enforcer" is occupied by the dioxygen ligand, which is coordinated in a side-on fashion. The oxygen-oxygen distance of 1.262 (8) Å clearly resolves the ambiguity between a Co^{III}-peroxo and a Co^{II}-superoxo description of the bonding in favor of the latter.[9] While there are many structurally characterized superoxo complexes, Tp′Co(O_2) seems to feature the first example of a symmetrically side-on bound superoxide.[10] Kitajima et al. have recently described a doubly side-on bound peroxide ligand (μ-η^2:η^2-O_2^{2-}) coordinated to two tris(pyrazolyl)borate copper fragments.[11] Thus it appears that metals in this particular coordination environment generally favor side-on coordination of O_2 (and possibly other ligands).[12]

To further characterize this unusual O_2 complex, Tp′Co(N_2) was exposed to a mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ (1.0:1.87:1.1, determined by mass spectrometry). The IR spectrum of the resulting mixture of dioxygen complexes exhibited three bands at 961, 937, and 908 cm^{-1}. This is the expected pattern for a side-on complex,[13] whereas end-on complexes should exhibit four bands (due to the M-$^{16}O^{18}O$/M-$^{18}O^{16}O$ isomerism).[14] The magnetic susceptibility of Tp′Co(O_2) was measured on a Faraday balance in the temperature interval 4-270 K. The compound is paramagnetic and has a temperature-independent effective magnetic moment of 3.88 μ_B (extrapolated to 298 K).[15] Tetrahedral cobalt(II) usually exhibits magnetic moments in the range of 4.6-4.8 μ_B, due to the spin-only moment of three unpaired electrons plus a sizable orbital contribution.[16] The superoxide ion is an odd-electron species with a magnetic moment of 1.89 μ_B.[17] The observed moment of Tp′Co(O_2) is consistent with strong antiferromagnetic coupling of the metal ion ($S = {}^3/_2$) and the superoxide ligand ($S = {}^1/_2$),[18] resulting in a ground state with $S = 1$ to which is added a significant orbital contribution.

We were initially puzzled by the observation that reactions of Tp′Co(N_2) with stoichiometric amounts of dioxygen yielded significant quantities of Tp′CoOH[19] as a side product even in rigorously dried solvents. Eventually, we found that addition of 1 equiv of Tp′Co(O_2) to a solution of Tp′Co(N_2) resulted in the formation of Tp′CoOH in 90% yield by NMR (based on total Tp′Co). When this reaction was carried out in toluene-d_8, no incorporation of deuterium into the hydroxyl group could be detected by IR spectroscopy. However, examination of the hydroxide complex by mass spectroscopy indicated some incorporation of deuterium in the *tert*-butyl groups of the tris(pyrazolyl)borate ligand. This observation suggests abstraction of a hydrogen from the ligand followed by deuterium atom abstraction from solvent as one reaction pathway. Further experiments to identify the source of the hydrogen atom are currently in progress.

The first step in this reaction most likely involves displacement of N_2 from Tp′Co(N_2) by Tp′Co(O_2) and formation of a dinuclear peroxo bridged cobalt complex. The severe steric demands of the Tp′ ligand may further destabilize the already weak O-O bond in the peroxide intermediate,[20] leading to bond homolysis. The resultant cobalt oxo complex is expected to display high reactivity.[21] Its ability to abstract hydrogen atoms suggests a description as Tp′Co^{II}-O•, i.e., an oxygen atom radical bound to a metal atom or oxide monoanion (O^-). We note that such species are thought to be important in the oxidative coupling of methane over metal oxides at elevated temperatures.[22] Efforts to modify our system to direct the attack of the oxygen atom at external substrates rather than the ligand are currently under way.

Acknowledgment. This research was supported by the National Science Foundation (CHE 8820354).

Supplementary Material Available: Tables of X-ray structure determination of Tp′Co(O_2) including crystal data, atomic coordinates and isotropic thermal parameters, and bond distances and angles (7 pages). Ordering information is given on any current masthead page.

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True Nature of Trihalotris(tetrahydrofuran)molybdenum(III), $MoX_3(THF)_3$ (X = Cl, Br, I). A Paramagnetic ^1H Nuclear Magnetic Resonance Study[†]

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$MoCl_3(THF)_3$ is extensively used for the synthesis of molybdenum complexes in the III and lower oxidation states.[1-5] Several improved preparation procedures[6-8] have been subsequently published after the original report.[9] However, its structural nature

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[†] Dedicated to Prof. Fausto Calderazzo on the occasion of his 60th birthday.

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Table I. Assignment of Paramagnetic ^1H Nuclear Magnetic Resonance δ Values to Structures I–IV[a]

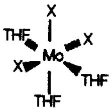
	I (α)	I (β)	II (α)	II (β)	III (α)	III (β)	IV (α)	IV (β)
X = Cl	65.7 (2)	8.2 (2)	25.0	3.7	6.73 (2)			
	56.2 (1)	6.1 (1)	17.9	3.4	6.49 (1)	2.34	6.2–6.0	2.34
X = Br	72.2 (2)	9.5 (2)	ca. 69	?	7.21 (2)			
	57.3 (1)	6.3 (1)	ca. 51	?	6.62 (1)	2.44	7.2–6.6	2.44

[a] See text for structures. Numbers in parentheses within each class are relative intensities.

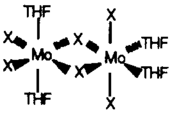
has never been fully addressed, probably because of its insolubility in most solvents and its paramagnetism.[27] Recently, multigram-scale preparations of the analogous $MoX_3(THF)_3$ (X = Br, I) compounds have appeared.[10,11] A single-crystal structural study of the iodide derivative shows an octahedral meridional arrangement of the ligands.[11,27] Structural studies of other MoX_3L_3 derivatives (X = Cl, Br, I; L = two-electron neutral donor) are limited to those few instances where single crystals suitable for X-ray diffraction have been obtained.[3b,5,10b,12] NMR investigations have not been reported, and EPR studies are difficult.[13]

We have discovered that octahedral Mo(III) complexes containing phosphine ligands exhibit relatively sharp, paramagnetically shifted ^1H NMR spectra, which allow for the first time an assessment of their structure *in solution*.[14] Paramagnetic NMR[15] studies of mononuclear octahedral d^3 systems are limited to a few compounds of chromium(III) and vanadium(II) and one compound of tungsten(III).[16] We have utilized this technique to investigate the nature of the tris(tetrahydrofuran) adducts of molybdenum(III) halides and have found an unexpectedly complex behavior. This communication reports the first paramagnetic ^1H NMR study of mononuclear molybdenum(III) coordination compounds, detailing the previously unknown chemical nature and behavior in solution of $MoX_3(THF)_3$ (X = Cl, Br), and the results of a preliminary kinetic investigation of their decomposition.

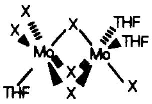
The ^1H NMR spectrum of a CD_2Cl_2 solution of crystalline $MoCl_3(THF)_3$ changes with time, and the initial pale purple solution deepens over time to a dark purple. A similar behavior was observed for the corresponding tribromide compound, where the color changes from orange to dark purple. The triiodide compound is not soluble enough in CD_2Cl_2 for an NMR study to be carried out, and the only resonances we could identify were those of free THF. The NMR peaks can be assigned to the compounds whose structures are illustrated in I–IV as shown in Table I. Free THF has resonances at δ 3.9 for the α-H and at δ 2.0 for the β-H atoms. In both cases (X = Cl, Br), the monomer resonances decrease in intensity with time. The edge-sharing bioctahedral dimer II is noticeable in the early part of the experiment. For X = Cl, it initially increases to a maximum of 19% of the total molybdenum concentration after ca. 6 min at 30 °C, but subsequently diappears. For X = Br, there is much less of compound II produced initially, and its decay is more rapid than for X = Cl. Compounds III and IV increase in concentration throughout the experiment, as does free THF.



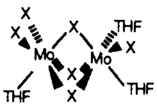
I



II



III



IV

The assignments appear reasonable in view of the following. Higher paramagnetic shifts are expected for the mononuclear I ($S = {}^3/_2$) than for II (for which metal–metal bonding or antiferromagnetic coupling can lower the effective magnetic moment) than for III and IV (where the closer approach of the two metals can give rise to a stronger metal–metal interaction). The observed shifts indicate, however, that even III and IV have residual paramagneticity. This is consistent with the available data from the literature and from other unpublished work of ours: although several edge-sharing bioctahedral compounds have short metal–metal separations (in the range 2.73–2.79 Å) and are diamagnetic,[17-19] the recently reported[20] $Mo_2Cl_6(PEt_3)_4$ compound exhibits a long metal–metal separation (3.730 (1) Å) and a high magnetic moment. Concerning confacial bioctahedral compounds, the known $[Mo_2X_7(PMe_3)_2]^-$ ions (X = Cl,[21] I[22]) show a slight paramagnetic shift for the PMe_3 proton resonance, and we have observed similar shifts for the $Mo_2Cl_6L_3$ neutral complexes (L = PEt_3, PMe_2Ph).[14] The assignment of structure II to the edge-sharing bioctahedral dimer results primarily from the observation of two resonances for the α protons. An all-axial or all-equatorial derivative should exhibit only one signal. Although we cannot exclude that a mixture of all-axial and all-equatorial isomers is present (in which case they must react at approximately the same rate), we favor the structural assignment shown in II on the bais of other known structures of edge-sharing bioctahedral derivatives of molybdenum[20] and other metals.[23,24] The α protons for the bromide analogue are much more paramagnetically shifted and indicate that II (X = Br) is almost as paramagnetic as I, whereas the metal–metal interaction in II (X = Cl) is substantial. The position of the β-H resonances for II (X = Br) could not be identified because the compound never accumulates to a sufficient

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extent and because these peaks probably overlap with the β-H resonances of 1 and with the α-H resonances of III and IV. The stereoisomerism suggested for the confacial bioctahedral structure is analogous to that reported for the $[Mo_2X_7(PMe_3)_2]^-$ (X = Cl, I) ions.[21,22]

The following points are also worthy of note. There is no extra peak in the NMR spectrum that could be assigned to a mononuclear facial isomer. Therefore, the $MoX_3(THF)_3$ compounds are present *in solution* as meridional isomers exclusively. Integration establishes that the amounts of free THF and THF of compounds III and IV *that are produced* are equivalent to each other and correspond to 1.5 mol per mole of $MoCl_3(THF)_3$ consumed. However, extrapolation of the data to zero time shows that the starting materials were already contaminated by free THF (for X = Cl, Br) and face-sharing dimers (for X = Cl).

An important point emerges from the latter observation. Most of the recommended procedures for the synthesis of $MoCl_3(THF)_3$ involve the use of CH_2Cl_2 as solvent or cosolvent for the synthesis or separation procedure.[1b,6,7] The product has been described before as orange, brownish-orange, pink, pinkish-purple, and even blue-purple.[1b,2c,6,7,9] We propose that these different colors are the result of variable amounts of dinuclear impurities. According to our study, the product can be expected to be a *mixture* of $MoCl_3(THF)_3$ and $Mo_2Cl_6(THF)_3$, containing perhaps minor amounts of $Mo_2Cl_6(THF)_4$ and free THF. Wedd and co-workers[1b] reported that $MoCl_3(THF)_3$ loses THF in benzene to afford a pinkish-red, diamagnetic solid, which they formulated as $Mo_3Cl_9(THF)_5$ on the basis of analytical data. A subsequent investigation by electronic spectroscopy suggested that association to $Mo_2Cl_6(THF)_3$ occurs instead.[25] The conversion of III and IV back to $MoCl_3(THF)_3$ in THF is very slow (less than 20% conversion over 48 h at room temperature).

The above NMR data can be interpreted in terms of the two-step process illustrated in Scheme I. A preliminary kinetic analysis for the bromide system indicates a second-order decay of the monomer concentration, for a k value of 0.431 ± 0.005 M^{-1} min^{-1} at 30 °C. The data for the chloride system are less accurate, but the two halide systems take approximately the same time to transform to the final dinuclear product. More kinetic studies are planned for the near future.

Scheme I

$$2MoX_3(THF)_3 \xrightarrow{k} Mo_2X_6(THF)_4 + 2THF \qquad (1)$$

$$Mo_2X_6(THF)_4 \rightarrow Mo_2X_6(THF)_3 + THF \qquad (2)$$

Similar equilibria might take place with different ligand systems. For instance, the acetonitrile derivatives $MoCl_3(MeCN)_3{\cdot}MeCN$,[8] $MoCl_3(MeCN)_3$,[9] and $Mo_2Cl_6(MeCN)_3$[26] have all been described. We are planning to reinvestigate these compounds as well as others and to study the monomer/dimer interconversion by paramagnetic ^1H NMR.

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Supplementary Material Available: A figure showing the linear relationship between the inverse concentration of $MoBr_3(THF)_3$ and time (1 page). Ordering information is given on any current masthead page.

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A Well-Defined Rhenium(VII) Olefin Metathesis Catalyst

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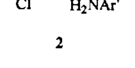
Molybdenum, tungsten, and rhenium are the three most active metals in classical olefin metathesis systems.[1] Molybdenum(VI)[2] and tungsten(VI)[3] alkylidene complexes of the type $M(CHR')(NAr)(OR)_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2) have been shown to be well-behaved olefin metathesis catalysts with an activity that can be controlled through the choice of OR. Although several rhenium alkylidene complexes have been reported,[4] none has shown any confirmable metathesis activity, even toward strained cyclic olefins such as norbornene. Since Re≡CR″ and M=NR″ (M = Mo or W) can be regarded as isoelectronic units, plausible candidates as olefin metathesis catalysts are complexes of the type $Re(CHR')(CR'')(OR)_2$. We report here that such a complex in which OR = $OCMe(CF_3)_2$ is a well-behaved olefin metathesis catalyst.

Treatment of orange $Re(NAr')_2$(CH-*t*-Bu)(CH_2-*t*-Bu) (**1**) (Ar′ = 2,6-$C_6H_3Me_2$)[4c] with excess HCl in dimethoxyethane at 0 °C affords [Re(C-*t*-Bu)(CH-*t*-Bu)(H_2NAr')Cl_2]$_2$ (**2**, eq 1) in 80% yield.[5] Two isomers of **2** are observed in solution. The structure of what we presume to be the major isomer has been determined by an X-ray study, details of which will be published in the full report. The structure is that shown in eq 1 in which the alkylidene



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(5) A solution of $Re(NAr')_2$(CH-*t*-Bu)(CH_2-*t*-Bu) (4.64 g, 8.2 mmol) in dimethoxyethane (100 mL) was cooled to 0 °C and treated with HCl (590 mL, 26 mmol). The orange solution immediately darkened, and a white precipitate formed. After stirring of the solution at 25 °C for 2.5 h, the solvent was removed in vacuo, leaving a beige powder, which was extracted away from insoluble $Ar'NH_3Cl$ with benzene and filtered through a pad of Celite. The filtrate was then reduced to dryness in vacuo and washed with pentane, to yield a faintly orange powder (3.4 g, 80%): ^1H NMR (C_6D_6) (major isomer) δ 14.49 (s, 2, C*H*-*t*-Bu), 6.7–6.5 (m, 6, H_{aryl}), 6.7 and 6.3 (d, 2, NH_2), 2.37 and 2.17 (s, 6, 2,6-$C_6H_3Me_2$), 1.39 and 1.01 (s, 18, CMe_3); ^{13}C NMR (THF-d_8, major isomer) δ 292.1 (*C*-*t*-Bu), 286.3 (*C*H-*t*-Bu, J_{CH} = 130 Hz), 144.2 (C_{ipso}), 128.7 (C_{meta}), 123.7 (C_{ortho}), 119.5 (C_{para}), 53.4 and 46.8 (CMe_3), 31.5 and 28.5 (CMe_3). Anal. Calcd for $C_{36}H_{60}Cl_4N_2Re_2$: C, 41.77; H, 5.84; N, 2.71. Found: C, 42.11; H, 6.00; N, 2.50.

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