amples of anti addition prior to **2** and others of its type.[16] The NMR data for **2** could have easily lead to the wrong assignment. It seems reasonable to conclude that the normal mode of attack by electrophilic acetylenes on η^1-C_5H_5 rings in stable metal complexes will be such as to afford the anti product, at least where other bulky ligands are coordinated to the metal.

The structure of **2** provides major confirmation of the postulate[15] of hyperconjugation in **1** whereby the electrons of the Pt–Cp bond are delocalized with those of the diene unit. This causes the Pt–Cp bond distance to be longer than the Pt–CH_3 one. Since such delocalization is not possible for **2**, the differences observed in the NMR and structural trans influences between the methyl and Cp groups of **1** should not be observed for the methyl and norbornadiene groups of **2**. This is indeed the case, for the bond distances of these latter ligands to platinum are the same in **2**. This was also evident in the ^{1}H NMR of **2**, where, although different resonances for the vinyl protons trans to the two ligands were resolved, the *J*(PtH(vinyl)) coupling constants were identical.[16] Comparing the two structures, the Pt–CH_3 distances in **1** and **2** are indistinguishable [**1**, 2.068 (8) and **2**, 2.054 (14) Å; 0.9σ] whereas the other Pt–C(sp^3) distances are quite different [Pt–Cp, 2.151 (8) and Pt–$C_7F_6H_5$, 2.054 (10) Å; 7.6σ]. Finally, the COD ligand in **2** is twisted in a manner similar to that in **1**, further substantiating the claim that the differences in the platinum–carbon(sp^3) bonds in **1** are not due to steric effects. This comparison of **1** and **2** is satisfyingly consistent with the postulate of hyperconjugative effects in **1**.

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Registry No. 1, 56200-09-0; **2**, 56200-13-6; $CF_3C{\equiv}CCF_3$, 692-50-2.

Supplementary Material Available: Listing of structure amplitudes (8 pages). Ordering information is given on any current masthead page.

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Structural Studies on Some (η^5-C_5H_5)M(CO)$_3$X Molecules: (η^5-C_5H_5)W(CO)$_3$Cl, (η^5-C_5H_5)Mo(CO)$_3$Cl, and (η^5-C_5H_5)Mo(CO)$_3$HgCl

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Single-crystal X-ray diffraction studies have been completed on three simple (η^5-C_5H_5)M(CO)$_3$X derivatives. Crystal data are as follows: for (η^5-C_5H_5)W(CO)$_3$Cl, $P2_1/n$, a = 7.9732 (19) Å, b = 10.695 (6) Å, c = 11.3719 (18) Å, β = 99.096 (16)°, R_F = 3.3% for 1690 reflections; for (η^5-C_5H_5)Mo(CO)$_3$Cl, $P2_1/c$, a = 7.9590 (17) Å, b = 10.7180 (28) Å, c = 14.9587 (33) Å, β = 130.968 (15)°, R_F = 2.4% for 1194 reflections; for (η^5-C_5H_5)Mo(CO)$_3$HgCl, $P\bar{4}2_1c$, a = 12.042 (1) Å, c = 15.319 (2) Å, R_F = 4.2% for 1460 reflections. The (η^5-C_5H_5)M(CO)$_3$Cl complexes are isostructural with W–Cl = 2.490 (2) Å and Mo–Cl = 2.498 (1) Å; in contrast to this, the average metal–carbon(ring) distances are W–C = 2.326 Å and Mo–C = 2.304 Å; i.e., the tungsten–ligand distance is less than the molybdenum–ligand distance in the direction of the halide ligand but is greater in the direction of the cyclopentadienyl ligand. In (η^5-C_5H_5)Mo(CO)$_3$HgCl, the average Mo–C(ring) distance is 2.303 Å, with Mo–Hg = 2.683 (1) Å and Mo–Hg–Cl = 160.02 (9)°.

Introduction

While definitive structural studies of [(η^5-C_5H_5)W(CO)$_3$]$_2$ and [(η^5-C_5H_5)Mo(CO)$_3$]$_2$ have been carried out (showing the metal–metal distances W–W = 3.222 (1) Å and Mo–Mo = 3.235 (1) Å)[1] and a large number of structural studies on species containing the [(η^5-C_5H_5)Mo(CO)$_3$] unit have been carried out,[2-12] there have been fewer structural studies of the analogous [(η^5-C_5H_5)W(CO)$_3$]-containing species[13-17] and no comparative studies of simple (η^5-cyclopentadienyl)tricarbonylmetal halides.

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(1) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.

(2) (η^5-C_5H_5)Mo(CO)$_3C_2H_5$: Bennett, M. J.; Mason, R. *Proc. Chem. Soc.* **1963**, 273. Bennett, M. J. Ph.D. Thesis, Sheffield University, England, 1965, pp 38–74.

(3) (η^5-C_5H_5)Mo(CO)$_3C_3F_7$: Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1967**, *6*, 1213.

(4) [(η^5-C_5H_5)Mo(CO)$_3$][(η^5-C_5H_5)Fe(CO)$_2$]$_2$SnCl: O'Connor, J. E.; Corey, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 3930.

(5) [(η^5-C_5H_5)Mo(CO)$_3$]Mn(CO)$_5$: Biryukov, B. P.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1968**, *9*, 655.

(6) (η^5-C_5H_5)Mo(CO)$_3CH_2CO_2H$: Ariyaratne, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Prout, C. K.; Swanwick, M. G. *J. Chem. Soc. A* **1968**, 1309.

(7) [(η^5-C_5H_5)Mo(CO)$_3$](μ_4-S)[(η^5-C_5H_5)Mo(CO)$_2$][Re(CO)$_3$]$_2$(μ_3-S): Vergamani, P. J.; Vahrenkamp, H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6326.

(8) [(η^5-C_5H_5)Mo(CO)$_3$]$_3$Tl: Rajaram, J.; Ibers, J. A. *Inorg. Chem.* **1973**, *12*, 1313.

(9) [(η^5-C_5H_5)Mo(CO)$_3$]$_2$Zn and [(η^5-C_5H_5)Mo(CO)$_3$]$_2Zn_2Cl_2(OEt_2)_2$: St. Denis, J.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 5427.

(10) [(η^5-C_5H_5)Mo(CO)$_3$]ZnBr(THF)$_2$ and [Bu_4N^+][(η^5-C_5H_5)Mo(CO)$_3^-$]: Crotty, D. E.; Corey, E. R.; Anderson, T. J.; Glick, M. D.; Oliver, J. D. *Inorg. Chem.* **1977**, *16*, 920.

(11) [(η^5-C_5H_5)Mo(CO)$_3$]$_2$Hg: Mickiewicz, M. H.; Raston, C. L.; White, A. H.; Wild, S. B. *Aust. J. Chem.* **1977**, *30*, 1685.

(12) [(η^5-C_5H_5)Mo(CO)$_3$][(η^5-C_5H_5)$_2$Nb]: Pasynskii, A. A.; Skripkin, Yu. V.; Eremenko, I. L.; Kalinnikov, V. T.; Aleksandrov, G. G.; Andrianov, V. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1979**, *165*, 49.

(13) (η^5-C_5H_5)W(CO)$_3$(σ-C_6H_5): Semion, V. A.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1968**, *9*, 1046.

(14) (η^5-C_5H_5)W(CO)$_3$(AuPPh$_3$): Wilford, J. B.; Powell, H. M. *J. Chem. Soc. A* **1969**, 8.

(15) [(η^5-C_5H_5)W(CO)$_3$]$_3$Ga: Conway, A. J.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1945.

(16) [(η^5-C_5H_5)W(CO)$_3$]$_2$(AlMe$_2$)$_2$: Conway, A. J.; Gainsford, G. J.; Schrieke, R. R.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 2499.

(17) (η^5-C_5H_5)W(CO)$_3$(GaMe$_2$): St. Denis, J. N.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1977**, *129*, 1.

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We now report the results of an X-ray crystallographic study of the simple species $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ in conjunction with redeterminations of the structures of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$[18] and $(\eta^5\text{-}C_5H_5)Mo(CO)_3HgCl$.[19]

Experimental Section

The three structural studies were carried out with use of a Syntex P2$_1$ automated four-circle diffractometer in conjunction with the Syntex XTL system. The XTL system is comprised of a Data General NOVA 1200 computer (24K of 16-bit word memory, with a parallel floating-point processor for 32- or 64-bit arithmetic), a Diablo moving-head disk unit (1.25 million 16-bit word capacity), a Versatec electrostatic printer/plotter, and the SUNYAB-modified version of the XTL interactive crystallographic program package.

Crystals were mounted on fibers (with GE varnish). In each case the fiber was set into an aluminum pin with beeswax and was mounted in a eucentric goniometer on the Syntex P2$_1$ diffractometer. Crystal alignment, determination of cell parameters, and collection of X-ray diffraction data were performed by standard methods[20] (see Table I). Data were corrected for Lorentz and polarization effects and absorption (via 2θ and ϕ interpolation between ψ scans of selected reflections) and were merged to a unique set of reflections. Systematically absent reflections were deleted. Any reflection with $I < 0$ had its intensity reset to zero.

Each structure was solved with use of a combination of Patterson, difference-Fourier, and full-matrix least-squares refinement techniques.

The analytical scattering factors of the appropriate neutral atoms[21] were used for computing the calculated structure factors; both the $\Delta f'$ and $i\Delta f''$ components[22] of anomalous dispersion were included for all nonhydrogen atoms. The function $\sum w(|F_o| - |F_c|)^2$ was minimized during the least-squares refinement process; the assigned weights are given by $w = [\sigma^2(|F_o|) + p^2|F_o|^2]^{-1}$, where p is the "ignorance factor".

1. Structural Study of $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$. This complex was obtained as a minor byproduct in some studies of mixed iridium-tungsten metal cluster complexes. The crystal used for the diffraction study had dimensions 0.23 × 0.13 × 0.10 mm. The systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ along with the C_{2h} diffraction symmetry indicate the space group $P2_1/n$. Two forms of data were collected and merged to a single set ($R(I) = 3.6\%$ for 1684 pairs). Relative absorption factors ranged from 2.1 to 1.0.

Full-matrix least-squares refinement of positional and anisotropic thermal parameters (with hydrogen atoms included in calculated trigonal positions with C–H = 0.95 Å)[23] led to convergence with $R_F = 3.3\%$, $R_{wF} = 4.0\%$, and GOF = 0.97 for all 1690 data ($R_F = 2.8\%$, $R_{wF} = 3.8\%$ for those 1519 data with $I > 3\sigma(I)$). A final difference-Fourier map showed no unexpected features. No correction for secondary extinction was necessary.

2. Structural Study of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$. This complex was prepared by standard literature methods via the route $Mo(CO)_6 \rightarrow [(\eta^5\text{-}C_5H_5)Mo(CO)_3^-][Na^+] \rightarrow (\eta^5\text{-}C_5H_5)Mo(CO)_3H \rightarrow (\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$.[24,25] The crystal used was of dimension 0.23 × 0.15 × 0.10 mm. We followed Chaiwasie and Fenn[18] in selecting the very obtuse monoclinic cell corresponding to the standard space group $P2_1/c$ (absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$). Two forms of data were collected and merged to a single set ($R(I) = 1.1\%$ for 1019 averaged pairs). Relative absorption factors ranged from 1.12 to 1.00.

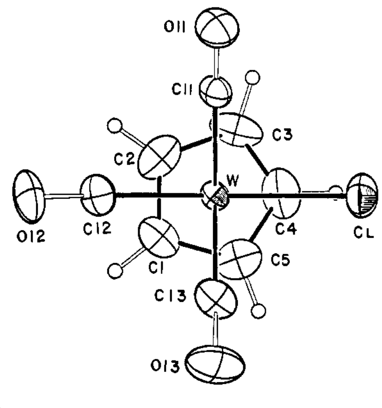

Figure 1. $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ molecule, projected on to the cyclopentadienyl plane.

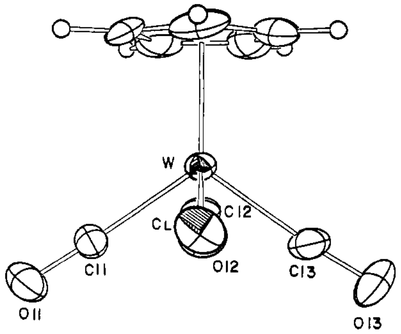

Figure 2. $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ molecule, viewed from the side.

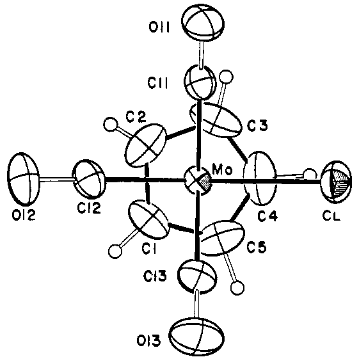

Figure 3. $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ molecule, projected on to the cyclopentadienyl plane.

Full-matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for nonhydrogen atoms, and isotropic thermal parameters for hydrogen atoms resulted in final convergence with $R_F = 2.4\%$, $R_{wF} = 2.1\%$, and GOF = 1.07 for all 1194 data ($R_F = 1.9\%$, $R_{wF} = 2.0\%$ for those 1073 data with $I > 3\sigma(I)$). A final difference-Fourier synthesis was "clean" ($\rho(\max) = 0.24$ e Å^{-3}), and no correction was necessary for secondary extinction.

3. Structural Study of $(\eta^5\text{-}C_5H_5)Mo(CO)_3HgCl$. The crystals used in this study were obtained as a minor component from the reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ with (i) sodium amalgam, (ii) acetic acid, and (iii) carbon tetrachloride. Other synthetic routes are available.[26] The crystal used had dimensions of 0.18 × 0.17 × 0.15 mm. The D_{4h} Laue symmetry and the systematic absences (hhl for $l = 2n + 1$, $h00$ for $h = 2n + 1$) confirm the noncentrosymmetric tetragonal space group $P\bar{4}2_1c$ (D_{2d}^4, No. 114) previously reported by Albright, Glick, and Oliver.[19] Two octants of data were collected ($+h, +k, \pm l$) and merged to a single set corresponding to the D_{2d} ($\bar{4}2m$) point group symmetry of the space group. (With anomalous dispersion included, we have $I(hkl) = I(khl) \neq I(hk\bar{l}) = I(kh\bar{l})$. The agreement index between the intensities was 2.5% for 1198 pairs of averaged reflections.

Normal refinement of positional and anisotropic thermal parameters, with hydrogen atoms included in calculated positions, led to convergence with the unexpectedly high residuals of $R_F = 7.5\%$ and $R_{wF} = 9.3\%$. However, the crystal is noncentrosymmetric; following

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(18) Chaiwasie, S.; Fenn, R. H. *Acta Crystallogr., Sect. B*, **1968**, *B24*, 525. This previous structural study of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ is of low precision. Based on 799 visually-estimated data, the discrepancy index is $R_F = 11.0\%$.

(19) Albright, M. J.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1978**, *161*, 221. This previously reported structural study of $(\eta^5\text{-}C_5H_5)Mo(CO)_3HgCl$ is based on 854 data with $I > 3\sigma(I)$. The discrepancy indices are $R_F = 5.8\%$ and $R_{wF} = 6.2\%$.

(20) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

(21) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101.

(22) See ref 21, pp 149–150.

(23) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(24) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 107.

(25) Fischer, E. O.; Pruett, R. L. *Inorg. Synth.* **1963**, *7*, 135.

(26) Mays, M. J.; Robb, J. D. *J. Chem. Soc. A* **1968**, 329.

Table I. Experimental Data for the X-ray Diffraction Studies

	(η^5-C_5H_5)W(CO)$_3$Cl	(η^5-C_5H_5)Mo(CO)$_3$Cl	(η^5-C_5H_5)Mo(CO)$_3$HgCl
	(A) Crystal Parameters		
cryst system	monoclinic	monoclinic	tetragonal
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{4}2_1c$ (No. 114)
a, Å	7.9732 (19)	7.9590 (17)	12.042 (1)
b, Å	10.695 (6)	10.7180 (28)	
c, Å	11.3719 (18)	14.9587 (33)	15.319 (2)
β, deg	99.096 (16)	130.968 (15)	
V, Å^3	957.5 (6)	963.5 (4)	2221.7 (5)
Z	4	4	8
mol wt	368.42	280.52	481.11
ρ(calcd), g cm^{-3}	2.56	1.93	2.88
μ, cm^{-1}	130.0	15.8	154.0
T, °C	25	24	25
	(B) Measurement of Data		
diffractometer	Syntex $P2_1$		
radiation	Mo Kα ($\bar{\lambda}$ 0.710 730 Å)		
monochromator	highly oriented graphite, equatorial mode, 2θ(mono) = 12.2°		
reflctns measd	$\pm h$, $+k$, $\pm l$ (2 forms)	$\pm h$, $+k$, $\pm l$ (2 forms)	$+h$, $+k$, $\pm l$ (2 forms)
2θ range, deg	3.0–50.0	3.5–45.0	3.0–45.0
scan type	coupled θ(cryst)–2θ(counter)		
scan speed, deg/min	3.0	2.5	3.0
scan range, deg	[2θ(Mo Kα_1) − 0.7]– [2θ(Mo Kα_2) + 0.7]	[2θ(Mo Kα_1) − 1.0]– [2θ(Mo Kα_2) + 1.0]	[2θ(Mo Kα_1) − 1.0]– [2θ(Mo Kα_2) + 1.0]
bkgd measd	stationary-crystal, stationary counter at beginning and end of scan, each for one-third of the time taken for the scan		
reflctns colld	3694 total, 1690 independent	2816 total, 1194 independent	3182 total, 1460 independent
data averaging $R(I)$	3.6% for 1684 pairs	1.1% for 1019 pairs	2.5% for 1198 pairs

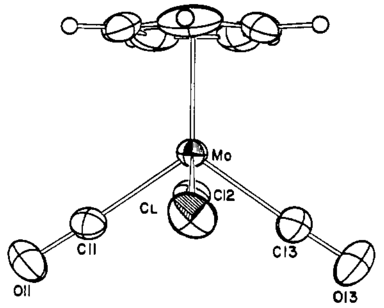

Figure 4. (η^5-C_5H_5)Mo(CO)$_3$Cl molecule, viewed from the side.

inversion of the coordinates of all atoms (x, y, z) → ($1 - x$, $1 - y$, $1 - z$), continued refinement led to convergence with the dramatically lowered residuals R_F = 4.2%, R_{wF} = 3.3%, and GOF = 0.91 for all 1460 data (R_F = 3.1% and R_{wF} = 3.4% for those 1274 reflections with $I > 3\sigma(I)$).

A correction for secondary extinction was included in the model. The resulting value of g was 3.3×10^{-7}; this enters the equation for the corrected observed structure factor amplitude in the form $|F_{o,cor}| = |F_{o,uncor}|(1.0 + gI_0)$. A final difference-Fourier synthesis showed no significant features.

Positional and thermal parameters for the three structural studies are collected in Table II.

Discussion

A. (η^5-C_5H_5)W(CO)$_3$Cl and (η^5-C_5H_5)Mo(CO)$_3$Cl Molecules. Interatomic distances and angles for these two species are compared in Table III. Characteristic views of the molecules are shown in Figures 1–4. The crystals are composed of discrete molecular units with no close intermolecular contacts. The two species are isomorphous. Nevertheless, we have solved the structure of the tungsten derivative with use of the nonstandard space group $P2_1/n$ (which provides a β angle of about 99° and near orthogonality of the crystallographic coordinate system, thus aiding in the least-squares refinement process), whereas we have followed Chaiwasie and Fenn[18] in using a very obtuse β angle (close to 131°) in the standard space group $P2_1/c$ in our analysis of the molybdenum complex. The redetermined structure of (η^5-C_5H_5)Mo(CO)$_3$Cl is in basic agreement with that determined previously from photographic data,[18] but estimated standard deviations are reduced to about 10% of their previous values, and there is also a substantial change in the derived Mo–Cl bond length (see below).

Dimensions within the (η^5-C_5H_5)W(CO)$_3$Cl and (η^5-C_5H_5)Mo(CO)$_3$Cl molecules are closely similar, principally as a result of the lanthanide contraction which causes a third-row transition-metal ion to have a covalent radius very close to that of the analogous second-row transition-metal ion in that group.[27] The following comparisons are of interest.

(1) The tungsten–chlorine bond length of 2.490 (2) Å is 0.008 Å shorter than the molybdenum–chlorine bond length of 2.498 (1) Å. (Note that this latter value is substantially shorter than that of 2.542 (9) Å reported originally by Chaiwasie and Fenn).[18] This apparent difference in covalent radius is in excellent agreement with the results of accurate crystallographic studies of [(η^5-C_5H_5)W(CO)$_3$]$_2$ and [(η^5-C_5H_5)Mo(CO)$_3$]$_2$ (W–W = 3.222 (1) Å and Mo–Mo = 3.235 (1) Å,[1] whence r(Mo) − r(W) = 0.0065 Å). However, this effect may be directional rather than isotropic (see items 2 and 3).

(2) The tungsten–carbon(ring) distances range from 2.260 (10) to 2.376 (9) Å, averaging 2.326 Å, and the tungsten–centroid[28] distance is 2.001 Å. The molybdenum–carbon(ring) distances range from 2.262 (6) to 2.353 (7) Å, averaging 2.304 Å, while the molybdenum–centroid distance is 1.992 Å. Thus, in the direction of the η^5-cyclopentadienyl system, the covalent radius of tungsten appears to be slightly *greater* than that of molybdenum.

(3) The tungsten–carbonyl bond lengths range from 1.992 (8) to 2.002 (12) Å, averaging 1.998 [5] Å;[29] the molybdenum–carbonyl bond lengths range from 1.980 (4) to 2.009 (6)

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(27) (a) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *B25*, 925–946. (b) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767.

(28) "Centroid" defines the centroid of the pentagon defined by the five carbon atoms of the cyclopentadienyl ring.

(29) Esd's of average distances, calculated via the scatter formula $\sigma = [\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$, are given in square brackets.

Table II. Positional and Thermal Parameters

(η^5-C_5H_5)W(CO)$_3$Cl

atom	x	y	z	atom	x	y	z
W(1)	0.15295 (3)	0.21300 (2)	−0.14322 (2)	C(2)	0.1668 (16)	0.3412 (10)	0.0160 (9)
Cl	0.1202 (3)	0.2446 (2)	−0.36260 (16)	C(3)	0.1753 (13)	0.4230 (7)	−0.0820 (11)
O(11)	0.5289 (8)	0.1944 (5)	−0.1911 (6)	C(4)	0.0212 (17)	0.4128 (8)	−0.1525 (9)
O(12)	0.2986 (9)	0.0079 (6)	0.0426 (5)	C(5)	−0.0820 (12)	0.3303 (9)	−0.1067 (9)
O(13)	−0.0573 (9)	−0.0242 (6)	−0.2375 (6)	H(1)[a]	−0.0309	0.2261	0.0564
C(11)	0.3925 (10)	0.1989 (5)	−0.1735 (6)	H(2)	0.2563	0.3279	0.0804
C(12)	0.2484 (11)	0.0826 (7)	−0.0250 (6)	H(3)	0.2683	0.4736	−0.0953
C(13)	0.0246 (11)	0.0609 (7)	−0.2056 (7)	H(4)	−0.0105	0.4576	−0.2247
C(1)	0.0085 (15)	0.2838 (7)	0.0035 (10)	H(5)	−0.1941	0.3077	−0.1416

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	2.95 (2)	2.050 (14)	3.004 (15)	0.114 (7)	0.733 (11)	0.008 (7)
Cl	5.37 (11)	6.29 (10)	3.30 (7)	0.83 (9)	0.73 (7)	0.78 (7)
O(11)	4.1 (3)	5.3 (3)	6.2 (3)	0.9 (2)	1.8 (3)	0.3 (2)
O(12)	8.5 (4)	5.2 (3)	6.0 (3)	1.5 (3)	1.0 (3)	2.9 (3)
O(13)	7.7 (4)	5.0 (3)	9.4 (4)	−3.0 (3)	1.4 (3)	−2.4 (3)
C(11)	3.2 (4)	2.7 (3)	4.2 (3)	0.3 (2)	0.8 (3)	0.6 (2)
C(12)	5.4 (4)	3.0 (3)	4.4 (3)	0.7 (3)	1.0 (3)	0.0 (3)
C(13)	5.7 (4)	3.2 (3)	4.9 (3)	−0.2 (3)	2.0 (3)	−0.9 (3)
C(1)	7.2 (6)	4.5 (4)	5.5 (4)	0.0 (4)	3.4 (4)	−1.0 (3)
C(2)	6.2 (6)	5.9 (5)	5.2 (5)	1.6 (5)	−0.0 (4)	−3.1 (4)
C(3)	6.4 (5)	2.2 (3)	10.4 (6)	−1.1 (3)	3.8 (5)	−2.7 (4)
C(4)	10.2 (8)	2.5 (3)	6.5 (5)	2.1 (4)	2.0 (5)	−0.4 (3)
C(5)	5.1 (5)	4.1 (4)	8.2 (6)	1.8 (3)	1.1 (4)	−1.8 (4)

(η^5-C_5H_5)Mo(CO)$_3$Cl

atom	x	y	z	atom	x	y	z
Mo(1)	0.01659 (4)	0.21495 (2)	0.35875 (2)	C(2)	0.1896 (9)	0.3412 (5)	0.5183 (5)
Cl(1)	−0.23414 (17)	0.24496 (10)	0.13987 (8)	C(3)	0.1077 (13)	0.4202 (4)	0.4247 (7)
O(11)	0.3453 (5)	0.1980 (2)	0.3105 (2)	C(4)	−0.1180 (12)	0.4137 (5)	0.3512 (5)
O(12)	0.3445 (5)	0.0111 (3)	0.5420 (2)	C(5)	−0.1753 (9)	0.3329 (5)	0.3961 (6)
O(13)	−0.2902 (5)	−0.0205 (3)	0.2639 (3)	H(1)[b]	0.005 (8)	0.239 (4)	0.543 (4)
C(11)	0.2265 (6)	0.2008 (3)	0.3279 (3)	H(2)[c]	0.310 (6)	0.329 (3)	0.573 (3)
C(12)	0.2257 (6)	0.0852 (4)	0.4744 (3)	H(3)[d]	0.188 (8)	0.461 (5)	0.419 (5)
C(13)	−0.1759 (6)	0.0639 (3)	0.2976 (3)	H(4)[e]	−0.211 (7)	0.453 (4)	0.279 (4)
C(1)	0.0104 (11)	0.2876 (5)	0.4989 (5)	H(5)[f]	−0.325 (8)	0.311 (4)	0.363 (4)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	3.404 (15)	2.566 (13)	3.043 (14)	0.162 (12)	2.296 (12)	0.044 (11)
Cl(1)	4.90 (5)	7.03 (6)	3.47 (4)	0.99 (4)	2.57 (4)	0.73 (4)
O(11)	5.69 (14)	6.12 (15)	6.75 (16)	1.00 (12)	4.99 (14)	0.80 (12)
O(12)	8.1 (2)	5.77 (15)	6.08 (15)	2.81 (15)	4.21 (15)	2.57 (14)
O(13)	8.1 (2)	5.40 (15)	9.1 (2)	−3.04 (15)	5.76 (16)	−2.10 (15)
C(11)	4.24 (17)	3.25 (15)	3.80 (16)	0.53 (14)	2.67 (15)	0.29 (13)
C(12)	5.6 (2)	3.74 (17)	4.38 (17)	0.76 (16)	3.57 (17)	0.48 (15)
C(13)	5.1 (2)	4.1 (2)	5.1 (2)	−0.53 (16)	3.66 (17)	−0.34 (16)
C(1)	10.3 (4)	4.5 (2)	6.6 (3)	−0.2 (3)	7.3 (3)	−0.7 (2)
C(2)	4.6 (3)	6.8 (3)	5.3 (3)	0.0 (2)	2.2 (2)	−3.3 (2)
C(3)	12.0 (5)	3.2 (2)	11.1 (4)	−2.3 (3)	10.1 (4)	−2.4 (3)
C(4)	10.6 (4)	4.0 (2)	5.8 (3)	2.9 (3)	4.8 (3)	0.3 (2)
C(5)	5.4 (3)	5.8 (3)	9.8 (4)	−0.4 (2)	5.5 (3)	−3.1 (3)

(η^5-C_5H_5)Mo(CO)$_3$HgCl

atom	x	y	z	atom	x	y	z
Mo	0.76670 (10)	0.70956 (10)	0.85181 (8)	Cp(2)	0.6505 (18)	0.6517 (27)	0.9641 (12)
Hg	0.85733 (5)	0.90493 (5)	0.89667 (4)	Cp(3)	0.6228 (16)	0.5983 (14)	0.8917 (20)
Cl	0.88749 (30)	1.10515 (28)	0.90499 (22)	Cp(4)	0.5856 (15)	0.6700 (35)	0.8305 (10)
O(1)	0.8089 (10)	0.8357 (10)	0.6774 (8)	Cp(5)	0.5860 (19)	0.7776 (19)	0.8731 (22)
O(2)	0.9814 (12)	0.6443 (12)	0.9538 (11)	H(1)[g]	0.6509	0.8065	0.9985
O(3)	0.8663 (10)	0.5254 (11)	0.7341 (9)	H(2)	0.6790	0.6176	1.0153
C(1)	0.7960 (12)	0.7913 (13)	0.7421 (11)	H(3)	0.6284	0.5203	0.8838
C(2)	0.9057 (16)	0.6746 (13)	0.9158 (14)	H(4)	0.5638	0.6536	0.7723
C(3)	0.8285 (13)	0.5924 (16)	0.7793 (11)	H(5)	0.5608	0.8470	0.8514
Cp(1)	0.6338 (17)	0.7525 (18)	0.9553 (17)				

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	2.69 (6)	2.99 (6)	3.15 (5)	−0.52 (4)	−0.22 (6)	−0.35 (5)
Hg	3.945 (31)	3.187 (29)	3.690 (23)	−1.007 (19)	−0.421 (28)	−0.498 (26)
Cl	4.24 (17)	2.98 (15)	3.51 (13)	−0.27 (12)	−0.38 (14)	0.03 (14)
O(1)	7.2 (8)	6.4 (7)	4.4 (6)	−1.0 (6)	1.2 (5)	0.2 (6)
O(2)	7.5 (9)	7.0 (9)	14.8 (11)	0.0 (7)	−7.2 (9)	0.2 (9)
O(3)	5.9 (7)	5.6 (7)	10.5 (8)	0.2 (5)	2.9 (7)	−2.9 (7)
C(1)	4.0 (8)	4.5 (9)	3.3 (7)	−0.7 (6)	1.5 (6)	0.5 (6)
C(2)	4.9 (9)	2.9 (8)	10.0 (14)	0.3 (7)	−2.0 (10)	−0.0 (8)
C(3)	3.2 (8)	5.6 (10)	5.6 (9)	−0.5 (7)	0.5 (6)	−2.8 (8)

Table II (*Continued*)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cp(1)	6.1 (12)	3.1 (9)	11.6 (17)	−1.7 (9)	3.0 (12)	−4.1 (11)
Cp(2)	6.9 (12)	11.6 (18)	4.2 (8)	−1.0 (14)	2.4 (9)	0.1 (11)
Cp(3)	5.6 (11)	3.9 (9)	12.5 (16)	−3.0 (7)	3.5 (14)	−2.1 (13)
Cp(4)	2.1 (9)	21.9 (31)	2.3 (7)	−2.4 (14)	0.2 (6)	−2.2 (12)
Cp(5)	4.4 (11)	6.7 (14)	16.7 (25)	2.8 (11)	5.1 (14)	8.4 (16)

[a] All hydrogen atoms were assigned isotropic thermal parameters of $B = 7.0$ Å^2. [b] $B_{iso} = 7.4$ (13) Å^2. [c] $B_{iso} = 3.9$ (10) Å^2. [d] $B_{iso} = 9.8$ (17) Å^2. [e] $B_{iso} = 8.4$ (13) Å^2. [f] $B_{iso} = 7.9$ (12) Å^2. [g] All hydrogen atoms were assigned isotropic thermal parameters of $B = 6.0$ Å^2.

Table III. Interatomic Distances (Å) with Esd's and Interatomic Angles (Deg) for (η^5-C_5H_5)M(CO)$_3$Cl

	dist	
atoms	M = W	M = Mo
M–Cl	2.490 (2)	2.498 (1)
M–C(11)	1.999 (8)	2.009 (6)
M–C(12)	2.002 (12)	1.980 (4)
M–C(13)	1.992 (8)	1.992 (4)
M–C(1)	2.299 (11)	2.267 (7)
M–C(2)	2.260 (10)	2.262 (6)
M–C(3)	2.350 (8)	2.323 (5)
M–C(4)	2.376 (9)	2.353 (7)
M–C(5)	2.346 (10)	2.315 (8)
M···centroid	2.001	1.992
C(11)–O(11)	1.138 (10)	1.134 (7)
C(12)–O(12)	1.136 (9)	1.137 (5)
C(13)–O(13)	1.145 (10)	1.140 (6)
C(1)–C(2)	1.390 (17)	1.380 (12)
C(2)–C(3)	1.427 (15)	1.381 (9)
C(3)–C(4)	1.360 (17)	1.360 (14)
C(4)–C(5)	1.365 (15)	1.346 (11)
C(5)–C(1)	1.432 (15)	1.343 (9)
C–H	0.95 (fixed)	0.76 (5)–0.97 (7)
	angle	
atoms	M = W	M = Mo
Cl–M–C(11)	77.83 (21)	77.22 (12)
Cl–M–C(12)	137.37 (22)	136.67 (14)
Cl–M–C(13)	77.70 (23)	77.86 (13)
Cl–M-centroid	110.90	111.76
C(11)–M–C(12)	77.94 (30)	78.41 (18)
C(11)–M–C(13)	109.15 (30)	109.79 (18)
C(12)–M–C(13)	77.88 (32)	77.48 (19)
M–C(11)–O(11)	178.1 (6)	177.2 (4)
M–C(12)–O(12)	178.3 (7)	178.8 (4)
M–C(13)–O(13)	175.5 (7)	177.4 (4)
C(5)–C(1)–C(2)	105.1 (9)	107.4 (6)
C(1)–C(2)–C(3)	110.2 (9)	107.8 (6)
C(2)–C(3)–C(4)	105.1 (9)	106.5 (7)
C(3)–C(4)–C(5)	111.7 (10)	109.2 (7)
C(4)–C(5)–C(1)	107.9 (9)	109.0 (7)

Å, averaging 1.993 [14] Å. Here, the bond lengths are statistically indistinguishable.

(4) The M(CO)$_3$Cl portion of the molecule has the usual irregular "four-legged piano stool" arrangement, typical of (η^5-C_5H_5)M(CO)$_3$X (M = Cr, Mo, W) derivatives. The trans Cl–W–C(12) and Cl–Mo–C(12) angles are, respectively, 137.37 (22) and 136.67 (14)°; the other trans angles are far less obtuse, with C(11)–W–C(13) = 109.15 (30)° and C(11)–Mo–C(13) = 109.79 (18)°. The cis angles are all acute with Cl–W–C(11) = 77.83 (21)°, Cl–W–C(13) = 77.70 (23)°, C(11)–W–C(12) = 77.94 (30)°, and C(12)–W–C(13) = 77.88 (32)° and with Cl–Mo–C(11) = 77.22 (12)°, Cl–Mo–C(13) = 77.86 (13)°, C(11)–Mo–C(12) = 78.41 (18)°, and C(12)–Mo–C(13) = 77.48 (19)°.

(5) The metal–carbonyl systems are close to linear with normal C–O distances: W–C–O = 175.5 (7)–178.3 (7)° with C–O = 1.136 (9)–1.145 (10) Å; Mo–C–O = 177.2 (4)–178.8 (4)° with C–O = 1.134 (7)–1.140 (6) Å.

Table IV. Interatomic Distances (Å) and Angles (Deg) for (η^5-C_5H_5)Mo(CO)$_3$HgCl[a]

	Distances		
Mo–Hg	2.683 (1)	C(1)–O(1)	1.136 (20)
Hg–Cl	2.442 (3)	C(2)–O(2)	1.142 (25)
Mo–C(1)	1.980 (16)	C(3)–O(3)	1.155 (22)
Mo–C(2)	1.985 (20)	Cp(1)–Cp(2)	1.24 (4)
Mo–C(3)	1.944 (18)	Cp(2)–Cp(3)	1.33 (4)
Mo–Cp(1)	2.312 (23)	Cp(3)–Cp(4)	1.35 (4)
Mo–Cp(2)	2.325 (21)	Cp(4)–Cp(5)	1.45 (5)
Mo–Cp(3)	2.274 (20)	Cp(5)–Cp(1)	1.42 (4)
Mo–Cp(4)	2.257 (20)	Hg···Cl^i	3.079 (3)
Mo–Cp(5)	2.347 (23)	Hg···Cl^{ii}	3.078 (4)
Mo···centroid	1.994		
	Angles		
Mo–Hg–Cl	160.02 (9)	Mo–C(3)–O(3)	177.7 (15)
Hg–Mo–C(1)	73.1 (5)	Cp(5)–Cp(1)–Cp(2)	111.8 (23)
Hg–Mo–C(2)	73.5 (6)	Cp(1)–Cp(2)–Cp(3)	110.1 (23)
Hg–Mo–C(3)	128.8 (5)	Cp(2)–Cp(3)–Cp(4)	110.8 (23)
Hg–Mo···centroid	111.95	Cp(3)–Cp(4)–Cp(5)	104.9 (23)
C(1)–Mo–C(2)	112.0 (7)	Cp(4)–Cp(5)–Cp(1)	102.1 (23)
C(1)–Mo–C(3)	78.9 (7)	Cl–Hg···Cl^i	89.66 (10)
C(2)–Mo–C(3)	78.8 (8)	Cl^i···Hg···Cl^{ii}	79.05 (9)
Mo–C(1)–O(1)	176.8 (14)	Cl···Hg···Cl^{ii}	83.59 (10)
Mo–C(2)–O(2)	173.3 (17)		

[a] i: $1-x, 1-y, z$. ii: $y, 1-x, -z$.

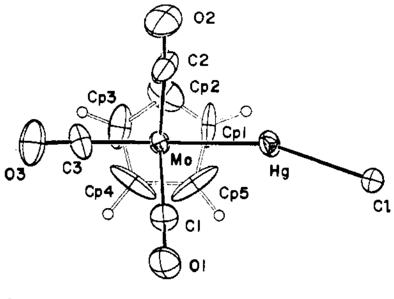

Figure 5. (η^5-C_5H_5)Mo(CO)$_3$HgCl molecule, projected on to the cyclopentadienyl plane.

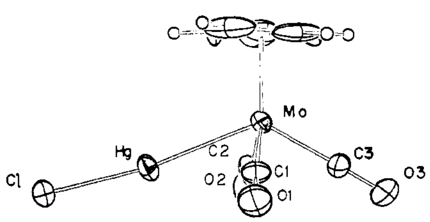

Figure 6. (η^5-C_5H_5)Mo(CO)$_3$HgCl molecule, viewed from the side.

(6) Alway and Barnett[30] have commented that both IR and ^{13}C NMR spectroscopy indicate that the carbonyl group trans to the halogen is back-bonded to a greater extent than the two cis carbonyls. The difference in metal–carbon bond length is at a level that is not detectable by conventional X-ray

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(30) Alway, D. G.; Barnett, K. W. *Adv. Chem. Ser.* **1978**, *No. 168*, 115–131.

diffraction studies. No differences between M–CO(trans) and M–CO(cis) distances are found from the present study.

B. $(\eta^5\text{-}C_5H_5)Mo(CO)_3HgCl$ Molecule. Interatomic distances and angles are collected in Table IV; the molecule is depicted in Figures 5 and 6. The overall structure agrees with that reported by Oliver, Albright, and Glick,[19] but esd's are reduced to approximately 35% of their previous values, and certain bond lengths and angles are now more in line with the expected values. The following points are worthy of mention.

(1) For correct refinement of the structure, the inclusion of corrections for anomalous dispersion[22] is of great importance. With Mo Kα radiation, the appropriate values (in order of decreasing significance) are $\Delta f'(\mathrm{Hg}) = -3.084$ and $\Delta f''(\mathrm{Hg}) = 9.223$, $\Delta f'(\mathrm{Mo}) = -1.825$ and $\Delta f''(\mathrm{Mo}) = 0.688$, and $\Delta f'(\mathrm{Cl}) = 0.132$ and $\Delta f''(\mathrm{Cl}) = 0.159$ (all values in units of electrons). In the noncentrosymmetric space group $P\bar{4}2_1c$, refinement in the correct hand led to $R_F = 4.2\%$ and $R_{wF} = 3.3\%$, while refinement in the incorrect hand led to convergence with $R_F = 7.5\%$ and $R_{wF} = 9.3\%$.

(2) The revised Mo–Hg and Hg–Cl bond lengths are 2.683 (1) and 2.442 (3) Å (previously reported as 2.673 (3) and 2.437 (8) Å)[19] and the Mo–Hg–Cl angle is 160.02 (9)° (previously 160.0 (2)°). The changes here are not the most significant in the structure (see below).

(3) The Mo–C(ring) distances range from 2.257 (20) to 2.347 (23) Å, averaging 2.303 Å (previously, 2.24–2.47 Å, average = 2.36 Å);[19] the present values are totally consistent with those within the $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ molecule, where the average Mo–C(ring) distance is 2.304 Å. Similarly, the Mo–centroid distance in $(\eta^5\text{-}C_5H_5)Mo(CO)_3HgCl$ is 1.994 Å as compared with 1.992 Å in the $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ molecule.

(4) The $Mo(CO)_3Hg$ portion of the molecule has a geometric arrangement similar to the $Mo(CO)_3Cl$ portion of the $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ molecule. Trans angles are Hg–Mo–C(3) = 128.8 (5)° and C(1)–Mo–C(2) = 112.0 (7)°, whereas cis angles are Hg–Mo–C(1) = 73.1 (5)°, Hg–Mo–C(2) = 73.5 (6)°, C(1)–Mo–C(3) = 78.9 (7)°, and C(2)–Mo–C(3) = 78.8 (8)°.

(5) The Mo–C–O angles and C–O bond lengths are 173.3 (17)–177.7 (15)° and 1.136 (20)–1.155 (22) Å, respectively (previously reported as 165–171° and 1.09–1.13 Å).[19]

(6) As indicated previously,[19] the η^5-cyclopentadienyl ligand is undergoing substantial librational motion about the Mo–centroid axis, resulting in unrealistic C(ring)–C(ring) distances.

(7) There are indications of loose association of molecules about the crystallographic $\bar{4}$ axis. Thus, the mercury atom is formally two-coordinate, but there are interations with chlorine atoms of two other molecules at distances Hg···Cl $(1 - x, 1 - y, z) = 3.079$ (3) Å and Hg···Cl $(y, 1 - x, -z) = 3.078$ (4) Å.

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Registry No. $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$, 12128-24-4; $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$, 12128-23-3; $(\eta^5\text{-}C_5H_5)Mo(CO)_3HgCl$, 12079-83-3.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes for the three structural studies (23 pages). Ordering information is given on any current masthead page.

Contribution from the School of Chemistry,
University of Sydney, Sydney 2006, Australia

Crystal and Molecular Structure of Racemic Tris(ethylenediamine)ruthenium(II) Tetrachlorozincate(II)

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The crystal and molecular structure of racemic $[Ru(C_2H_8N_2)_3][ZnCl_4]$ has been determined from X-ray data collected by counter methods. The pale yellow crystals are orthorhombic, of space group $Pna2_1$, with $a = 15.976$ (5) Å, $b = 7.683$ (4) Å, $c = 14.160$ (3) Å, $V = 1738.1$ (8) Å^3, and $Z = 4$. The structure was solved by standard Patterson and Fourier techniques and refined by full-matrix least-squares methods to a conventional R index (on F) of 0.033. The divalent ruthenium is hexacoordinated in distorted octahedral symmetry. The average N–Ru–N bite angle of the rings is 81.6 (3)°. The average dihedral angle is 55.4 (1)°. The twist angle is 52.9 (7)°. The weighted mean $\mathrm{Ru^{II}}$–N distance of 2.132 (3) Å is within experimental uncertainty identical with the Ru–N of 2.11 (2) Å in the corresponding Ru(III) complex. A Λ cation exhibits a [$\delta\delta$ (74% λ, 26% δ)] configuration. There are no strong hydrogen bonds to the complex cation. The occurrence of the $\delta\delta\lambda$ conformation is ascribed to metal–ligand distances sufficiently long to reduce the ligand–ligand interactions favoring the $\delta\delta\delta$ conformation. The role of hydrogen bonding in the structures of $M(en)_3$ complexes is discussed.

Introduction

The crystal and molecular structure of (±)-$[Ru(C_2H_8N_2)_3][ZnCl_4]$ has been determined for two reasons. First, in studies of electron exchange between $Ru(en)_3^{2+}$ and $Ru(en)_3^{3+}$ one needs to know the stereochemical differences between the two oxidation states in order to assess any Franck–Condon barriers to electron transfer. The difference in Ru–N bond lengths between $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ is only 4 pm,[1] so it is a reasonable inference that a similar small difference exists for the ethylenediamine complexes. However, because of the apparent very large difference in electron-transfer rates between the hexaamine and tris(ethylenediamine) complexes of cobalt(II) and cobalt(III), it seemed prudent to determine directly the structure of $Ru(en)_3^{2+}$, for comparison with the known structure of $Ru(en)_3^{3+}$.[2]

The second reason relates to clarification of earlier work on the conformations of tris(ethylenediamine)metal complexes. Calculations[3] have indicated that, because of longer metal–ligand distances, there are smaller ligand–ligand interactions

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[1] Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304.

[2] Peresie, H. J.; Stanko, J. A. *Chem. Commun.* **1970**, 1674.

[3] Gollogly, J. R.; Hawkins, C. J.; Beattie, J. K. *Inorg. Chem.* **1971**, *10*, 317.

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