are quantitatively reproducible independent of sample and regardless of the direction of pressure change. However, while all samples behave qualitatively the same with regard to absorption *intensity*, for experimental reasons related to diamond cell techniques, the intensity data presented in Figure 1 are from a single sample with points obtained only for *increasing* pressure.

The absorption spectra in the region of the $^1\delta\delta^* \leftarrow {}^1\delta^2$ transition of $Re_2Cl_8^{2-}$ and the pressure dependence of the transition energy, integrated absorption intensity, and the metal–metal stretching frequency are illustrated in Figure 1. Unlike the abrupt two-state result reported for $Re_2I_8^{2-}$,[14] the $^1\delta\delta^* \leftarrow {}^1\delta^2$ transition undergoes a monotonic shift to lower energy with increasing pressure. The integrated absorption intensity increases slightly at low pressures (below ~2 GPa), then decreases monotonically with further increases in pressure.

Two factors affect $\delta$ overlap in $Re_2X_8^{2-}$ complexes, namely the torsional angle $\chi$ and the Re–Re distance. The observation of an initial increase in the intensity of the $^1\delta\delta^* \leftarrow {}^1\delta^2$ transition suggests that at low pressures the $\delta$ overlap increases. This likely arises from shortening of the metal–metal distance prior to any significant torsional deformation. Resonance Raman measurements show that the ambient pressure Re–Re stretching frequency for the $Cl^-$ complex is 272 $cm^{-1}$.[18,19] This vibration increases in frequency (to 357 $cm^{-1}$ at ca. 15 GPa) over the entire pressure range (Figure 1). A continuous decrease in the metal–metal bond distance is probably the dominant factor in accounting for the frequency increase.

At pressures above ~2 GPa, the repulsive interactions of the halides begin to dominate the torsional potential, resulting in an increase in torsional angle and a net decrease in the amount of $\delta$ overlap.[1,11] Decreasing $\delta$ overlap should be manifested in two ways. First, the largely covalent $^1\delta^2$ ground state will be destabilized relative to the more ionic $^1\delta\delta^*$ excited state.[5] Second, the oscillator strength for the $^1\delta\delta^* \leftarrow {}^1\delta^2$ transition should decrease.[5,15]

Given the above theoretical considerations and spectroscopic results, our observations on $Re_2Cl_8^{2-}$ are consistent with an initial shortening of the Re–Re bond followed by a gradual change in the torsional angle and further shortening of the Re–Re bond with increasing pressure.

A final observation concerns the behavior of the p$\pi$ (Cl) to $\delta^*$ (Re) charge-transfer transition of $Re_2Cl_8^{2-}$. This transition remains at constant energy (313 nm) over the entire pressure range examined. The only effect of increasing pressure is to broaden the absorption envelope. If interactions between the medium and the molecular orbitals of the complex[20] were primarily responsible for the observed behavior of the $^1\delta\delta^* \leftarrow {}^1\delta^2$ transition, the energies of *all* electronic transitions would be altered by pressure. Rather, it appears that over the pressure range studied, the main effect of applied pressure is to induce structural changes which in turn alter the intramolecular properties, i.e., those determined by the extent of $\delta$ overlap between the two metal atoms.

The evidence developed herein strongly suggests that for $Re_2Cl_8^{2-}$ in $CH_2Cl_2$, elevated pressure results in an increase in the magnitude of the repulsive steric potential of the halides relative to the $\delta$ bonding potential[2] such that the minimum in the *net* torsional potential energy shifts smoothly along the torsional coordinate from the eclipsed to the staggered geometry. This picture is very different from that required to interpret the results of Carroll et al.,[14] which appear to involve a pressure-dependent equilibrium between two *distinct* conformers for $Re_2Br_8^{2-}$ and $Re_8I_8^{2-}$ in poly(methyl methacrylate). The disparity between our results and those of Carroll et al. may be due to the specific complexes examined, the media employed, or other effects. Further study of these systems is indicated and is proceeding in this laboratory.

**Acknowledgments.** This work was performed at Los Alamos National Laboratory under the auspices of the U. S. Department of Energy. Additional suport by the National Science Foundation (Grant CHE 84-03836 at the University of Texas at Austin) is gratefully acknowledged. We thank Steven Agnew, Basil Swanson, Vince Miskowski, and Michael Hopkins for technical assistance and helpful discussions. D.E.M. acknowledges the support of the Director's Fellowship Program at LANL.

**Registry No.** $(Bu_4N)_2Re_2Cl_8$, 14023-10-0; $Re_2Cl_8^{2-}$, 19584-24-8.

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(18) Clark, R. J. H.; Franks, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 2763.

(19) Clark, R. J. H.; Stead, M. J. *Inorg. Chem.* **1983**, *22*, 1214.

(20) Drickamer, H. G. *Annu. Rev. Phys. Chem.* **1982**, *33*, 25 and references therein.

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# Formation of Furans and 1-Rhena-4-oxacyclohexa-2,5-diene Compounds from Reactions of $Cp^*ReO_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with $PPh_3$ in Alkynes

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Recent literature shows an increasing interest in the chemistry of metal oxide compounds. Several new high-valent organometallic oxides have been reported, e.g., heptavalent $Cp^*ReO_3$ ($Cp^*{=}C_5(CH_3)_5$) and pentavalent dimer $(Cp^*ReO_2)_2$.[1] Here we describe (i) the reduction reactions of $Cp^*ReO_3$ with $PPh_3$ in alkynes, which may ultimately lead to furans, and (ii) the X-ray structure of an intermediate of this reaction, which features a unique six-membered ring built from two alkynes and one rhenium oxygen fragment.

As a means to create a vacant coordination site an oxo ligand can be removed from $Cp^*ReO_3$ by phosphines.[1a–c] When $Cp^*ReO_3$ was allowed to react with $PPh_3$ in pure alkynes for a short time at room temperature, and the resulting crude reaction mixture chromatographed over silica, rhenium monooxide adducts I were obtained in about 40% yield, eq 1, besides unconverted

$$\begin{aligned}&Cp^*ReO_3 + PPh_3 + RCCR' \rightarrow\\ &\qquad Cp^*(O)Re(RCCR') + OPPh_3 \quad (1)\\ &\qquad \text{Ia,b:}\ R = R' = Me, Et\\ &\qquad \text{Ic:}\ R = Me, R' = i\text{-}Pr\\ &\qquad \text{Id:}\ R = Ph, R' = H\end{aligned}$$

$Cp^*ReO_3$. Adduct formation occurred with the alkynes mentioned (Ia–d); with sterically more demanding alkynes, e.g., $Me_3SiCCSiMe_3$ and 2,2,7,7-tetramethyloct-4-yne, $(Cp^*ReO_2)_2$ was formed.

Air-sensitive adducts I are oily substances, which are difficult to purify. They were formulated as the monooxide alkyne adducts on the basis of their $^1H$ NMR, $^{13}C$ NMR, and IR characteristics[2] and their subsequent reaction with $CpTiCl_3$ ($Cp = C_5H_5$). In the latter reaction complexes II, $Cp^*(Cl)_2Re(RCCR')$, were formed quantitatively, eq 2.

$$\begin{aligned}&\text{Ia,b} + CpTiCl_3 \rightarrow Cp^*(Cl)_2Re(RCCR') + {}^1/_4(CpTiClO)_4\\ &\qquad \text{IIa,b:}\ R = R' = Me, Et^2\\ &\qquad\qquad\qquad\qquad\qquad\qquad (2)\end{aligned}$$

Elemental analysis of IIb combined with the stoichiometry of eq 2 suggests the general formula of I to be $Cp^*(O)Re(RCCR')$.[3]

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(1) (a) Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem.* **1984**, *96*, 364–365. (b) Herrmann, W. A.; Voss, E.; Floel, M. *J. Organomet. Chem.* **1985**, *297* C5–C7. (c) Herrmann, W. A. *J. Organomet. Chem.* **1986**, *300*, 111–139. (d) Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1984**, *3*, 1313–1314.

(2) Analytical and spectroscopic details are presented in the supplementary material.

(3) For other $d^4$ rhenium oxide acetylene adducts, see: Mayer. J. M.; Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 7454–7462.

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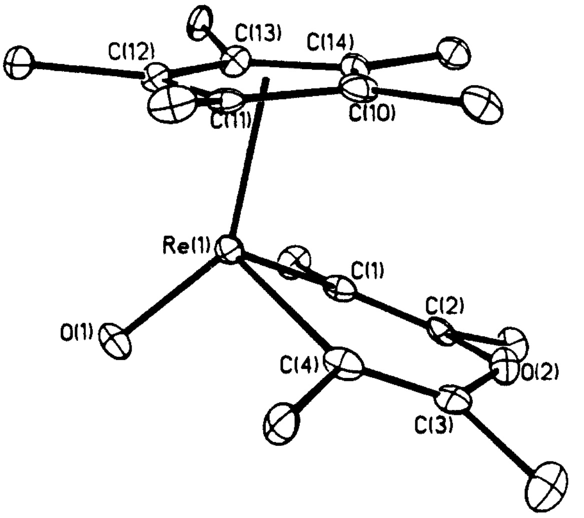
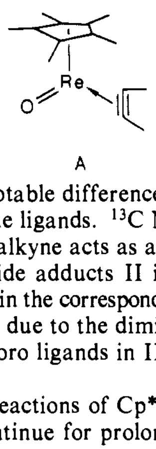
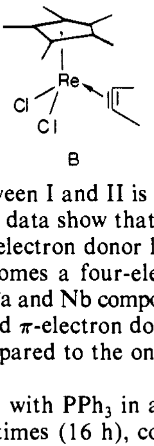


**Figure 1.** Molecular structure of IIIa. Bond lengths (Å): Re(1)–C(1) 2.094 (11); Re(1)–C(4) 2.096 (13); C(1)–C(2) 1.329 (18); C(3)–C(4) 1.298 (18); C(2)–O(2) 1.366 (14); C(3)–O(2) 1.389 (16); Re(1)–O(1) 1.716 (8); Re(1)–C(12) 2.138 (11); Re(1)–C(11) 2.248 (9); Re(1)–C(10) 2.549 (11). Bond angles (deg): C(1)–Re(1)–C(4) 85.6 (5); Re(1)–C(1)–C(2) 125.9 (8); C(1)–C(2)–O(2) 126.4 (10); C(2)–C(3)–O(2) 122.6 (9).

The spectroscopic data are in agreement with structures A and B for I and II, respectively.



A



B

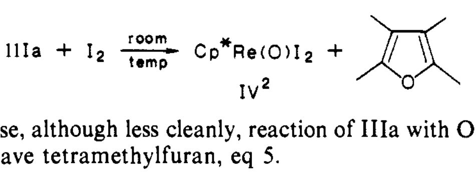
The most notable difference between I and II is the behavior of the acetylene ligands. $^{13}$C NMR data show that in the oxide adducts I the alkyne acts as a two-electron donor ligand, while in the dichloride adducts II it becomes a four-electron donor ligand,[4] just as in the corresponding Ta and Nb compounds.[5] This change will be due to the diminished $\pi$-electron donor capacity of the two chloro ligands in II compared to the one oxo ligand in I.

When the reactions of Cp*ReO$_3$ with PPh$_3$ in alkynes were allowed to continue for prolonged times (16 h), compounds of molecular formula "Cp*ReO$_2$(RCCR′)$_2$"[2] were obtained with but-2-yne, hex-3-yne, and phenylacetylene, eq 3.

$$\mathrm{Cp^*ReO_3 + PPh_3 + RCCR'} \xrightarrow[\text{room temp}]{16\text{ h}} \text{“}\mathrm{Cp^*ReO_2(RCCR')_2}\text{”} + \mathrm{OPPh_3} \quad (3)$$

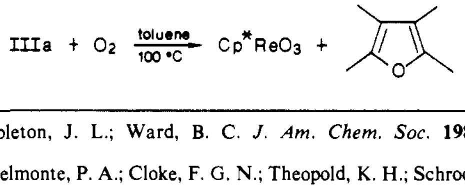
IIIa,b: R = R′ = Me, Et
IIIc,d: R = Ph, R′ = H

Dark-red IIIa (from but-2-yne) reacted with I$_2$ in benzene quantitatively to yield tetramethylfuran as the organic product, eq 4.



(4)

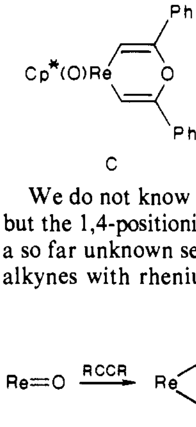
Likewise, although less cleanly, reaction of IIIa with O$_2$ in hot toluene gave tetramethylfuran, eq 5.



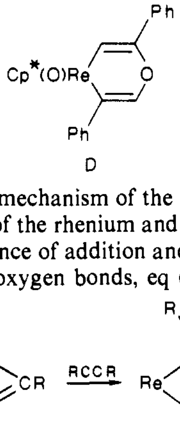
(5)

X-ray analysis of IIIa[6] showed a quite unexpected and novel organometallic structure, see Figure 1. The most remarkable feature of the X-ray structure is the rhenium- and oxygen-containing six-membered ring, a 1-rhena-4-oxacyclohexa-2,5-diene, in the following called rhenapyran, which can be viewed as being built from two molecules of alkynes and one rhenium oxygen fragment. In particular the 1,4-positioning of the rhenium and the oxygen atom is fascinating. Another noteworthy feature in the structure of IIIa is the slipped coordination of the Cp* ring. The structure of IIIa clearly shows the displacement of the rhenium atom from the center of the Cp* ring. The largest Re–C(ring) distances is 2.549 (11) Å, the shortest 2.138 (11) Å. The carbon–carbon distances in the ring are quite the same (1.407 (17)–1.443 (16) Å), indicating no true $\eta^5 \rightarrow \eta^3$ slip.[7,8] Since steric interactions do not seem to be important, an explanation may be that the oxo ligand exerts a trans effect, which results in a diminished interaction of the rhenium with the C(10)–C(14) bond of the Cp* ring.

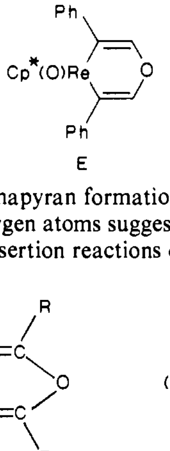
Monooxide alkyne adducts I and rhenapyran compounds III could be prepared from both terminal and internal alkynes. The most important factor which governs the reactions seems to be the steric one. For example, we could not prepare adducts of 2,2,7,7-tetramethyloct-4-yne or bis(trimethylsilyl)acetylene. Not surprisingly, steric factors became even more pronounced in the formation of the rhenapyrans, witness the failure of 2-methylpent-2-yne to give the corresponding rhenapyran. Furthermore, the fact that for the rhenapyran products of phenylacetylene only isomers with structures C and D were observed and no E is illustrative of the steric limitations.



C

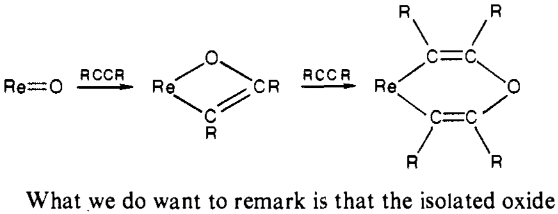


D



E

We do not know the mechanism of the rhenapyran formation, but the 1,4-positioning of the rhenium and oxygen atoms suggests a so far unknown sequence of addition and insertion reactions of alkynes with rhenium oxygen bonds, eq 6.



(6)

What we do want to remark is that the isolated oxide adducts I could not be converted to the corresponding compounds III.[9]

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(4) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288–3290.

(5) (a) Belmonte, P. A.; Cloke, F. G. N.; Theopold, K. H.; Schrock, R. R. *Inorg. Chem.* **1984**, *23*, 2365–2367. (b) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387–393.

(6) Crystal data for IIIa: C$_{18}$H$_{27}$O$_2$Re, $M$ = 461.6, orthorhombic, space group $P2_12_12_1$ (No. 19), $a$ = 13.413 (5) Å, $b$ = 14.061 (5) Å, $c$ = 17.804 (7) Å, $U$ = 3358 (3) Å$^3$, $T$ = 200 K, $Z$ = 8, $D_c$ = 1.83 g cm$^{-3}$, $F(000)$ = 1807.5 electrons, graphite monochromated Mo K$\alpha$ X-radiation, $\lambda$ = 0.71069 Å, $\mu$(Mo K$\alpha$) = 73.4 cm$^{-1}$. Experiments were conducted at 200 K on a Nicolet P3m diffractometer fitted with an LT-1 cooling device. 3544 Diffracted intensities were measured; of these 2821 with $I > 3\sigma(I)$ were used in structure determination. There are two independent molecules of IIIa in the asymmetric unit of the crystal structure. The mutual differences in bonding distances and angles are very small. Final residuals $R$ = 0.038, $R_w$ = 0.039.

(7) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929–935.

(8) Einstein, F. W. B. Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1985**, *5*, 53–59.

(9) Furthermore, when purified but-2-yne adduct Ia was reacted with fresh Cp*ReO$_3$ and PPh$_3$ in hex-3-yne, only the tetraethyl-substituted compound IIIb was observed, eq 7. The mixed dimethyldiethylrhenapyran Cp*(O)-

$$\underset{\text{Ia}}{\mathrm{Cp^*(O)Re(MeCCMe)}} + \mathrm{Cp^*ReO_3 + PPh_3} \xrightarrow{\text{EtCCEt}} \underset{\text{IIIb}}{\mathrm{Cp^*(O)ReC_4(Et)_4O}} + \text{Ia} + \mathrm{OPPh_3} \quad (7)$$

$\overline{\text{ReC(Me)=C(Me)—O—C(Et)=C}}\text{(Et)}$ was not formed. However, this complex could be made by starting the reduction of Cp*ReO$_3$ with PPh$_3$ in but-2-yne and replacing the but-2-yne by hex-3-yne after 25 min, without chromatographic isolation of the products of the reaction with but-2-yne!!

Therefore, we assume that the reactions proceed via a common labile intermediate which upon workup decomposes to give adducts I or, alternatively, reacts further with alkyne to afford rhenapyrans III.

**Supplementary Material Available:** Details of the analytical and spectroscopic results (3 pages). Ordering information is given on any current masthead page.

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## Synthesis and Characterization of Polynuclear Chromium(III) Alkyls. Crystal Structure of a Paramagnetic $\mu_3$-Methylidyne Complex with Short Nonbonded Cr–Cr Contacts

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*Received August 27, 1986*

Organometallic chemistry is dominated by diamagnetic molecules. Recently, however, appreciation has been growing for the importance of radical reactions and metallaradicals in this area of chemistry.[1] Herein we describe some paramagnetic chromium(III) alkyls and the facile conversion of a methyl ligand into a $\mu_3$-methylidyne fragment.

Addition of 1 equiv of TlCp to a stirred $Et_2O$ solution of $MeCrCl_2(THF)_3$[2] at room temperature resulted in a rapid color change from green to dark red. After 30 min the solution was filtered, the solvent evaporated, and the solid residue recrystallized from $Et_2O$ to yield dark red crystals of bis($\mu$-chloro)dimethylbis($\eta^5$-cyclopentadienyl)dichromium (**1**) in 90% yield (Scheme I).[3] In an analogous reaction of $EtCrCl_2(THF)_3$ the corresponding ethyl dimer **2** was formed in 78% yield.

The molecular structure of **1** was determined by X-ray diffraction (Figure 1).[4] The dimeric molecule has crystallographic $C_i$ symmetry and features the pseudooctahedral coordination geometry of a three-legged piano stool around chromium. Two bridging chloride ligands hold the dimer together, and the methyl groups stand trans to each other. The Cr–Cr distance of 3.29 Å is too long to allow for metal–metal bonding, giving each chromium a 15-electron configuration. The magnetic susceptibility of **1** was measured in the temperature range 3–300 K, and the temperature dependence of $\chi_m$ is characteristic of an antiferromagnetically coupled dimer ($\mu_{eff}$(300 K) = 3.58 $\mu_B$). The data were fitted by using the Heisenberg–Dirac–Van Vleck (HDVV) model for a dimer of two $S = {}^3/_2$ ions giving $J = -72$ cm$^{-1}$.[5]

Alkyl dimers **1** and **2** are air sensitive both in solution and in the solid state. They dissolve readily in common organic solvents, and such solutions are stable at room temperature for several hours. Added nucleophiles rapidly cleave the dimers, forming a series of mononuclear chromium(III) alkyl complexes (see Scheme I).[6]

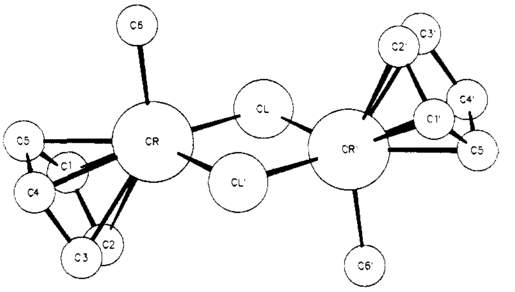


**Figure 1.** Molecular structure of **1**. Selected bond distances: Cr–Cr′, 3.287 (1); Cr–C6, 2.073 (3); Cr–Cl, 2.355 (1); Cr–Cl′, 2.357 (1) Å. Interatomic angles: Cr–Cl–Cr′, 88.5 (1)°; Cl–Cr–Cl′, 91.5 (1)°; Cl–Cr–C6, 94.2 (1)°; Cl′–Cr–C6, 95.0 (1)°.

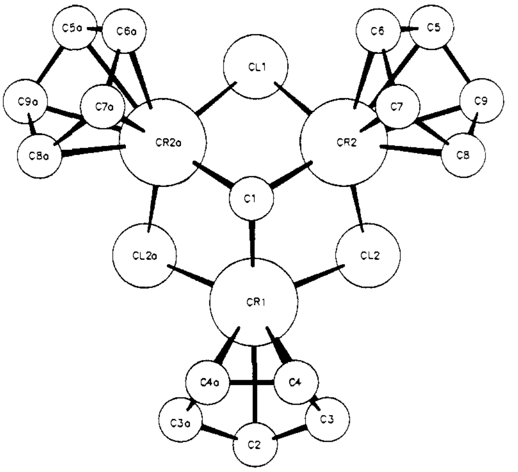
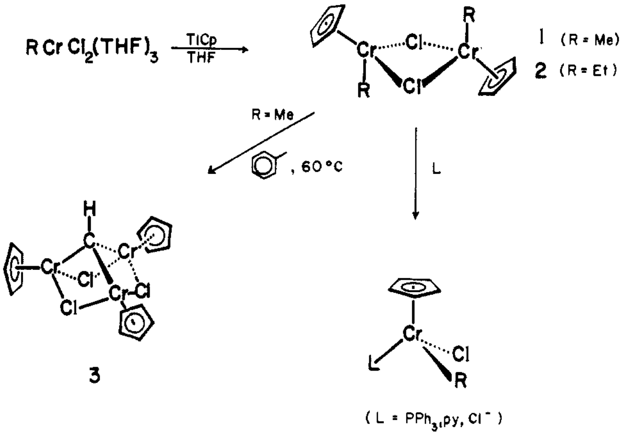


**Figure 2.** Molecular structure of **3**. Selected bond distances: Cr1–Cr2, 2.837 (2); Cr2–Cr2a, 2.793 (2); Cr1–C1, 1.949 (14); Cr2–C1, 1.935 (10); Cr1–Cl2, 2.360 (4); Cr2–Cl2, 2.357 (4); Cr2–Cl1, 2.348 (4) Å. Interatomic angles: Cr1–C1–Cr2, 93.8 (5)°; Cr2–C1–Cr2a, 92.4 (6)°; Cr1–Cl2–Cr2, 73.9 (1)°; Cr2–Cl1–Cr2a, 73.0 (1)°.

**Scheme I**



When a toluene solution of **1** was heated to 60 °C for several hours, the color of the solution changed from dark red to purple. At the same time methane, ethane, and ethylene were evolved. Filtration, removal of solvent, and extraction of the residue with THF yielded purple needles of the trinuclear chromium complex **3** in 24% yield.[7] The nature of this compound became clear only as the result of a crystal structure determination (Figure 2).[8] the molecule exhibits crystallographic $C_s$ symmetry only (Cl1, C1,

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[1] (a) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* **1976**, *14*, 345. (b) Brown, T. L. *Ann. N. Y. Acad. Sci.* **1980**, 80. (c) Halpern, J. *Angew. Chem.* **1985**, *97*, 308. (d) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.

[2] Nishimura, K.; Kuribayashi, H.; Yamamoto, A.; Ikeda, S. *J. Organomet. Chem.* **1972**, *37*, 317.

[3] **1**: IR (Nujol) 3080 (wk), 1108 (m), 1017 (m), 1003 (m), 839 (m), 827 (s), 812 (s), 802 (s) cm$^{-1}$; $^1$H NMR ($CD_2Cl_2$) 112 (br), 90 (br) ppm. Anal. Calcd for $C_{11}H_{16}Cl_2Cr_2$: C, 43.00; H, 4.81. Found: C, 42.60; H, 4.76. **2**: IR (KBr) 2945 (s), 2846 (s), 1450 (m), 1364 (m), 1117 (s), 1018 (s), 1006 (s), 843 (m), 821 (vs), 797 (vs), 473 (m) cm$^{-1}$. Anal. Calcd for $C_{14}H_{20}Cl_2Cr_2$: C, 46.30; H, 5.55, Cl, 19.52. Found: C, 46.42; H, 5.63; Cl, 19.60.

[4] Dark red crystals from $Et_2O$; orthorhombic *Pccn*; $a$ = 15.667 (3) Å, $b$ = 11.421 (3) Å, $c$ = 7.858 (2) Å; $Z$ = 4; $R$ = 0.034, $R_w$ = 0.049.

[5] (a) Martin, R. L. In *New Pathways in Inorganic Chemistry*; Ebsworth, Maddock, Sharp, Eds.; Cambridge University: Cambridge, 1968; Chapter 9. (b) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986; Chapter 5. (c) Cairns, C. J.; Busch, D. H. *Coord. Chem. Rev.* **1986**, *69*, 1.

[6] Satisfactory analytical data have been obtained on all complexes. Details of the characterization will be published in a full paper.

[7] **3**: IR (KBr) 3117 (wk), 1606 (wk), 1432 (s), 1355 (wk), 1116 (m), 1014 (s), 808 (s), 804 (s) cm$^{-1}$; $^1$H NMR ($CD_2Cl_2$) 31.0 (br) ppm, $\mu_3$-CH not detected. Anal. Calcd for $C_{16}H_{16}Cl_3Cr_3$: C, 40.83; H, 3.43; Cl, 22.60. Found: C, 40.85; H, 3.53; Cl, 22.85.

[8] Purple crystals from THF/pentane; orthorhombic $Pmn2_1$; $a$ = 14.743 (1) Å, $b$ = 9.5695 (7) Å, $c$ = 6.3521 (5) Å, $Z$ = 2; $R$ = 0.053, $R_w$ = 0.043.

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