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**The Crystal Structure of $\text{HRe}_2\text{Mn}(\text{CO})_{14}$.
A Neutral, "Electron-Deficient," Polynuclear
Carbonyl Hydride¹**

Sir:

The reduction of $\text{Mn}_2(\text{CO})_{10}$ or $\text{Re}_2(\text{CO})_{10}$ with NaBH_4 (and subsequent acidification) has given rise to an unusual group of polynuclear carbonyl hydrides: $\text{H}_3\text{Re}_3(\text{CO})_{12}$,² $\text{H}_3\text{Mn}_3(\text{CO})_{12}$,³ $\text{H}_7\text{B}_2\text{Mn}_3(\text{CO})_{10}$,³ and $\text{HRe}_3(\text{CO})_{14}$.^{4a} Only one of these complexes, $\text{H}_7\text{B}_2\text{Mn}_3(\text{CO})_{10}$, has so far been examined crystallographically,⁵ although attempts have been made to study $\text{H}_3\text{Re}_3(\text{CO})_{12}$.⁶ We now wish to report the structure of $\text{HRe}_2\text{Mn}(\text{CO})_{14}$,^{4b} which no doubt will be closely related to $\text{HRe}_3(\text{CO})_{14}$.⁷

$\text{HRe}_2\text{Mn}(\text{CO})_{14}$ crystallizes in the monoclinic space group $\text{P}2_1/\text{n}$ (No. 14) with $a = 9.31$, $b = 15.82$, $c = 14.38$ Å, $\beta = 106.4^\circ$, $V = 2032$ Å³; $\rho_{\text{obsd}} = 2.64$ g cm⁻³ ($\rho_{\text{calcd}} = 2.68$ g cm⁻³ for $Z = 4$, $M = 820$). A single-crystal X-ray crystallographic analysis, based on complete three-dimensional data (Mo $\text{K}\alpha$; $\sin \theta_{\text{max}} = 0.38$) collected with a Buerger automated diffractometer, has led to the location of all nonhydrogen atoms. The present discrepancy index is $R_F = 10.39\%$ for the 2100 nonzero reflections. The over-all geometry of the molecule is shown in Figure 1. The metal atoms are in a nonlinear configuration, the $\text{Re}\cdots\text{Re}-\text{Mn}$ angle being 98.1° . The $\text{Re}-\text{Mn}$ bond length of 2.960 Å is in good agreement with the value of 2.97 Å predicted from the $\text{M}-\text{M}$ distances in $\text{M}_2(\text{CO})_{10}$ ($\text{Mn}-\text{Mn} = 2.923$ Å,⁸ $\text{Re}-\text{Re} = 3.02$ Å⁹). However, the $\text{Re}\cdots\text{Re}$ distance of 3.39 Å in $\text{HRe}_2\text{Mn}(\text{CO})_{14}$ is ~ 0.37 Å longer than a normal $\text{Re}-\text{Re}$ single bond. It is proposed that the hydrogen atom known¹⁰ to be present in $\text{HRe}_2\text{Mn}(\text{CO})_{14}$ occupies a bridging position between the two rhenium atoms. The otherwise normal octahedral coordination of the rhenium atoms leads us to believe

(1) Work supported by NSF Grants GP-6720 (H. D. K.) and GP-4225 (M. R. C.), and by ARPA Grant SD-88 (M. R. C.).

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

(3) W. Fellmann, D. K. Huggins, and H. D. Kaesz, Abstracts, Presented at the VIIIth International Conference on Coordination Chemistry, Vienna, Sept 1964, V. Gutmann, Ed., Springer-Verlag, Berlin, 1965, pp 255-257.

(4) (a) W. Fellmann and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, **2**, 63 (1966). (b) $\text{HRe}_2\text{Mn}(\text{CO})_{14}$ is obtained in 10% yield by acidification of a dry mixture of $\text{NaMn}(\text{CO})_5$ and a salt containing lower carbonyl anions of rhenium (obtained from the treatment of $\text{Re}_2(\text{CO})_{10}$ with NaBH_4 in tetrahydrofuran³).

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

(6) We have examined crystals of $\text{H}_3\text{Re}_3(\text{CO})_{12}$, but have not yet found a specimen which gives an interpretable diffraction pattern. Professor L. F. Dahl has informed us that he has encountered similar difficulties both with $\text{H}_3\text{Re}_3(\text{CO})_{12}$ and $\text{H}_3\text{Mn}_3(\text{CO})_{12}$.

(7) The structure of $\text{HRe}_3(\text{CO})_{14}$ is under investigation in the laboratories of Professor L. F. Dahl.

(8) L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

(9) L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

(10) The number of hydrogen atom(s) in this and the above-mentioned derivatives has been confirmed by calibrated mass spectra: J. M. Smith, K. Mehner, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 1759 (1967).

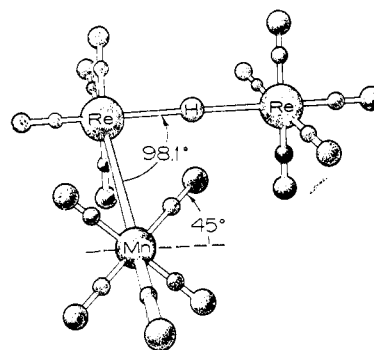


Figure 1. The stereochemistry of $\text{HRe}_2\text{Mn}(\text{CO})_{14}$.

that the $\text{Re}-\text{H}-\text{Re}$ bridge is probably linear [a similar scheme has been suggested for the $\text{HCr}_2(\text{CO})_{10}^-$ ion¹¹]. If a symmetrical, linear $\text{Re}-\text{H}-\text{Re}$ linkage is assumed, then the resulting $\text{Re}-\text{H}$ distance of 1.695 Å is in remarkably good agreement with the $\text{Re}-\text{H}$ distance of 1.68 ± 0.01 Å determined by a neutron-diffraction study¹² of K_2ReH_9 .

An interesting observation in the present study is that the carbonyls in the $(\text{OC})_4\text{Re}-\text{Mn}(\text{CO})_5$ portion of the molecule are in a strictly staggered conformation (as are those in $\text{Mn}_2(\text{CO})_{10}$,⁸ $\text{Tc}_2(\text{CO})_{10}$,¹³ and, presumably, the isomorphous⁹ $\text{Re}_2(\text{CO})_{10}$), whereas the carbonyl groups in the hydrogen-bridged portion of the molecule are in an eclipsed configuration. (The author's drawing of the $\text{HCr}_2(\text{CO})_{10}^-$ ion¹¹ indicates that this too adopts an eclipsed configuration.) Furthermore, the sets of radial carbonyl groups in the $(\text{OC})_5\text{Mn}-\text{Re}(\text{CO})_4$ moiety bend slightly toward each other, a feature noted also for $\text{Mn}_2(\text{CO})_{10}$ ⁸ and $\text{Tc}_2(\text{CO})_{10}$.¹³

The structure of $\text{HRe}_2\text{Mn}(\text{CO})_{14}$ taken together with the chemistry (treatment of this compound with CO gives $\text{HRe}(\text{CO})_5$ and $\text{MnRe}(\text{CO})_{10}$)⁴ suggests a description of the bonding which correlates the two. The $\text{HRe}(\text{CO})_5$ unit might be regarded as a neutral ligand in a radial position on $\text{LMnRe}(\text{CO})_9$ held through hydrogen bridging *via* a two-electron three-center bond.¹⁴ More extensive studies on $\text{HRe}_3(\text{CO})_{14}$ strengthen this idea: ¹³CO-enriched CO reacts with $\text{HRe}_3(\text{CO})_{14}$ to produce $\text{Re}_2(^{13}\text{CO})_9(^{13}\text{CO})$, with the ¹³CO group in the *radial* position.¹⁵ CH_3CN and $(\text{C}_6\text{H}_5)_3\text{P}$ similarly give monosubstituted derivatives $\text{LRe}_2(\text{CO})_9$ but with $(\text{C}_6\text{H}_5)_3\text{P}$ *axial* substitution is observed.¹⁶

The concept of a neutral transition metal hydride acting as a ligand in metal complexes suggests the formulas of a large class of electron-deficient polynuclear metal hydrides. A few such possibilities based on known complex hydrides and known carbonyls would be: $(\text{OC})_5\text{ReH}\cdot\text{M}(\text{CO})_5$ and $(\pi-\text{C}_5\text{H}_5)_2\text{ReH}\cdot\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), $(\text{OC})_4\text{CoH}\cdot\text{Fe}(\text{CO})_4$, or $\text{L}_2(\text{X})\text{PtH}\cdot\text{M}(\text{CO})_{n-1}$ [where $\text{M}(\text{CO})_n$ is any of a number of known carbonyls]. These compounds would be

(11) L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *ibid.*, **88**, 366 (1966).

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(13) M. F. Bailey and L. F. Dahl, *ibid.*, **4**, 1140 (1965).

(14) Such a bonding system has historically been termed "electron deficient"; cf. R. E. Rundle, *Record. Chem. Progr.* (Kresge Hooker Sci. Lib.), **23**, 195 (1962); this merely refers to molecules in which some of the bonding or nonbonding orbitals are empty.

(15) R. W. Harrill and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, **2**, 69 (1966).

(16) R. W. Harrill, Ph.D. Dissertation, University of California at Los Angeles, 1967, to be published.

related by loss of a proton to the corresponding polynuclear carbonyl anions¹⁷ and could, therefore, in some cases be very strong proton-releasing acids. The electron-deficient polynuclear carbonyl hydrides would also be isoelectronic with polynuclear protonated metal carbonyl species such as $(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeHMn}(\text{CO})_5^+$ or $(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{WHW}(\text{CO})_3(\pi\text{-C}_5\text{H}_5)^+$ reported by Wilkinson and co-workers.¹⁸ The question of the placement of the hydrogen atoms is the same in these two classes of compound.

(17) See U. Anders and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 539 (1967), and references cited therein.

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(19) Work performed during the temporary residence of R. B. and sabbatical leave residence of H. D. K. at Harvard University.

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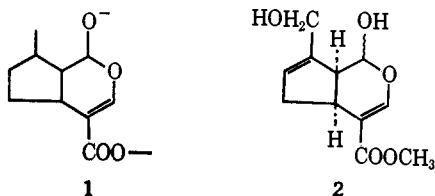
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The Total Synthesis of Racemic Genipin

Sir:

Since the pioneering work of Schmid on the structure of plumieride,¹ the group of monoterpenes containing part structure **1** has rapidly expanded. The suggestion² that such compounds are intermediates in the biosynthesis of indole alkaloids has recently been supported by preliminary experiments³ which, however, need confirmation with multiply labeled compounds. Until now no member of this class of natural products has been prepared from the elements, but the present communication reports on a synthesis of genipin (**2**).⁴



The bicyclic ethyl ester **3**⁵⁻⁷ on base hydrolysis was transformed to the acid **4**, mp 53–55° (lit.⁸ mp 51–52°). Reduction with lithium in liquid ammonia followed by esterification with methanol in the presence of *p*-toluenesulfonic acid afforded a mixture of methyl esters containing approximately 90% of **5**.

When the diene **5** was treated with osmium tetroxide in dimethylformamide and the resulting osmate ester cleaved with hydrogen sulfide,⁹ a crystalline tetrol (**6**), mp 163–165°, was formed in 50% yield. Although

(1) O. Halpern and H. Schmid, *Helv. Chim. Acta*, **41**, 1109 (1958).
(2) R. Thomas, *Tetrahedron Letters*, 544 (1961); E. Wenkert, *J. Am. Chem. Soc.*, **84**, 98 (1962).

(3) A. R. Battersby, R. T. Brown, R. S. Kapil, J. A. Martin, and A. O. Plunkett, *Chem. Commun.*, 890 (1966).

(4) C. Djerassi, T. Nakano, A. N. James, L. H. Zalkow, E. J. Eisenbraun, and J. N. Shoolery, *J. Org. Chem.*, **26**, 1192 (1961).

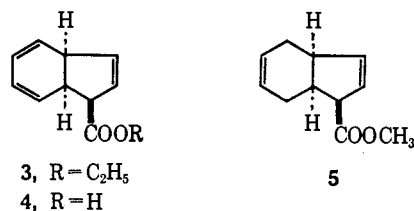
(5) K. F. Bangert and V. Boekelheide, *J. Am. Chem. Soc.*, **86**, 905 (1964).

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(7) G. W. Fonken and W. Moran, *Chem. Ind. (London)*, 1841 (1963).

(8) T. J. Katz and P. J. Garrat, *J. Am. Chem. Soc.*, **86**, 5194 (1964).

(9) D. H. R. Barton and D. Elad, *J. Chem. Soc.*, 2090 (1956).

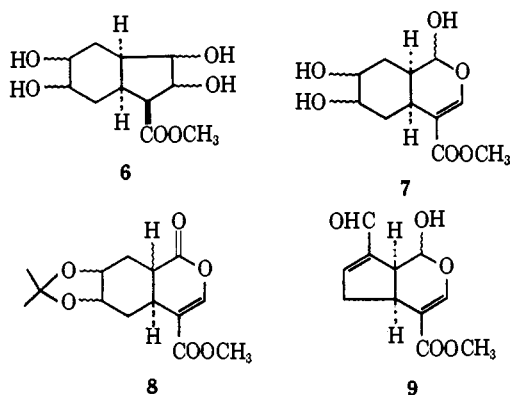


3, R = C₂H₅

4, R = H

5

this material was a mixture of two epimers it was used directly for further transformation. Taking advantage of earlier work which demonstrated that *cis*-cyclopentane-1,2-diols are cleaved much more rapidly with lead tetraacetate than *cis*-1,2-cyclohexanediols,¹⁰ the mixture of tetrols **6** was exposed to 1 equiv of this reagent in glacial acetic acid solution. Oxidation was complete within seconds and chromatography of the resulting mixture of products gave three triols: **7a** [11%; mp 156–157°; infrared absorptions (KBr) 3550, 1700, 1640 cm⁻¹; ultraviolet absorptions in EtOH 240 mμ (ε 10,500), in 0.01 *N* NaOH 273 mμ (ε 19,000)], **7b** [12%; mp 176–177°; infrared absorptions (KBr) 3500, 3355, 1690, 1635 cm⁻¹; ultraviolet absorptions same as those of **7a**], and **7c** [22%; mp 202–208°; infrared absorptions (KBr) 3425, 3250, 1690, 1635 cm⁻¹; ultraviolet absorptions same as those of **7a**]. Investigations aimed at clarifying the configurations of the three triols **7** are incomplete but isomers **7a** and **7b** on consecutive treatments with acetone and with dicyclohexylcarbodiimide–dimethyl sulfide¹¹ yielded the same lactone, **8**, mp 109–110°, having infrared and ultraviolet absorptions identical with those of **7a**. This tentatively indicates that the two triols differ only in the configuration of the hemiacetal carbon atom. Triol **7c** did not yield an acetone but was quantitatively cleaved by periodic acid.



The resulting crude dialdehyde was cyclized by the agency of piperidine acetate,¹² and the desired bicyclic aldehyde **9** was obtained in 68% yield in the form of a liquid with infrared absorptions (CHCl₃) at 2800, 1700, 1670, 1630 cm⁻¹. Reduction of the aldehyde **9** with lithium tri-*t*-butoxyaluminumhydride¹³ in ether gave racemic genipin (**2**), mp 116–117°. Identity with natural genipin¹⁴ was established by comparison of infrared,

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(14) We are grateful to Professor C. Djerassi, Stanford University, for a sample of natural genipin.