Table III. Second-Order Rate Constants for the Reaction of $Re(CO)_5^-$ with M_2

M_2	k,[a] s^{-1} M^{-1}	$-E_{1/2}$,[b] V
$Co_2(CO)_8$	13 ± 1	0.9
$Mn_2(CO)_{10}$	1.4 ± 0.3	1.7
$Cp_2Mo_2(CO)_6$	20 ± 2	1.4

[a] Error limits are 95% confidence limits. [b] Reference 7.

did not occur—none of the anions reacted with $Re_2(CO)_{10}$.

Examination by infrared stopped-flow kinetics studies[5] showed that reactions 1–3 were first order in $[Re(CO)_5^-]$ and in dimer.[6]

$$\text{rate} = k[Re(CO)_5^-][M_2] \qquad (4)$$

$$M = Mn(CO)_5,\ CpMo(CO)_3,\ Co(CO)_4$$

A typical plot of the decrease in absorbance due to $Re(CO)_5^-$ at 1860 cm^{-1} is shown in Figure 2; plots for each dimer at different concentrations are given in the supplementary material. The fits to the plots under pseudo-first-order conditions (the dimer in at least a 10-fold excess) show a first-order dependence on $Re(CO)_5^-$. The dependence on the dimers is shown by the data in Table II. The rate constants, k, were obtained as the slope of plots (supplemental data) of k_{obs} versus $[M_2]$ and are shown in Table III.

The rate law observed is typical for electron-transfer reactions with a first-order dependence on the oxidant and the reductant. The dependence on the dimer is $Cp_2Mo_2(CO)_6 > Co_2(CO)_8 > Mn_2(CO)_{10}$, as shown in Table III. This dependence does not correlate with the reduction potentials for the dimers, which are also given in Table III. This casts doubt on an outer-sphere mechanism for the electron transfer. Possible inner-sphere mechanisms requiring dissociation of a ligand from the anion or the dimer are precluded because the electron transfer occurs more rapidly than ligand dissociation. An inner-sphere mechanism involving nucleophilic attack of the anion on the dimer is indicated. Possible sites for nucleophilic attack would be (1) the metal–metal antibonding orbital, (2) the metal center, and (3) a carbon of a carbonyl. Attack at the metal center would seem unlikely since the most sterically constrained metal (seven-coordinate) reacts more rapidly.[7,8] It is difficult to distinguish between the other two possibilities at this point. On the basis of the known preference for nucleophilic attack at CO's with less electron density and the rapid reaction of $Cp_2Mo_2(CO)_6$,[9,10] we favor attack at the carbonyl. Future studies will be directed toward this question.

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Supplementary Material Available: Plots of k_{obs} versus $[M_2]$ and of kinetic data for reactions of $Re(CO)_5^-$ with M_2 (9 pages). Ordering information is given on any current masthead page.

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(5) A schematic of the infrared stopped-flow instrument is shown in Figure 1. The infrared source is a tunable carbon monoxide laser (Edinburgh Instruments PL3). The beam passes through an iris diaphragm and the Irtran-2 cell (Wilmad Glass Co., Inc.) and into the HgCdTe detector (Infrared Associates, Inc.). The signal from the detector is processed by a stopped-flow operating system (OLIS). The stopped-flow system is composed of Teflon and KelF components. The syringes are driven by an air cylinder (Power Drive Inc.) through a Berger ball mixer (Research Instruments and Mfg. and Commonwealth Technology Inc.). The stopcocks and tubing are from Hamilton.

(6) For $M_2 = Co_2(CO)_8$ the plots of k_{obs} versus $[Co_2(CO)_8]$ have a substantial intercept. This may indicate a process that is independent of $[Co_2(CO)_8]$ or may be a result of the instability of $Co_2(CO)_8$ in THF solution. Since the other dimers do not show such an intercept, we favor the latter explanation.

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Preparation and X-ray Structure of (Tetramethyldibenzotetraaza[14]annulene)chromium Dimer, $[(tmtaa)Cr]_2$. A Multiply Bonded Complex of Dichromium(II) without Bridging Ligands

Understanding the factors that promote or inhibit the formation of metal–metal multiple bonds remains even today a very challenging and interesting goal.[1] This is especially puzzling in the chemistry of Cr(II) where the well-known ability of the d^4 electronic configuration to form unusually short Cr–Cr quadruple bonds[2] contrasts with theoretical calculations that predict for the quadruple bond either little[3] or no contribution[4] to the ground state. Furthermore, the occurrence of Cr–Cr quadruple bonds, with the only three exceptions being $Cr_2Me_8Li_4$,[5a] $Cr_2(C_4H_8)_4Li_4$,[5b] and $Cr_2(PMe_3)_2(CH_2SiMe_3)_2(\mu\text{-}CH_2SiMe_3)_2$[6] is confined to a homogeneous series of compounds containing ligands with the characteristic geometry of the bridging three-center chelating systems.[1,7] In order to identify a possible role of the ligands in forcing the formation of Cr–Cr bonds, we started an extensive study of new classes of Cr(II) compounds, containing ligands with most diverse geometries.[8-10] Herein we report an example where the formation of a Cr–Cr multiple bond without the assistance of bridging atoms is caused by the unique geometry of a macrocyclic ligand.

Reaction of $Me_8Cr_2(LiTHF)_4$[5] with 2 equiv of tetramethyldibenzotetraaza[14]annulene ($tmtaaH_2$) in toluene proceeds smoothly with evolution of methane (Scheme I)[11] and formation

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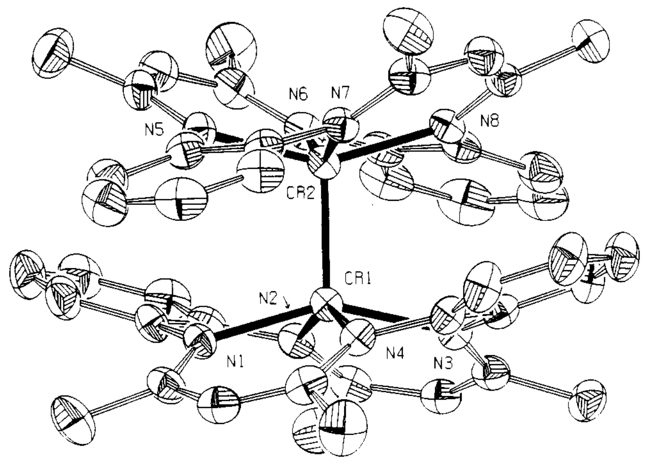
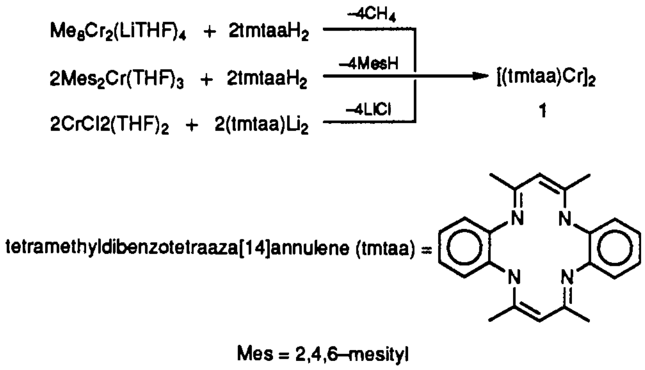


Figure 1. Thermal ellipsoid plot of **1** drawn at the 40% probability level. Selected bond distances (Å) and angles (deg): Cr(1)–Cr(2) = 2.096 (1), Cr(1)–N(1) = 2.004 (3), Cr(1)–N(2) = 1.996 (4), Cr(1)–N(3) = 1.999 (3), Cr(1)–N(4) = 1.998 (4); Cr(2)–Cr(1)–N(1) = 104.8 (1), N(1)–Cr(1)–N(2) = 80.1 (1), N(1)–Cr(1)–N(4) = 92.4 (2), N(2)–Cr(1)–N(3) = 93.4 (2), N(3)–Cr(1)–N(4) = 80.1 (2); N(1)–Cr(1)–Cr(2)–N(5) = 7.8 (2).

Scheme I



of moderately air-sensitive brick-red crystals of $[(\mathrm{tmtaa})\mathrm{Cr}]_2$ (**1**). Compound **1** has been obtained either by reaction of $\mathrm{CrCl_2(THF)_2}$[12a] with $(\mathrm{tmtaa})\mathrm{Li}_2$ or also by reacting $\mathrm{Mes_2Cr(THF)_3}$[12b] with $\mathrm{tmtaaH_2}$ (Scheme I). The dimeric nature of **1** has been demonstrated by a single-crystal X-ray structure determination.[13] The unit cell contains two discrete dimeric units (Figure 1). The two tmtaa moieties possess the usual saddle-shaped geometry and are rotated by approximately 90° relative to one another, as result of steric interactions.

The Cr–Cr bonding distance (2.096 (1) Å) falls between those observed in quadruply bonded chromium acetates[2b] and those in the so-called "supershort"-bonded complexes,[2a] suggesting also in this case that a multiple bond is binding the two [Cr(tmtaa)] moieties. The occurrence of such a bond is quite striking. In fact, in the case of other macrocyclic ligands (porphyrin[14] and Schiff base[15]), only monomeric square-planar complexes are formed, in sharp contrast with the dinuclear structures of analogous Mo derivatives.[16] Questions arise about which factors in **1** enhance the tendency of the metal to form the multiple bond. The N–N trans-annular distance of the tmtaa ring of **1** (3.88 (1) Å) is remarkably similar to that observed in the structure of the free ligand (3.815 Å)[17] and is significantly shorter than that observed in mononuclear and square-planar porphyrin[14] or Schiff base complexes[15] [4.07 and 4.05 Å, respectively]. On the other hand, the Cr–N bonding distances (Cr–N = 1.993 (3)–2.009 (3) Å) are comparable with those observed in a monomeric porphyrin complex (2.033 Å),[14] in Cr(acacen) (2.089 Å),[15] or in $\mathrm{(THF)_2Cr[N(SiMe_3)_2]_2}$ (2.033 Å).[18] Furthermore, the normal geometry of the free ligand is not perturbed by the coordination of chromium.[17] Therefore, we conclude that the position of chromium outside the $\mathrm{N_4}$ plane ($\mathrm{Cr{-}N_4}$ = 0.50 (2) Å) in **1** is just the result of the small ring dimensions. Preliminary HF–SCF calculations,[19] carried out on the monomeric Cr(tmtaa) fragment and Cr(porphyrin), show that the deviation of chromium from the molecular plane modifies the shape of the d_{yz} and d_{xz} orbitals with respect to those in the symmetric square-planar complexes. As a result, in the region above the molecular plane, the lobes of these orbitals become bigger and more diffuse. While the shape of d_{z^2} is not changed significantly, the formation of a Cr–Cr multiple bond may be caused by an increased ability of d_{yz} and d_{xz} to overlap. Our preliminary calculations showed that there is hardly any overlap between the δ-bonding $d_{x^2-y^2}$ orbitals, the d_{xy} orbital being mainly engaged in bonding with the ligand. The possible absence of a δ bond might be responsible for the residual paramagnetism of complex **1** (μ_{eff}/Cr = 0.49 μ_{B}, corrected for the underlying diamagnetism), which cannot be attributed to chromic impurities on the basis of the reproducibility of the measurements carried out at both variable temperatures and variable fields, on different samples obtained from different solvents and after several recrystallizations. Further study to understand the magnetic properties and the bonding of **1** is in progress.

Acknowledgment. The crystallographic part of this work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). X-ray data were kindly collected by A. J. M. Duisenberg. We are indebted to Seunghee Lee (Columbia University) for a generous loan of $\mathrm{tmtaaH_2}$.

Supplementary Material Available: A plot showing the full atom-labeling scheme and tables of crystal data, positional and thermal param-

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(11) Neat $\mathrm{tmtaaH_2}$ (1.6 g, 4.8 mmol) was added to a toluene solution (30 mL) of $\mathrm{Me_8Cr_2Li_4(THF)_4}$ (1.3 g, 2.37 mmol). The resulting mixture was heated gently until no more gas evolution was observed. Brick-red crystals of $[(\mathrm{tmtaa})\mathrm{Cr}]_2$ were obtained upon cooling the resulting solution to –30 °C (yield 0.90 g, 1.14 mmol, 48%). Anal. Calcd (found) for $\mathrm{C_{58}H_{60}Cr_2N_8}$: C, 71.70 (71.68); H, 6.18 (6.17); N, 11.54 (11.55); Cr, 10.51 (10.49). IR (KBr, Nujol mull, cm^{-1}): 1580 (w), 1550 (s), 1395 (s), 1370 (m), 1280 (m), 1195 (s), 1170 (w), 1125 (m), 1075 (m), 1060 (m), 1030 (s), 990 (m), 940 (m), 915 (m), 860 (w), 850 (w), 750 (s), 720 (m), 670 (w), 620 (w), 570 (m), 530 (m).

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eters, bond distances, bond angles, and torsion angles (12 pages). Ordering information is given on any current masthead page.

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Alkoxide and Thiolate Rhenium(VII) Oxo–Alkyl Complexes and $Re_2O_5(CH_2CMe_3)_4$, a Compound with a $[O_2Re–O–ReO_2]^{4+}$ Core

We recently reported synthetic routes to the Re(VII) dioxo compounds $ReO_2(CH_2CMe_3)_2X(py)$ (X = Br, Cl, F).[1] Rhenium(VII) compounds supported by only two oxo groups are rare, presumably because a convenient general synthesis has not been available.[2] The synthesis of the halide complexes gave us the opportunity to prepare a range of compounds via simple substitution reactions. Herein, we report the synthesis of the alkoxide and thiolate Re(VII) dioxo compounds $ReO_2(CH_2CMe_3)_2(ER)$ and describe the synthesis and structure of $Re_2O_5(CH_2CMe_3)_4$, the first example of a rhenium oxo compound containing a $[O_2Re–O–ReO_2]^{4+}$ core.

Reactions of $ReO_2(CH_2CMe_3)_2F(py)$ with Me_3SiSR reagents give $ReO_2(CH_2CMe_3)_2(SR)$ (R = Me (**1**), Ph (**2**)) (eq 1). IR

$$\mathrm{ReO_2(CH_2CMe_3)_2F(py)} + \mathrm{Me_3SiSR} \xrightarrow[\text{pentane}]{12\ \text{h}} \underset{\mathbf{1}\ \text{or}\ \mathbf{2}}{\mathrm{ReO_2(CH_2CMe_3)_2(SR)}} + \mathrm{Me_3SiF} \quad (1)$$

$$\text{R} = \text{Me}\ (\mathbf{1})\ (65\%),\ \text{Ph}\ (\mathbf{2})\ (47\%)$$

spectra recorded for **1** and **2** show the two-band pattern characteristic of a *cis*-MO_2 moiety [e.g., $\nu(ReO_2)$ = 985, 949 cm^{-1} for **1**].[3] Room-temperature ^1H NMR spectra for **1** and **2** each reveal singlets corresponding to two equivalent neopentyl ligands, but at low temperatures singlets arising from two different neopentyl groups are observed for both compounds. This, together with the IR data, indicates that the molecules have trigonal-bipyramidal (tbp) geometries in which rapidly exchanging neopentyl ligands occupy axial and equatorial positions or both neopentyl ligands occupy axial positions and rotation about the Re–S bond is slow at low temperatures. The latter structure for **2** is found in the solid state from an X-ray crystallographic study (Figure 1).[4]

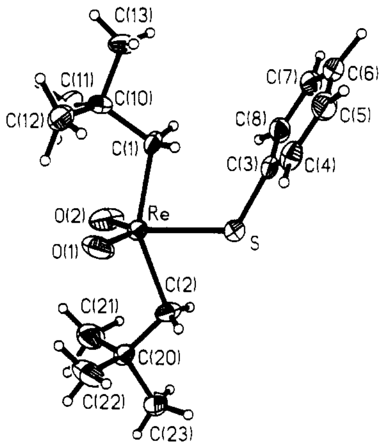

Figure 1. ORTEP plot of $ReO_2(CH_2CMe_3)_2(SPh)$ (**2**) showing the atom-numbering scheme (50% probability ellipsoids). Selected distances (Å) and angles (deg): Re–S, 2.395 (2); Re–O(1), 1.692 (7); Re–O(2), 1.694 (6); Re–C(1), 2.160 (7); Re–C(2), 2.188 (8); S–C(3), 1.774 (7); S–Re–O(1), 121.2 (2); S–Re–O(2), 120.8 (2); O(1)–Re–O(2), 117.7 (3); S–Re–C(1), 79.6 (2); S–Re–C(2), 69.8 (2); C(1)–Re–C(2), 149.5(3); Re–S–C(3), 118.3 (3).

The most unusual structural feature of **2** is the large O(1)–Re–O(2) angle [117.7 (3)°]; O=M=O angles in d^0 compounds usually fall in the range 100–110° [e.g., ∠O=Mo=O = 110.5 (3)° in tbp $MoO_2(L\text{-}NS_2)$].[5] There is no obvious electronic reason for an open angle in **2**. There are, however, four intramolecular contacts between the neopentyl methyl groups [C(11), C(12), C(21) and C(22)] and the oxo ligands, which average 0.3 Å less than the van der Waals contact distance of 3.4 Å,[6] that may explain the large angle.

The alkoxide complexes $ReO_2(CH_2CMe_3)_2(OR)$ (R = CH_2CMe_3 (**3**), *t*-Bu (**4**)) are prepared by the salt metathesis reactions shown in eq 2, and $ReO_2(CH_2CMe_3)_2(OMe)$ (**5**) is prepared by alcohol/alkoxide exchange, eq 3. Each compound

$$\mathrm{ReO_2(CH_2CMe_3)_2Br(py)} + \mathrm{LiOR} \xrightarrow[0\ ^\circ\text{C ether}]{6\ \text{h dark}} \underset{\mathbf{3}\ \text{or}\ \mathbf{4}}{\mathrm{ReO_2(CH_2CMe_3)_2(OR)}} + \mathrm{LiBr} \quad (2)$$

$$\text{R} = \mathrm{CH_2CMe_3}\ (\mathbf{3})\ (69\%),\ t\text{-Bu}\ (\mathbf{4})\ (82\%)$$

$$\mathrm{ReO_2(CH_2CMe_3)_2(O\text{-}}t\mathrm{\text{-}Bu)} + \mathrm{MeOH} \xrightarrow[\mathrm{CH_3CN}]{0.5\ \text{h dark}} \underset{\mathbf{5}\ (79\%)}{\mathrm{ReO_2(CH_2CMe_3)_2(OMe)}} + t\text{-BuOH} \quad (3)$$

shows IR bands arising from the ReO_2 group [e.g., 955, 923 cm^{-1} ($Re^{18}O_2$; 898, 878 cm^{-1}) for **4**] that are lower in energy than those observed for five-coordinate **1** and $ReO_2(CH_2CMe_3)_2Br$ (1001, 961 cm^{-1}).[1] This is consistent with the alkoxide ligand being a stronger π-donor to the Re(VII) center than a halide or thiolate and therefore competing more effectively with the oxo ligands for multiple bonding.

Efforts to obtain a high-quality X-ray structure of an alkoxide

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(4) Crystal data for $C_{16}H_{27}O_2SRe$ at −40 (1) °C: dark orange blocks from a cold (−20 °C) CH_3CN solution, 0.24 × 0.36 × 0.40 mm, triclinic, space group $P\bar{1}$, a = 9.196 (2) Å, b = 10.067 (2) Å, c = 11.122 (2) Å, α = 102.22 (1)°, β = 103.24 (1)°, γ = 105.25 (1)°, d_{calcd} = 1.69 g cm^{-3}, Z = 2, μ = 67.61 cm^{-1}. X-ray diffraction data were collected on a Nicolet R3m/V diffractometer using a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) in the θ–2θ scan mode. Lorentz and polarization corrections and an empirical absorption correction (PSICOR) were applied to the data. A total of 3858 reflections were collected in the range $4° < 2\theta < 50°$ ($\pm h, \pm k, l$); 3259 were unique reflections (R_{int} = 0.0289), and 2853 with $F_o > 6\sigma(F_o)$ were used in the structure solution. An extinction correction was applied in the final cycles of refinement. $R(F)$ = 0.0346; $R_W(F)$ = 0.0358. Structure factors from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

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