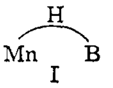
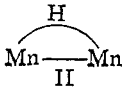
Mass Spectra of Polynuclear Metal Carbonyl Hydrides[1]

Sir:

We have subjected to calibrated mass spectrometric analysis[2] the several polynuclear metal carbonyl hydrides and borohydride, $H_3Re_3(CO)_{12}$,[3] $HRe_3(CO)_{14}$,[4] $HRe_2Mn(CO)_{14}$,[4] $H_3Mn_3(CO)_{12}$,[5] $H_7B_2Mn_3(CO)_{10}$[5,6] (and their deuterated derivatives), synthesized in these laboratories. We confirm in each case the number of hydrogen atoms originally proposed from elemental analysis, and for $H_7B_2Mn_3(CO)_{10}$ also proposed from three-dimensional difference maps in the X-ray diffraction analysis.[6] Furthermore, the behavior of the hydrogen atoms on fragmentation may give some insight into their mode of attachment in these molecules. Recent communications on some of the same[7] and closely related derivatives[7,8] prompts us to give this preliminary report of our results.

$H_7B_2Mn_3(CO)_{10}$ is the only derivative whose structure is known.[6] All seven hydrogen atoms were found to be in bridging positions, six in the two-electron, three-center Mn–H–B bridging (I), and one in hydrogen bridging across a metal–metal bond (II). This latter situation is somewhat analogous to the CO bridging across a metal–metal bond (III), except that in the latter (III) four electrons and two σ bonds are involved in the bridge, while in the former (II) the bridge consists of a two-electron, three-center system.


I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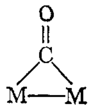
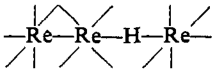

III

The parent ion and the first four mass multiplets in the spectrum of $H_7B_2Mn_3(CO)_{10}$ can be assigned to the series $H_7B_2Mn_3(CO)_n$, $6 \leq n \leq 10$. The peak of mass 474 was measured accurately by calibration against $(C_4F_9)_3N$ and is therefore known to correspond to $^{1}H_7{}^{11}B_2{}^{55}Mn_3({}^{12}C^{16}O)_{10}{}^+$. *None of the hydrogen atoms are lost in the parent and the first three ions* (n = 10, 9, 8, 7 in the above formula). This is deduced from analysis of the intensities in the multiplets arising from the distribution of ^{10}B, ^{11}B, and ^{13}C (Mn is monoisotopic). This is in marked contrast with the behavior of $HMn(CO)_5$,[8] containing terminal bonded H, in which a competition between loss of H and loss of CO was observed everywhere in the spectrum. In the multiplet for $H_7B_2Mn_3(CO)_6{}^+$ some small alteration in the intensities is observed, denoting the onset of some loss of hydrogen. Lower m/e regions of the spectrum are complicated by the overlap of $H_7B_2Mn_3(CO)_5{}^+$ and its lower members with those of the series starting with $H_6B_2Mn_2(CO)_7{}^+$ (because m/q of HMn $\simeq$ m/q of 2CO). We intend to sort this out with improved resolution.

The spectrum of $HRe_3(CO)_{14}$ shows the parent ion and a progressive series showing loss of 14 CO groups. Except for the last three members, $HRe_3(CO)_2{}^+$, HRe_3CO^+, and $HRe_3{}^+$ (in which 25, 30, and 60% of the ions, respectively, have lost H), *none of the other members of this long series $Re_3(CO)_n$ shows any loss of H*, which loss would be expected for a terminal Re–H. A possible position for H in $HRe_3(CO)_{14}$ was discussed elsewhere.[4] The simple rules of valence suggest a metal carbonyl framework $Re(CO)_5$–$Re(CO)_4$–$Re(CO)_5$. The hydrogen would have to be bound to the central Re atom in order to maintain a closed valence shell for that atom and a diamagnetic structure for the molecule. However, from (i) infrared spectra in the carbonyl region,[4] (ii) the great ease with which $HRe(CO)_5$ is split out to give $Re_2(CO)_{10}$ or $LRe_2(CO)_9$ in the treatment of $HRe_3(CO)_{14}$ with CO or other ligands,[4] and (iii) from the present behavior of H in the fragmentation pattern of the parent ion, a bridging position for hydrogen is strongly suggested. The most compatible model with over-all symmetry and other suggested[9] linear metal–hydrogen–metal bridging would be the structure IV.


IV (CO groups omitted for clarity)

Other more intense fragmentation series observed in the spectrum of $HRe_3(CO)_{14}$ are those starting with $HRe_2(CO)_9{}^+$ and $HRe(CO)_5{}^+$. Both display competitive loss of H and CO, but this is much more prominent in the $HRe(CO)_5{}^+$ series. In addition to these, we were surprised to find the fragment $Re_2(CO)_{10}{}^+$ at relative intensity significantly above any of the peaks of the parent series, $HRe_3(CO)_n$ (and significantly above the level of detection by infrared of any possible $Re_2(CO)_{10}$ impurity in the samples of $HRe_3(CO)_{14}$). The fragment $Re(CO)_6{}^+$ was also observed. These could only come from CO transfer during fragmentation of the proposed structure (at operating pressures, the probability of recombination of CO with metal fragments is extremely small and could not account for the intensity of those peaks). This unusual CO transfer has not to our knowledge been reported for polynuclear derivatives such as $Mn_2(CO)_{10}$,[10] $Co_2(CO)_8$,[10] and others[11] studied thus far. We therefore checked the mass spectrum of $Re_2(CO)_{10}$. In addition to the two expected series, starting with $Re_2(CO)_{10}{}^+$ and $Re(CO)_5{}^+$ a distinct peak for $Re(CO)_6{}^+$ was observed (at relative intensity 5% compared to the most intense peak, Re^+, of the $Re(CO)_n{}^+$ series), clearly demonstrating the CO transfer process in this molecule of known structure.

The mixed carbonyl $HRe_2Mn(CO)_{14}$ was subjected to analysis. The parent ion peak and those of its CO-loss series which could be discerned (down to $HRe_2Mn(CO)_7{}^+$) did not show any H loss. The mass spectrum was obscured by the presence of some

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[1] Work supported by National Science Foundation Grant GP 4175; taken in part from the dissertation of J. M. S., University of California at Los Angeles, Los Angeles, Calif., 1966.

[2] Associated Electrical Industries, Ltd., Model MS-9 spectrometer, source chamber at 220° and ionizing potential of 62 ev.

[3] D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Am. Chem. Soc.*, 86, 4841 (1964).

[4] W. Fellmann and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, **2**, 63 (1966).

[5] W. Fellmann, D. K. Huggins, and H. D. Kaesz, Abstracts of Papers presented at the VIIIth International Conference on Coordination Chemistry, Sept 1964, V. Gutmann, Ed., Springer-Verlag, Berlin, pp 255–257.

[6] H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965).

[7] B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. H. Robinson, *Chem. Commun.*, 851 (1966).

[8] W. F. Edgell and W. M. Risen, *J. Am. Chem. Soc.*, 88, 5451 (1966).

[9] L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *ibid.*, 88, 366 (1966); see also U. Anders and W. A. G. Graham, *Chem. Commun.*, 499 (1965).

[10] R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, **69**, 1618 (1965).

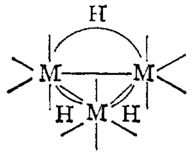
[11] R. B. King, *J. Am. Chem. Soc.*, **88**, 2075 (1966).

$HRe_3(CO)_{14}$ impurity (unavoidably present from the preparative method)[4] which overlapped with some of the members in the degradation series of $HRe_2Mn(CO)_{14}$.

The spectrum of $H_3Re_3(CO)_{12}$ shows most prominently the parent ion and the progressive series showing loss of 12 CO groups. The intensity patterns reveal that hydrogen loss is competing effectively with CO loss in all the multiplets. In $H_3Mn_3(CO)_{12}$, we find no hydrogen loss from the parent ion $H_3Mn_3(CO)_{12}$, contrary to earlier report.[7] However, this is not true for other members of the progressive CO-loss series, similar to that discussed for $H_3Re_3(CO)_{12}$ above. With the Mn derivative, the series corresponding to single metal atom fragments $[Mn(CO)_n^+]$ is the most intense, while the series of three metal atom fragments $[Re_3(CO)_n^+]$ is the most intense in the Re case, parallel to the greater chemical stability of $H_3Re_3(CO)_{12}$.

The position of the hydrogen atoms in these derivatives has not been established with certainty; however, infrared[3] and Raman[12] studies indicate that the hydrogen atoms must be in bridging positions. These must be exclusively of type II since metal–metal bonding is required for each Re atom to achieve a closed valence shell. Observation of competition in the mass spectrum between loss of H and CO in the parent ion series is consistent with hydrogen bridging across a metal–metal bond. In polynuclear metal carbonyls containing carbonyl bridging groups (always accompanied by metal–metal bonds, type III) it has been shown that terminal CO and bridging CO groups may progressively be lost from the parent metal cluster such as in the series $Co_2(CO)_n^+$, $0 \leq n \leq 8$ in $Co_2(CO)_8$,[10] and $Co_4(CO)_n^+$, $0 \leq n \leq 12$ in $Co_4(CO)_{12}$.[11]

In addition, spectra of the derivative $H_3Re_3(CO)_{12}$ show at weaker intensity the series $M_2(CO)_n^+$, $0 \leq n \leq 10$, and $M(CO)_m^+$, $0 \leq m \leq 5$. These further illustrate the transfer of CO during fragmentation in the parent structure which by all other indications[3,9] consists of a triangle of $M(CO)_4$ groups joined by M–M bonding and M–H–M bridging (V). A very low intensity peak (less than 1% of the most intense peak of the ion $H_3Re_3(CO)_3^+$ of the parent series) was observed at a position corresponding to $Re_2(CO)_{11}^+$.



V (CO groups omitted for clarity)

Mass spectral analysis is also valuable in studying reaction intermediates through isotopic labeling. For instance, the product from sequence 1 was found to be

$$H_3Re_3(CO)_{12} \xrightarrow{\text{Na-Hg}} [Na_2HRe_3(CO)_{12}]? \xrightarrow{D_3PO_4} D_2HRe_3(CO)_{12} \quad (1)$$

only about 70% deuterated. We imply that the intermediate anionic species must retain on the average approximately one hydrogen atom per Re_3 fragment. (The final product does not exchange H in acid medium.) A higher percentage of deuteration (about 90%) was achieved using $NaBD_4$ and D_3PO_4 in the reduction and acidification steps, respectively, of the original synthesis sequence 2.

$$Re_2(CO)_{10} \xrightarrow[\text{(iii) } D_3PO_4\text{, cyclohexane}]{\text{(i) } NaBD_4\text{, tetrahydrofuran} \atop \text{(ii) remove solvent}} \underset{(90\%\text{-D})}{D_3Re_3(CO)_{12}} \quad (2)$$

Characterization of the intermediate species is in progress.

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[12] J. M. Smith, W. Fellmann, and L. H. Jones, *Inorg. Chem.*, **4**, 1361 (1965).

Nucleosides. XL. The Introduction of a 2,3′-Imino Bridge into Pyrimidine Nucleosides[1]

Sir:

We wish to report the first synthesis of a nitrogen bridge analog (**4**) of an anhydronucleoside (**5**). Such compounds might serve as useful chemical precursors for the synthesis of nucleosides containing amino groups in the sugar moiety and lead to analogs of potential biochemical utility.

Previous studies in our laboratory[2] showed that treatment of 2,5′- or 2,2′-anhydronucleosides of uracil with liquid ammonia at room temperature led to the known[3] 2′,3′-O-isopropylidineisocytidine and 1-β-D-arabinofuranosylisocytosine, respectively, in good yields. Such isocytosine nucleosides, when treated with alkali, were readily converted to their uracil analogs.[2] It was envisioned that if anhydronucleosides of uracil contained a leaving group in the "down" configuration in the sugar moiety, treatment of such compounds with liquid ammonia should lead to isocytosine nucleosides which could then undergo an intramolecular displacement reaction by the 2-amino group with the formation of nitrogen-bridged "anhydro" nucleosides.

As a model compound, the 2,5′-anhydro derivative of 3′-O-mesylthymidine (**2**) was prepared by reaction of the known[4] iodonucleoside **1** with silver acetate in methanol (see Chart I). A crystalline product (from 95% methanol) was obtained (65%), mp 182–183° dec, $[\alpha]^{26}D$ +52° (DMF), $\lambda_{max}^{H_2O}$ 249 mμ, λ_{min} 218 mμ. *Anal.* Found for $C_{11}H_{14}N_2O_6$: C, 43.76; H, 4.70; N, 9.16; S, 10.70. Proof that **2** is a 2,5′-anhydronucleoside is shown by the dissimilarity of its melting point, optical rotation, and ultraviolet spectral properties from the known[4,5] 2,3′-anhydro isomer **6**. The nmr spectra of **2** and **6** in DMSO-d_6 also differ appreciably.[6]

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[1] This investigation was supported in part by funds from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service (Grant No. CA 08748).

[2] I. L. Doerr and J. J. Fox, *J. Org. Chem.*, in press.

[3] D. M. Brown, A. Todd, and S. Varadarajan, *J. Chem. Soc.*, 868 (1957); D. M. Brown, D. B. Parihar, A. Todd, and S. Varadarajan, *ibid.*, 3028 (1958).

[4] A. M. Michelson and A. R. Todd, *J. Chem. Soc.*, 816 (1955).

[5] J. J. Fox and N. C. Miller, *J. Org. Chem.*, **28**, 936 (1963).

[6] Compound **2** showed a pair of doublets centered at δ 4.69 and 4.17 ($H_{5'}$,$H_{5'}$, $J_{5',5'} \sim 12.5$ cps; $J_{4',5'} = J_{4',5'} \sim 1.0$ cps) while compound **6** showed a multiplet (2 H) centered at δ 4.50 ($H_{4'}H_{5',5'}$).