complexes, shifts in the relatively low frequency $NH_3$ rocking modes (600–800 cm$^{-1}$) can be significant to entropy changes in redox couples.

In this note we present the results of calculations based on eqs 1 and 2 for the hexaammine couples of cobalt(III/II) and ruthenium(III/II). These couples were chosen since the vibrational properties of hexaammine complexes have been studied in detail by a number of workers.[9] Table I presents the vibrational frequencies observed or estimated for chloride salts of the complexes of interest. It is assumed that the solid-state frequencies are comparable to the actual frequencies in solution (reported[9] skeletal frequencies from Raman spectra of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]^{3+}(aq)$ differ by ≤10 cm$^{-1}$). The least satisfactory compilation is for $[Ru(NH_3)_6]^{2+}$, for which surprisingly few vibrational data are available.[10] The far-infrared spectrum of $[Ru(NH_3)_6]Cl_2$ was therefore determined in this work to provide a value for the $T_{1u}$ bending vibrations.[11] Details of the estimates used are given in the footnotes of Table I. It is clear that frequency shifts in the cobalt case are significant, with the observed $T_{1u}$ M–N stretching band ($\nu_3$) shifting ~150 cm$^{-1}$, while, in the ruthenium case, the observed shift is ~50 cm$^{-1}$. The much reduced M–N force constant for Co$^{II}$ relative to Co$^{III}$ can be attributed to the $(d\pi)^5(d\sigma^*)^2$ to $(d\pi)^6$ change in electronic configuration at the metal center.

From the data in Table I and eq 1, the values of $\Delta S_{in}(vib)°$ at 298 K for the $[Co(NH_3)_6]^{3+/2+}$ and $[Ru(NH_3)_6]^{3+/2+}$ couples are estimated to be 15 ± 2 and 2 ± 2 eu, respectively. The estimated error in these values is based on an assumption that the vibrational frequencies in Table I are within 10 cm$^{-1}$ of the true value in aqueous solution, but larger errors in the assumed vibrational frequencies, especially for the estimated $\nu_6$ $T_{1u}$ mode, could lead to a values of $\Delta S_{in}(vib)°$ outside the ranges given.

Another important contribution to $\Delta\Delta S_{rc}$ for these two couples arises from the $\Delta S_{in}(el)°$ values, which are estimated[12] to be ~2.0–2.5 cal deg$^{-1}$ mol$^{-1}$ for the conversion of low-spin cobalt(III) to high-spin cobalt(II) complexes and −1.4 cal deg$^{-1}$ mol$^{-1}$ for reduction of low-spin ruthenium(III) to low-spin ruthenium(II). The total $\Delta S_{rc}$ difference between the two couples due to changes in the vibrational and electronic partition functions is therefore estimated as 16 ± 3 eu, which accounts for much of the estimated[2a] experimental difference of ~27 eu. Unfortunately, the hexaamminecobalt(III/II) couple is not conveniently studied electrochemically, so the actual $\Delta S_{rc}°$ value has not been determined. However, given the consistent differences between $\Delta S_{rc}°$ values for Co(III/II) and Ru(III/II) couples,[1,2] the calculations here suggest that approximately half of the difference in $\Delta S_{rc}°$ values for these complexes is attributable to the inner-sphere vibrational term, with the $\Delta S_{in}(el)°$ term accounting for an additional ~4 eu. The remaining difference may be related primarily to the outer-sphere contributions arising from the large Co–N distance change in the cobalt couple.

Although complete vibrational assignments are not available for other related complexes with L = en, bpy, and $H_2O$, the known vibrational frequency shifts for the Co couples are consistent with the same explanation for the observed higher $\Delta S_{rc}°$ values in comparison to those for low-spin/low-spin Ru and Fe couples. For example, $[Fe(bpy)_3]^{3+/2+}$ and $[Co(bpy)_3]^{3+/2+}$ couples have $\Delta S_{rc}°$ values of 2 and 22 eu in water, respectively.[1c] The observed M–N stretching frequencies[8] in the Fe complexes are essentially unchanged between the iron(III) and iron(II) complexes, while the same frequencies shift lower by ~130 cm$^{-1}$ in going from cobalt(III) to cobalt(II). Assuming comparable shifts in other bending and stretching modes of the $ML_3$ unit, much of the 20 eu difference in $\Delta S_{rc}°$ values could be attributable to the vibrational entropy component, as demonstrated here for the hexaammine case.

In general, changes in vibrational frequencies and electronic degeneracies are expected to dominate intramolecular contributions to redox entropy changes (rotational entropy changes are likely small, on the order of 10$^{-1}$ eu, for typical bond length changes). The emergence of gas-phase methods[14] for assessing entropies of electron attachment and ionization of metal complexes could lead to direct comparisons of experimental and calculated intramolecular entropy changes for redox processes. Details of the statistical mechanical evaluation of entropy changes for a variety of transition-metal complex redox couples will be given in a future article.

Finally, it should be noted that any chemical change at a metal center that leads to significant alteration of the skeletal frequencies of the complex can have an appreciable vibrational contribution to the entropy change of the reaction. Spin equilibrium is an excellent example of such a process, and evaluation of the thermochemistry of such processes with respect to intramolecular vibrational entropies has been illuminating but surprisingly limited.[15]

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(11) Far-IR spectra were obtained for $[Ru(NH_3)_6]Cl_2$ in a polyethylene pellet. The complex was produced via zinc reduction of an aqueous solution of $[Ru(NH_3)_6]Cl_3$ under argon followed by precipitation with $NH_4Cl$. Isotope studies to confirm the band assignments have not been completed. Assignment of the observed band at ~245 cm$^{-1}$ as the $T_{1u}$ mode must be considered tentative.

(12) In the case of octahedral low-spin d$^6$ $ML_6$ complexes of Ru$^{II}$ and Co$^{III}$, the electronic partition function, $q_{el}$, is equal to 1 for these $^1A_{1g}$ complexes. For Ru$^{III}$ and high-spin Co$^{II}$ the calculation of $q_{el}$ is complicated by the effects of spin–orbit coupling and Jahn–Teller distortion. For $O_h$ Ru$^{III}$, the ground state including spin–orbit coupling is $J = {}^1/_2$, with the $J = {}^3/_2$ state higher in energy by $3\lambda/2$ (~1800 cm$^{-1}$ higher on the basis of the free ion value of $\zeta$). Since the higher state is not significantly populated at 298 K, $q_{el} \simeq (2(1/2) + 1) = 2$, and $\Delta S_{in}(el)°$ for Ru$^{III/II}$ $\simeq R \ln(1/2)$. For high-spin $O_h$ Co$^{II}$, the ground state is also a Kramers doublet with $J = {}^1/_2$, but the two higher lying states ($J = {}^3/_2$ and $J = {}^5/_2$) are thermally accessible. The value of $q_{el}$ will therefore be >2, but the necessary parameters are not available to allow an accurate estimate. For a range of $\lambda$ values of $0.75\lambda_0$–$1.0\lambda_0$ and an $A$ value[13] of 1.5 and with distortions from cubic symmetry ignored, $q_{el}$ is estimated to be ~ 2.6–3.2.

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## X-ray Diffraction Study of Pentacarbonyl($\mu$-hydrido)(nonacarbonyldimanganese)rhenium, $HMn_2Re(CO)_{14}$

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and Thomas F. Koetzle*[‡]

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Among the large number of polynuclear transition-metal complexes containing bridging hydride ligands, those which contain a hydride bridging two *different* metals are rare.[1] Reliable, high-yield methods for the synthesis of such species are still being

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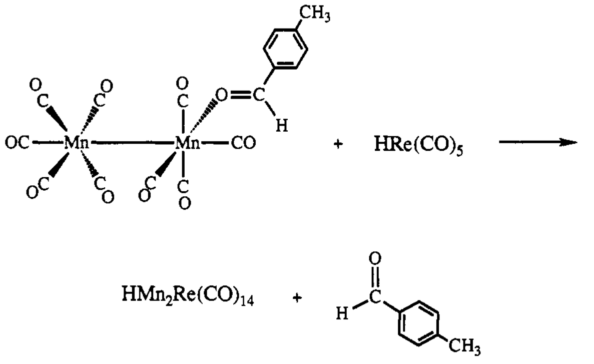
**Table I.** Experimental Data for the X-ray Diffraction Study of $HMn_2Re(CO)_{14}$

| | | | |
|---|---|---|---|
| formula | $C_{14}HO_{14}Mn_2Re$ | $V$, Å$^3$ | 2018.6 (9) |
| mol wt | 689.23 | $\rho$(calcd.), g cm$^{-3}$ | 2.267 (1) |
| space group | $P2_1/n$, No. 14 | $\mu$, cm$^{-1}$ | 73.06 |
| $a$, Å | 9.286 (1) | $T$, °C | 21 |
| $b$, Å | 15.852 (3) | λ, Å | 0.710 69$^a$ |
| $c$, Å | 14.288 (2) | transm coeff | 0.9972–0.7637 |
| $\beta$, deg | 106.32 (1) | $R$ | 0.031 |
| $Z$ | 4 | $R_w$ | 0.042 |

$^a$Graphite monochromated, Mo K$\bar{\alpha}$.

developed. An approach that has been used successfully in several cases[2] is the reaction of a metal hydride "donor" with a coordinatively unsaturated "acceptor" obtained from a metal complex containing a labile ligand such as THF. Recently, we reported[3] the synthesis and structural characterization of $Mn_2(CO)_9(\eta^1$-aldehyde) complexes. The weakly bound $\eta^1$-aldehyde ligand in these complexes is displaced readily by $CH_3CN$, suggesting that such aldehyde complexes might serve as sources of $Mn_2(CO)_9$ moieties in the synthesis of heterometallic cluster complexes. We now report the X-ray crystal structure of a mixed Mn-Re system, the open, L-shaped $HMn_2Re(CO)_{14}$, which has been prepared in the manner outlined above; see eq 1.



(1)

## Experimental Section

All manipulations were carried out under an inert atmosphere by using Schlenk techniques or a Vacuum Atmospheres drybox. NMR spectra were recorded on a Bruker AM-300 spectrometer; IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. $Mn_2(CO)_9(\eta^1$-tolualdehyde)[3] and $HRe(CO)_5$[4] were prepared by published procedures. Elemental analyses (C, H) were carried out by Galbraith Laboratories. Analyses for Mn and Re were carried out at Brookhaven by using X-ray fluorescence.

**$HMn_2Re(CO)_{14}$.** $Mn_2(CO)_9(\eta^1$-tolualdehyde) (351 mg, $7.28 \times 10^{-4}$ mol) was dissolved in hexane (5 mL), and $HRe(CO)_5$ (266 mg, $8.12 \times 10^{-4}$ mol) was added by vacuum transfer. The solution was stirred for 30 min at 0 °C to give an orange precipitate in an orange solution. The precipitate was collected by filtration, washed with hexane (2 × 5 mL), and dried under vacuum to give $HMn_2Re(CO)_{14}$ (407 mg, 81% yield). $^1H$ NMR ($C_6D_6$): $\delta$ -19.66 (s).[5] IR (hexane): 2147 w, 2086 w, 2047 s, 2014 m, 1989 m, 1984 m, 1974 m, 1961 w, 1933 w cm$^{-1}$. Anal. Calcd for $C_{14}HMn_2O_{14}Re$: C, 24.40; H, 0.15; Mn, 15.9; Re, 27.0. Found: C, 24.31; H, 0.35; Mn, 16.1; Re, 27.6. Red crystals were obtained by slow cooling of a toluene solution of $HMn_2Re(CO)_{14}$ to -15 °C.

**Table II.** Atomic Positional and Equivalent Isotropic Displacement Parameters$^a$

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| Re | 0.04545 (3) | 0.16536 (2) | 0.12469 (2) | 2.612 (5) |
| Mn1 | −0.1004 (1) | 0.35969 (7) | 0.09960 (8) | 2.78 (2) |
| Mn2 | −0.1270 (1) | 0.38396 (6) | 0.29639 (6) | 1.76 (2) |
| O1 | −0.2835 (6) | 0.0973 (4) | 0.0679 (5) | 5.1 (2) |
| O2 | 0.666 (8) | 0.1230 (4) | 0.3431 (4) | 5.2 (2) |
| O3 | 0.0350 (7) | 0.1909 (5) | −0.0942 (4) | 5.4 (2) |
| O4 | 0.3674 (6) | 0.2473 (4) | 0.1858 (5) | 5.3 (2) |
| O5 | 0.1614 (7) | −0.0149 (4) | 0.1051 (5) | 5.1 (2) |
| O6 | −0.0908 (8) | 0.3617 (5) | −0.1037 (5) | 5.6 (2) |
| O7 | −0.4079 (7) | 0.2857 (5) | 0.0470 (5) | 5.6 (2) |
| O8 | −0.2393 (9) | 0.5273 (4) | 0.0603 (6) | 6.7 (2) |
| O9 | 0.2055 (6) | 0.4373 (4) | 0.1672 (5) | 5.4 (2) |
| O10 | 0.0006 (8) | 0.5557 (4) | 0.2859 (5) | 5.4 (2) |
| O11 | −0.1404 (7) | 0.4015 (5) | 0.4996 (4) | 5.9 (2) |
| O12 | −0.4394 (7) | 0.4498 (6) | 0.2138 (6) | 7.9 (2) |
| O13 | 0.1849 (6) | 0.3129 (4) | 0.3568 (4) | 4.2 (1) |
| O14 | −0.2579 (7) | 0.2106 (4) | 0.2723 (5) | 5.5 (2) |
| C1 | −0.1648 (8) | 0.1235 (5) | 0.0866 (5) | 3.3 (2) |
| C2 | 0.0596 (9) | 0.1403 (5) | 0.2649 (6) | 3.4 (2) |
| C3 | 0.0362 (8) | 0.1842 (5) | −0.0160 (6) | 3.5 (2) |
| C4 | 0.2532 (8) | 0.2181 (5) | 0.1649 (6) | 3.6 (2) |
| C5 | 0.1228 (8) | 0.0512 (5) | 0.1123 (6) | 3.4 (2) |
| C6 | −0.0919 (9) | 0.3568 (5) | −0.0242 (6) | 3.6 (2) |
| C7 | −0.2895 (9) | 0.3118 (5) | 0.0695 (6) | 3.7 (2) |
| C8 | −0.1853 (9) | 0.4634 (6) | 0.0775 (6) | 4.0 (2) |
| C9 | 0.0915 (9) | 0.4062 (5) | 0.1441 (6) | 3.8 (2) |
| C10 | −0.0486 (9) | 0.4909 (5) | 0.2894 (6) | 3.7 (2) |
| C11 | −0.1358 (8) | 0.3947 (6) | 0.4196 (6) | 3.6 (2) |
| C12 | −0.318 (1) | 0.4249 (6) | 0.2433 (7) | 4.8 (2) |
| C13 | 0.0652 (9) | 0.3406 (5) | 0.3310 (5) | 3.5 (2) |
| C14 | −0.2048 (8) | 0.2764 (6) | 0.2813 (6) | 3.6 (2) |
| H | 0.00 (1) | 0.266 (7) | 0.154 (8) | 8 (3)$^b$ |

$^a$For anisotropically refined atoms, the equivalent isotropic displacement parameters are defined as $B = {}^1/_3[B_{22} + (B_{11} + B_{33} + 2B_{13} \cos\beta)/\sin^2\beta]$. $^b$Refined isotropically.

A crystal of dimensions 0.15 × 0.20 × 0.25 mm was used for the X-ray structure analysis; measurements were carried out at 21 °C on an Enraf-Nonius CAD-4 diffractometer using Mo K$\bar{\alpha}$ radiation. Experimental data are given in Table I. On the basis of observed systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, the space group was assigned as $P2_1/n$. Altogether, 4386 independent reflections up to $((\sin\theta)/\lambda)_{max} = 0.64$ Å$^{-1}$ were sampled by $\omega$-$2\theta$ scans using variable speed to attain approximately constant statistical precision. Measured intensities were corrected for Lorentz and polarization effects and for absorption based on azimuthal scan intensity data for four reflections ($\chi \geq 85°$). A total of 2956 reflections with $F_o^2 \geq 2\sigma(F_o^2)$ were used for the structure solution and refinement.[6] The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least squares techniques with anisotropic displacement parameters for all non-hydrogen atoms, minimizing $\sum w(F_o - |F_c|)^2$ with weights $w = [\sigma^2(F_o)]^{-1}$ and $\sigma(F_o) = [\sigma_c^2(F_o^2) + 0.045^2(F_o^4)]^{1/2}/2F_o$. No extinction correction was applied. Upon convergence, a final difference Fourier map showed a peak in the expected[7] position bridging Mn and Re for the $\mu_2$-hydride ligand. The hydrogen positional and isotropic displacement parameters refined satisfactorily together with those of the rest of the structure model (total of 280 parameters).

## Results

The title compound was prepared according to eq 1. The atomic coordinates and equivalent isotropic displacement parameters from the X-ray diffraction study are given in Table II.[5] The molecular structure with bond distances is shown in Figure 1, while bond angles are listed in Table III.

---

(1) (a) For a review of metal complexes with bridging hydrides, see: Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251–274. (b) For a general review of heterometallic complexes, see: Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 6, Chapter 40.

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(3) (a) Bullock, R. M.; Rappoli, B. J.; Samsel, E. G.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 261–263. (b) Bullock, R. M.; Rappoli, B. J. *J. Am. Chem. Soc.*, in press.

(4) Warner, K. E.; Norton, J. R. *Organometallics* **1985**, *4*, 2150–2160.

(5) The value of the equivalent isotropic displacement parameter $B$ for atom Mn2 is significantly lower than that for atom Mn1, consistent with the possible presence of a small amount of $(CO)_5Re(\mu$-$H)Mn(CO)_4Re(CO)_5$ impurity in the crystal. In the $^1H$ NMR spectrum, a singlet of low intensity, observed at $\delta$ -19.24, is tentatively assigned to this impurity.

(6) *Enraf-Nonius Structure Determination Package, SDP*; Enraf-Nonius: Delft, Holland, 1987.

(7) The location of the $\mu_2$-hydride is consistent with the results of an energy minimization calculation carried out as described in: Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509–2516.

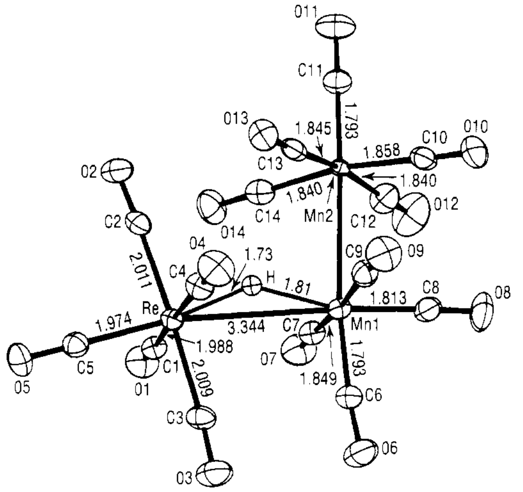

**Figure 1.** ORTEP drawing of $HMn_2Re(CO)_{14}$ molecule showing atomic nomenclature and bond distances, with ellipsoids drawn to enclose 50% probability. Bond distances not shown: Mn1-Mn2 = 2.916 (1) Å, Re-C4 = 2.031 Å, Mn1-C9 = 1.867 Å, C1-O1 = 1.138 Å, C2-O2 = 1.134 Å, C3-O3 = 1.120 Å, C4-O4 = 1.118 Å, C5-O5 = 1.120 Å, C6-O6 = 1.141 Å, C7-O7 = 1.133 Å, C8-O8 = 1.125 Å, C9-O9 = 1.130 Å, C10-O10 = 1.132 Å, C11-O11 = 1.160 Å, C12-O12 = 1.156 Å, C13-O13 = 1.155 Å, C14-O14 = 1.146 Å. Esd's in bond distances: M-M, 0.001 Å; M-C, 0.007-0.009 Å; M-H, 0.10-0.11 Å, C-O, 0.008-0.010 Å.

## Discussion

The L-shaped metal skeleton of $HMn_2Re(CO)_{14}$ is similar to that found in the isomorphous $HMnRe_2(CO)_{14}$,[8] in $HRe_3(CO)_{14}$,[9] and in $(C_5H_5)_2(CO)Ta(H)Mn_2(CO)_9$.[10] Single hydride bridges normally are associated with an increase in the metal-metal separation,[11] and this is the case for $HMn_2Re(CO)_{14}$: The hydride-bridged Mn-Re distance of 3.344 (1) Å is thus substantially longer than the Mn-Re distances of 2.909 (1) Å found in $MnRe(CO)_{10}$[12] and 2.960 (3) Å in $HMnRe_2(CO)_{14}$ where the hydride bridges the Re-Re bond.[8] In our current study, the M-H bond distances (Mn1-H = 1.81 (10) Å; Re-H = 1.73 (11) Å) have relatively high esd's, as expected for X-ray-determined values. This precludes any conclusions regarding possible asymmetry of the bridge, such as has been detected in the two complexes with M-($\mu_2$-H)-M′ bridges for which neutron diffraction results are available.[13] The Mn-Mn distance of 2.916 (1) Å is comparable to the values of 2.9038 (6) Å in $Mn_2(CO)_{10}$, determined by X-ray diffraction at 23 °C,[14,15] 2.938 (1) Å in $(C_5H_5)_2Ta(H)Mn_2(CO)_9$,[10] and 2.89 (1) Å in $[Mn_3(CO)_{14}]^-$, which has a linear metal skeleton.[16]

**Table III.** Bond Angles (deg)

| | | | |
|---|---|---|---|
| Mn1-Re-C1 | 86.6 (2) | C7-Mn1-C8 | 89.6 (4) |
| Mn1-Re-C2 | 101.5 (2) | C7-Mn1-C9 | 173.8 (3) |
| Mn1-Re-C3 | 81.6 (2) | C7-Mn1-H | 96 (3) |
| Mn1-Re-C4 | 88.6 (2) | C8-Mn1-C9 | 91.6 (4) |
| Mn1-Re-C5 | 169.1 (2) | C8-Mn1-H | 165 (3) |
| Mn1-Re-H | 20 (3) | C9-Mn1-H | 81 (3) |
| C1-Re-C2 | 89.5 (3) | Mn1-Mn2-C10 | 85.8 (2) |
| C1-Re-C3 | 90.7 (3) | Mn1-Mn2-C11 | 177.0 (2) |
| C1-Re-C4 | 175.1 (3) | Mn1-Mn2-C12 | 89.0 (3) |
| C1-Re-C5 | 91.3 (3) | Mn1-Mn2-C13 | 82.6 (2) |
| C1-Re-H | 95 (3) | Mn1-Mn2-C14 | 84.4 (2) |
| C2-Re-C3 | 176.9 (3) | C10-Mn2-C11 | 95.3 (3) |
| C2-Re-C4 | 90.5 (3) | C10-Mn2-C12 | 90.2 (4) |
| C2-Re-C5 | 89.1 (3) | C10-Mn2-C13 | 89.4 (3) |
| C2-Re-H | 84 (3) | C10-Mn2-C14 | 170.1 (3) |
| C3-Re-C4 | 89.5 (3) | C11-Mn2-C12 | 93.8 (4) |
| C3-Re-C5 | 87.8 (3) | C11-Mn2-C13 | 94.6 (3) |
| C3-Re-H | 99 (3) | C11-Mn2-C14 | 94.5 (3) |
| C4-Re-C5 | 93.5 (3) | C12-Mn2-C13 | 171.6 (4) |
| C4-Re-H | 80 (3) | C12-Mn2-C14 | 88.7 (4) |
| C5-Re-H | 170 (3) | C13-Mn2-C14 | 90.3 (3) |
| Re-Mn1-Mn2 | 99.19 (3) | Re-C1-O1 | 177.2 (6) |
| Re-Mn1-C6 | 87.3 (3) | Re-C2-O2 | 177.3 (7) |
| Re-Mn1-C7 | 88.7 (2) | Re-C3-O3 | 176.5 (7) |
| Re-Mn1-C8 | 176.2 (2) | Re-C4-O4 | 179.1 (7) |
| Re-Mn1-C9 | 90.5 (2) | Re-C5-O5 | 177.3 (7) |
| Re-Mn1-H | 19 (3) | Mn1-C6-O6 | 174.3 (7) |
| Mn2-Mn1-C6 | 173.5 (3) | Mn1-C7-O7 | 176.2 (7) |
| Mn2-Mn1-C7 | 86.9 (2) | Mn1-C8-O8 | 177.6 (8) |
| Mn2-Mn1-C8 | 84.2 (2) | Mn1-C9-O9 | 176.4 (7) |
| Mn2-Mn1-C9 | 87.2 (2) | Mn2-C10-O10 | 179.2 (6) |
| Mn2-Mn1-H | 82 (3) | Mn2-C11-O11 | 179.5 (7) |
| C6-Mn1-C7 | 93.5 (3) | Mn2-C12-O12 | 176.9 (8) |
| C6-Mn1-C8 | 89.3 (4) | Mn2-C13-O13 | 177.0 (6) |
| C6-Mn1-C9 | 92.5 (3) | Mn2-C14-O14 | 177.6 (7) |
| C6-Mn1-H | 104 (3) | Re-H-Mn1 | 141 (6) |

In $HMn_2Re(CO)_{14}$, the hydride-bridged Mn-Re carbonyls are eclipsed, while the $Mn_2(CO)_9$ unit is staggered. The Mn-Mn-Re angle is opened to 99.19 (3)°, reflecting the strain introduced by the interaction of equatorial carbonyls on Re with those on Mn2 (O2···O13 = 3.19 Å; O2···O14 = 3.21 Å). The observed conformation is similar to that reported[8] for $HMnRe_2(CO)_{14}$, Mn-Re-Re = 98.09 (7)°. By contrast, $HRe_3(CO)_{14}$[9] has the carbonyls of both terminal Re atoms staggered with respect to the central Re; the additional steric strain thus introduced causes the Re-Re-Re angle to be further opened to 107°.

As can be seen in Figure 1, the octahedral coordination of carbonyls about Re is distorted substantially by the presence of the hydride ligand. For example, angle Mn1-Re-C2 is 101.5 (2)° while Mn1-Re-C3 is 81.6 (2)°.[17] Distortions at Mn1 are smaller, e.g., Re-Mn1-C6 = 87.3 (3)°, and in general, the bonding within the $Mn_2(CO)_9$ unit is similar to that found in $Mn_2(CO)_{10}$. Thus, the axial Mn1-C6 and Mn2-C11 distances (mean 1.793 (8) Å) are shorter than the equatorial Mn-C distances (mean 1.850 (4) Å), and the Mn-Mn-C (equatorial) angles are acute (mean 85.7 (8)°). Mn1-C8 (1.813 (9) Å) is shorter than the other equatorial Mn-C bonds, reflecting the relatively lesser trans-influence of the Mn-H-Re bridge compared to CO, and this distance has therefore been excluded in the calculation of the mean value above. The difference between axial and equatorial Re-C distances, while still significant, is somewhat smaller than for Mn, viz., Re-C5 1.974 (8) Å vs. the mean Re-C (equatorial) 2.010 (9) Å.[18]

While some syntheses of hydride-bridged heterometallic complexes have employed displacement of $CH_3CN$ and other solvents

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[17] The O3···O6 contact of 2.94 Å is the shortest such intramolecular interaction found here.

[18] In fact the differences Re-C(equatorial)$_{mean}$ − Re-C5 = 0.036 (12) Å and Mn-C(equatorial)$_{mean}$ − Mn1-C8 = 0.037 (10) Å are essentially identical while Mn-C(equatorial)$_{mean}$ − Mn-C(axial)$_{mean}$ = 0.057 (9) Å. Thus, the relative trans-influences are Mn-Mn < Mn-H-Re < CO. The precision of this study is not sufficient to detect differences between axial and equatorial C-O distances; overall mean values are 1.144 (4) Å at Mn and 1.126 (4) Å at Re.

by a metal hydride, $Mn_2(CO)_9(CH_3CN)$ cannot be used in place of $Mn_2(CO)_9(\eta^1$-tolualdehyde) in the synthesis of $HMn_2Re(CO)_{14}$. When a $C_6D_6$ solution of $Mn_2(CO)_9(CH_3CN)$ (0.045 M) was treated with excess $HRe(CO)_5$ (1.0 M) and heated to 60 °C for 22 h, about half of the $Mn_2(CO)_9(CH_3CN)$ was consumed. The main products observed by $^1H$ NMR were $HMn(CO)_5$ ($\delta$ −7.87) and a bridging hydride species at $\delta$ −15.4 assigned as $HRe_3(CO)_{14}$; however, no formation of $HMn_2Re(CO)_{14}$ was observed. Clearly, the high lability of the complexed aldehyde is a critical requirement for the success of the synthesis of $HMn_2Re(CO)_{14}$. Warner and Norton[4] have reported the formation of heterometallic complexes from the reaction of metal alkyls with metal hydrides. For example, they reported that $HMnRe_2(CO)_{14}$ and $CH_3CHO$ resulted from the reaction of $CH_3Mn(CO)_5$ and $HRe(CO)_5$ in benzene. In view of our results indicating that $HRe(CO)_5$ reacts quickly with the $Mn_2(CO)_9(\eta^1$-aldehyde) complex, it is possible that a related aldehyde complex was an unobserved intermediate in their reaction as well.

We believe that the displacement of the aldehyde ligand of $Mn_2(CO)_9(\eta^1$-tolualdehyde) by metal hydrides will provide convenient access to a series of hydride-bridged heterometallic complexes, and we are continuing synthetic and crystallographic work in this area.

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**Registry No.** $HMn_2Re(CO)_{14}$, 120307-19-9; $Mn_2(CO)_9(\eta^1$-tolualdehyde), 120307-17-7; $HRe(CO)_5$, 16457-30-0; Re, 7440-15-5; Mn, 7439-96-5.

**Supplementary Material Available:** Tables S1 (further experimental data) and S2 (anisotropic displacement parameters) (4 pages); Table S3 (structure factors) (30 pages). Ordering information is given on any current masthead page.

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# Kinetic Studies of $PPh_3$ Substitution of Sulfur-Coordinated Thiophenes in $Cp'(CO)_2Re(Th)$: A Model for Thiophene Adsorption onto Hydrodesulfurization Catalysts

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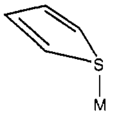
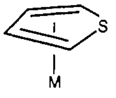
A point of central importance to the mechanism(s) of thiophene hydrodesulfurization (HDS) on heterogeneous catalysts is the mode of thiophene (T) adsorption and activation on a metal site.[2] Of the several known modes of thiophene coordination in transition-metal complexes,[3] the S- and $\eta^5$-bound forms are most often suggested for thiophene adsorption to catalyst surfaces. While there is much evidence to support $\eta^5$-coordination and activation of thiophene in organometallic complexes and on catalysts,[4–6] there is little such evidence for the S-bonded form. This arises from the weak donor ability of the thiophene sulfur atom. Thus, in the only known S-bound thiophene complexes, $Ru(NH_3)_5(T)^{2+}$,[7] $CpFe(CO)_2(T)^+$,[8] $CpFe(NCMe)_2(2,5\text{-}Me_2T)^+$,[9] $W(CO)_3(PCy_3)_2(T)$,[10] and $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2^+$, in which thiophene is part of a chelate ligand,[11] the thiophene is very weakly coordinated and easily displaced. This suggests that it would also be weakly coordinated to a metal site on a catalyst. However, recently we reported[12] a stable S-bound thiophene complex $Cp^*(CO)_2Re(T)$ and showed that the diene portion of the thiophene is activated to bind to $Fe(CO)_3$, giving a dinuclear complex $Cp^*(CO)_2Re(\mu\text{-}T)Fe(CO)_3$, in which the thiophene is S-bound to the Re and $\eta^4$-bound through the four carbons to the $Fe(CO)_3$.

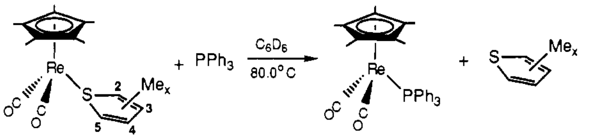


S-bound



$\eta^5$-bound

In addition to $Cp^*(CO)_2Re(T)$, we have prepared[13] a series of $Cp^*(CO)_2Re(Th)$ and $Cp(CO)_2Re(Th)$ complexes, where Th is thiophene, a methyl-substituted thiophene, or dibenzothiophene. These complexes allow us to compare the reactivity of these different S-bound thiophenes. In this paper, we report studies of the mechanism and compare the rates of substitution of a series of methyl-substituted thiophenes by $PPh_3$ according to eq 1. Of particular interest is the effect of methyl groups in the 2- and 5-positions on the rates of thiophene dissociation from these complexes. It has generally been stated[14,15] that such methyl groups would sterically inhibit thiophene adsorption to an HDS catalyst. This statement, however, was based on the assumption that S-bound thiophene is perpendicular to the surface, with the coordinated metal atom lying in the plane of the thiophene. In this configuration, methyl groups in the 2- and 5-positions would be expected to sterically weaken S-bonding to the metal. However, it is now known[3b,8b,11,13] that the metal does not lie in the thiophene plane (i.e., the sulfur is pyramidal), as shown for $Cp(CO)_2Re(Th)$ in eq 1. Thus, 2,5-methyl groups may pose less of a steric problem than previously suggested. Kinetic studies of the reaction in eq 1 offer one approach to assessing steric effects of 2,5-methyl groups on thiophene bonding to metals.



(1)

x = 0, 1, 2, 4 and the cyclopentadienyl ligand is $C_5H_5$ or $C_5Me_5$

## Experimental Section

**General Procedures.** The complexes, $Cp(CO)_2Re(Th)$ and $Cp^*(CO)_2Re(Th)$, where $Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$, and Th = T, 2-MeT, 3-MeT, $2,5\text{-}Me_2T$, $Me_4T$, and dibenzothiophene (DBT), were prepared as described elsewhere.[12,13] The $PPh_3$ was purified by recrystallization from warm hexanes and cooling to −20 °C. The $C_6D_6$ was distilled under Ar from Na/benzophenone. The products, $Cp(CO)_2Re(PPh_3)$ and $Cp^*(CO)_2Re(PPh_3)$, were identified[16] by their $^1H$ NMR and

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