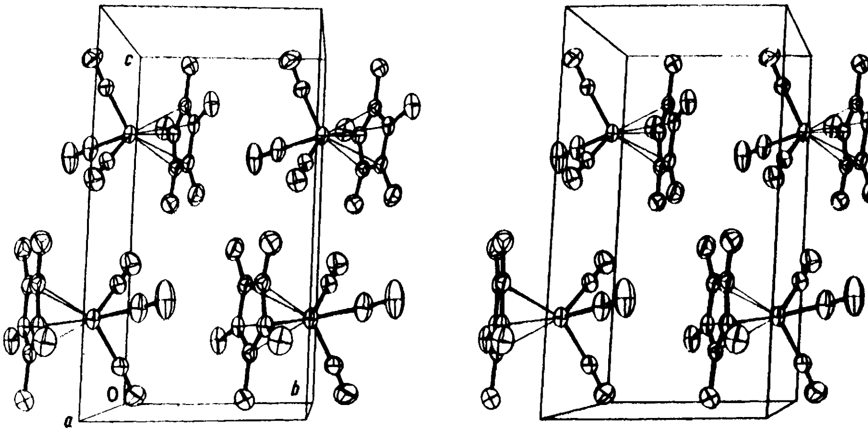


FIGURE 3 Stereoscopic view of the unit-cell packing of [$Mo(\eta$-$C_5Me_5)(CO)_2(NO)$]

The considerable displacement of the ring-methyl groups out of the ring plane *exo* to the metal atom, in (η-C_5Me_5)-containing structures, has previously been noted.[5,6,12–16] The phenomenon has been attributed to intramolecular steric interactions,[5,6,12,13] or to electronic effects.[16] As displayed in Table 4, all three [$M(\eta$-$C_5Me_5)(CO)_2(NO)$] complexes also have methyl groups which are displaced away from the metal, 0.034 to 0.120 Å out of the least-squares plane of the ring-carbon atoms. However, steric crowding cannot be reasonably invoked since the shortest contact distance of 2.92 Å between any methyl-hydrogen atom and any of the nitrogen, carbon, or oxygen atoms (of CO and NO) is sufficiently greater than the sum of the H · · · N, H · · · C, or H · · · O van der Waals radii. Consistent with this lack of steric interaction, neither the out-of-plane deviation nor the X–M–X angle (see above) are seen to be dependent upon

TABLE 3

Comparison of structural parameters for $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ (M = Cr, Mo, or W) with estimated standard deviations in parentheses *

	Cr	Mo	W
(*a*) Bond lengths (Å)			
M–C(1)	2.198(4)	2.346(5)	2.354(22)
M–C(2)	2.192(4)	2.366(5)	2.358(21)
M–C(3)	2.205(4)	2.349(5)	2.318(23)
M–C(4)	2.205(4)	2.348(5)	2.345(22)
M–C(5)	2.231(4)	2.242(5)	2.367(21)
M–Cent	1.846	2.016	2.008
M–X(1)	1.765(4)	1.891(6)	1.891(25)
M–X(2)	1.809(5)	1.942(6)	1.911(26)
M–X(3)	1.841(5)	1.923(5)	1.886(24)
X(1)–O(1)	1.160(5)	1.153(6)	1.179(29)
X(2)–O(2)	1.152(5)	1.150(7)	1.182(30)
X(3)–O(3)	1.164(5)	1.163(6)	1.200(27)
(*b*) Bond angles (°)			
X(1)–M–X(2)	95.7(2)	93.0(3)	91(1)
X(1)–M–X(3)	95.5(2)	92.4(2)	95(1)
X(2)–M–X(3)	93.4(2)	92.4(2)	91(1)
X–M–Cent	121.7	123.4	123
M–X(1)–O(1)	175.7(4)	177.4(5)	175(2)
M–X(2)–O(2)	176.2(4)	175.6(5)	176(2)
M–X(3)–O(3)	177.9(5)	176.6(5)	174(2)

* X = C or N. Cent = centroid of C_5 ring.

the M–Cent distance (Cent = centroid of C_5 ring). It appears, therefore, that the effect can only be explained on electronic grounds in which the ring-carbon atoms assume a small amount of sp^3 character.[16]

TABLE 4

Least-squares planes for $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ (M = Cr, Mo, or W) *

(*a*) Equations of planes

M = Cr: $0.4938X + 0.8671Y - 0.0657Z + 7.5941 = 0$
M = Mo: $0.9779X + 0.1987Y - 0.0643Z + 1.3313 = 0$
M = W: $0.9795X + 0.1926Y - 0.0591Z + 1.3096 = 0$

(*b*) Deviation (Å) of atoms from planes

Atom	M = Cr	M = Mo	M = W
C(1)	−0.003	0.004	0.017
C(2)	−0.000	−0.005	−0.017
C(3)	0.004	0.005	0.010
C(4)	−0.005	−0.002	0.002
C(5)	0.005	−0.001	−0.012
M	1.846	2.016	2.008
C(6)	−0.095	−0.097	−0.038
C(7)	−0.123	−0.103	−0.128
C(8)	−0.092	−0.118	−0.163
C(9)	−0.123	−0.078	−0.090
C(10)	−0.052	−0.161	−0.115

* The atoms of the five-membered ring were used to compute the planes.

Unfortunately, the unresolved disorder of the CO and NO ligands precludes any possible correlation between X–O (X = C or N) bond lengths and i.r. spectroscopic studies. However, consistent with the observed C–O and N–O stretching frequencies (Table 1) and similar to the results found for $[Cr(\eta\text{-}9H\text{-}C_{13}H_9)(CO)_2(NO)]$ [1] and $[M(\eta\text{-}C_5H_5)(CO)_2(NO)]$ (M = Cr,[1] Mo,[2] or W [2]), the M–X–O angles for all three $[M(\eta\text{-}C_5Me_5)(CO)_2(NO)]$ complexes are very nearly linear.

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