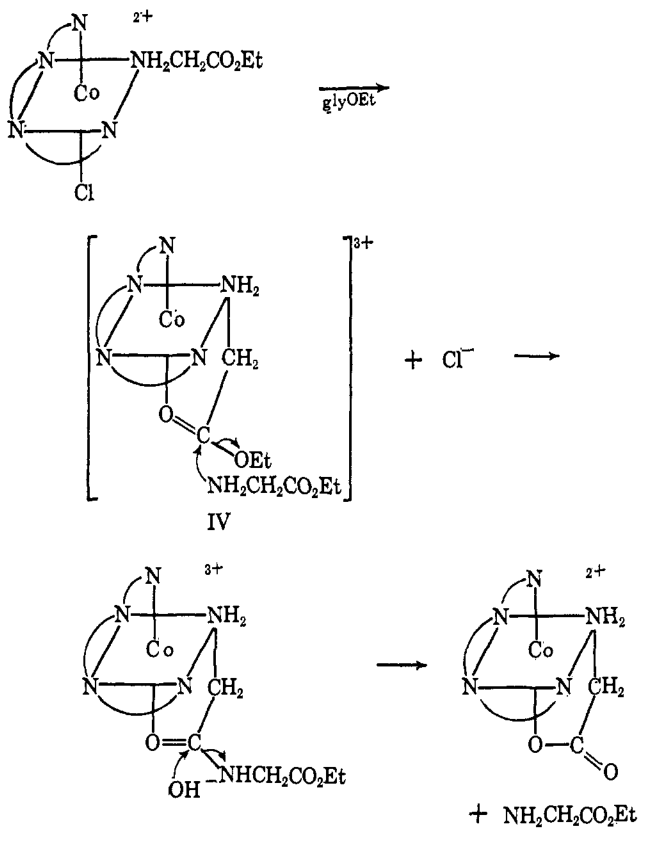
the results of 3890 ± 10 cpm/mg and approximately 200 ± 50 cpm/mg, respectively, establish that *no significant exchange of coordinated and free glycine ethyl ester has occurred during the reaction.* Thus formation of the peptide bond must involve condensation of the coordinated ester and must occur on the complex. Subsequent hydrolysis of the C^{14}-labeled β-[Co(trien)glyglyOEt]$(ClO_4)_3 \cdot H_2O$ at pH $\simeq$10 and 25° and examination of the β_2-[Co(trien)gly]$(ClO_4)_2 \cdot 0.5H_2O$ isolated from the resulting solution (4930 ± 10 cpm/mg) shows 96% retention of activity in the chelated glycine residue, and indicates a similar retention in the N-terminal glycine of the β_2-[Co(trien)-glyglyOEt]$^{3+}$ ion. These results are consistent with, but do not unequivocally establish, the following mechanism for peptide formation and subsequent hydrolysis. Formation of the peptide bond prior to chelation is also allowed by the results, but prior coordination of the incoming ester followed by condensation is excluded.



IV

Preliminary results indicate that the intermediate IV condenses with dipeptide esters to give a coordinated tripeptide ester, which leads to the possibility that this process may be useful as a general method for N-terminal addition of integral amino acid residues to peptide esters. Experiments to distinguish between the mechanistic possibilities are presently being conducted. Also the scope and versatility of this reaction are being investigated.

Acknowledgment. The authors are grateful to Dr. H. Rosenberg, Department of Biochemistry, John Curtin School of Medical Research, for a gift of C^{14}-labeled glycine and use of the Packard Scintillation Counter and to the Microanalytical Department for C, H, and N analyses.

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Chlorosilyl Derivatives of Transition Metals and Evidence for a Conformational Effect on Metal Carbonyl Stretching Bands

Sir:

The chemistry of silicon–transition metal compounds has been developed to a much smaller extent than that of germanium, tin, and lead; this situation may result in part from a lack of suitable preparative methods. We reported recently[1] that triphenylsilane, known[2] to react readily with cobalt carbonyl, would react under more vigorous conditions with the carbonyls of manganese and rhenium, affording $(C_6H_5)_3SiM(CO)_5$ (M = Mn, Re). We now communicate further studies showing that the silane–metal carbonyl reaction is a rather general one, providing a convenient route to new compounds both expected and unexpected. The reactions of trichlorosilane are particularly interesting, and a number are summarized in Table I. Yields vary widely, but the formation of $Cl_3SiMn(CO)_5$ is almost quantitative. On the basis of their infrared spectra, the products are structurally analogous to known derivatives of germanium, tin, and lead. It may be noted that silicon–molybdenum and silicon–nickel bonds have not been reported previously.

Table I. Trichlorosilane Reactions[a]

Reactant	Product[b]	Mp, °C[c]	CO stretching fundamentals, cm^{-1} [d]
$Mn_2(CO)_{10}$	$Cl_3SiMn(CO)_5$	130–131	2123, 2035
$Re_2(CO)_{10}$	$Cl_3SiRe(CO)_5$	169–169.5	2139, 2037, 2028
$Fe(CO)_5$	$[Cl_2SiFe(CO)_4]_2$	Dec >200	2094, 2053, 2048, 2038
$Fe_3(CO)_{12}$	$(Cl_3Si)_2Fe(CO)_4$	94–96	2125, 2078 2071, 2061
$[C_5H_5(CO)_3Mo]_2$	$Cl_3SiMo(CO)_3C_5H_5$	149–151	2041, 1976, 1959
$[C_5H_5(CO)_2Fe]_2$	$Cl_3SiFe(CO)_2C_5H_5$	128–130	2039, 1995
$[C_5H_5(CO)Ni]_2$	$Cl_3SiNi(CO)C_5H_5$	38–40	2062

[a] In sealed tubes in the 100–180° temperature range using excess Cl_3SiH. [b] Products characterized by elemental analysis and mass spectrum. In several cases other products are formed which have not yet been fully characterized. [c] Kofler hot-stage microscope. [d] In cyclohexane solution.

The trichlorosilyl derivatives of Table I are of interest in view of the numerous compounds of the trichlorostannyl ligand now known. The latter is regarded as a strong π acceptor and a weak σ donor.[3] Strong π-acceptor character for the Cl_3Sn ligand is also consistent with trends in CO stretching force constants in $Cl_3SnMn(CO)_5$ and related compounds, as we have pointed

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(1) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).

(2) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 1133 (1965).

(3) R. V. Lindsay, Jr., G. W. Parshall, and V. G. Stolberg, *ibid.*, **87**, 658 (1965); G. W. Parshall, *ibid.*, **88**, 704 (1966).

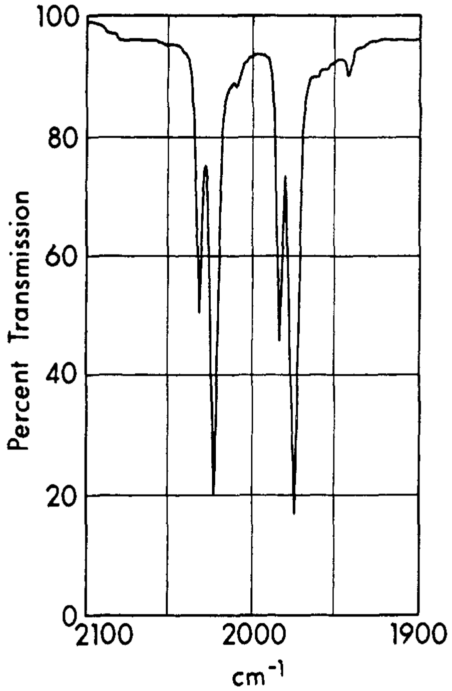


Figure 1. Carbonyl region of the infrared spectrum of CH$_3$Cl$_2$SiFe(CO)$_2$C$_5$H$_5$. Precise band positions are 2031, 2022, 1983, and 1973 cm^{-1} (cyclohexane solution, about 1 mg/ml, 0.5-mm cells).

out.[1] We have now extended the force constant approach to the corresponding Cl$_3$Si and Cl$_3$Ge[4] compounds and conclude that *there is little difference among Cl$_3$Si, Cl$_3$Ge, and Cl$_3$Sn as ligands.*[5] We suggest that the Cl$_3$Sn group is not unique, except for the ease with which it may be generated in reactions with tin(II) chloride.

Reactions with methyldichlorosilane yield methyldichlorosilyl analogs of many of the compounds of Table I. The infrared spectra of these methylsilyl derivatives reveal some unexpected features in the form of "extra" terminal carbonyl bands. The most striking example is provided by CH$_3$Cl$_2$SiFe(CO)$_2$C$_5$H$_5$, of which the spectrum is shown in Figure 1. The spectrum of Cl$_3$SiFe(CO)$_2$C$_5$H$_5$ is shown in Figure 2 for comparison. Repeated crystallization and fractional sublimation of the methyl derivative does not alter its spectrum, and its molecular weight in cyclohexane is normal (calculated, 291; found (osmometer), 294). Moreover, the nmr spectrum at 33° shows only two sharp peaks at τ 6.2 and 9.3 in a 5:3 ratio.[6]

The appearance of more than two CO stretching bands for a compound having only two CO groups leads one to postulate that isomers are present. We believe that these are most likely to be the two conformations of the molecule shown in Newman projection as I and II. Rapid interconversion would account for the simple nmr spectrum. The phenomenon is being studied in greater detail, and a similar effect has been observed in organotin derivatives such as CH$_3$Cl$_2$SnFe(CO)$_2$C$_5$H$_5$.[7]

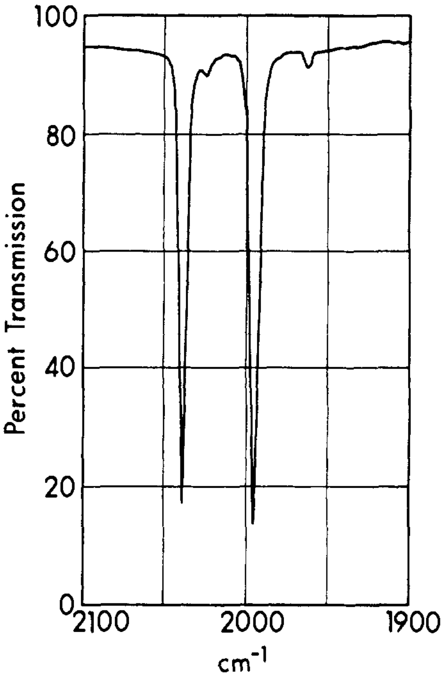
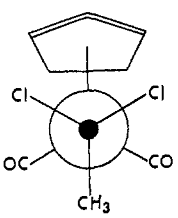
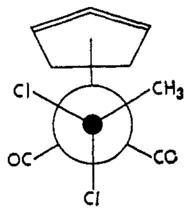


Figure 2. Carbonyl region of the infrared spectrum of Cl$_3$SiFe(CO)$_2$C$_5$H$_5$. Precise band positions are 2039 and 1995 cm^{-1} (cyclohexane solution, about 1 mg/ml, 0.5-mm cells).

Isomerism of the tautomeric type, involving equilibria between bridged and nonbridged forms, is well established in metal carbonyls and certain of their derivatives.[8] The present communication, however, is the first report of a *conformational* effect on terminal metal carbonyl frequencies.[9,10] The generality of this phenomenon remains to be established, but it should evidently be borne in mind when a choice between structures is being made on the basis of predicted and observed numbers of carbonyl stretching bands.



I



II

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(4) The compound Cl$_3$GeMn(CO)$_5$ has been prepared from Cl$_3$GeH and Mn$_2$(CO)$_{10}$: A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. B. Antonova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1284 (1965). We prepared it by reaction of chlorine with (C$_6$H$_5$)$_3$GeMn(CO)$_5$, and observe ν(CO) at 2130 (m), 2048 (s), 2038 (m) cm^{-1} in cyclohexane.

(5) Actual values of the approximate force constants (mdynes/A) are: Cl$_3$SiMn(CO)$_5$, k_1 = 16.86, k_2 = 17.17, k_i = 0.222; Cl$_3$GeMn(CO)$_5$, k_1 = 16.90, k_2 = 17.36, k_i = 0.210; Cl$_3$SnMn(CO)$_5$,[1] k_1 = 16.91, k_2 = 17.31, k_i = 0.204. For an explanation of nomenclature and fuller discussion, see ref 1.

(6) Attempts to measure the low-temperature nmr spectrum have not as yet been successful because of the tendency of solutions of the compound to become very viscous at about −20°.

(7) Research in progress in this laboratory by Mr. James Hoyano.

(8) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963); G. Bor, *ibid.*, **19**, 2065 (1963); F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967); R. D. Fischer, A. Vogler, and K. Noack, *J. Organometal. Chem.* (Amsterdam), 7, 135 (1967); K. Noack, *ibid.*, 7, 151 (1967).

(9) The doubling of *acyl* carbonyl frequencies in compounds of the type CXH$_2$COMn(CO)$_5$ (F. Calderazzo, K. Noack, and U. Schaerer, *ibid.*, **6**, 265 (1966)) is entirely analogous to that produced by rotational isomerism in conventional organic ketones.

(10) A referee has drawn attention to the fact that four strong carbonyl bands were observed by R. B. King in the compound π-C$_3$H$_5$(CO)$_2$Mo(π-C$_5$H$_5$): *Inorg. Chem.*, **5**, 2242 (1966). This was attributed by King to a kind of *cis–trans* isomerism involving a bidentate π-allyl group. We agree with the referee's suggestion that isomerism in the π-allyl case may arise from a conformational effect very similar to what is suggested here; *i.e.*, in I and II, replace Cl by CH$_2$, CH$_3$ by H, Si by C, and Fe by Mo. This viewpoint implies that the π-allyl group is monodentate in character, presumably with some freedom of rotation about the π-allyl–metal bond.

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Received March 10, 1967

The Crystal Structure of $HRe_2Mn(CO)_{14}$. A Neutral, "Electron-Deficient," Polynuclear Carbonyl Hydride[1]

Sir:

The reduction of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ with $NaBH_4$ (and subsequent acidification) has given rise to an unusual group of polynuclear carbonyl hydrides: $H_3Re_3(CO)_{12}$,[2] $H_3Mn_3(CO)_{12}$,[3] $H_7B_2Mn_3(CO)_{10}$,[3] and $HRe_3(CO)_{14}$.[4a] Only one of these complexes, $H_7B_2Mn_3(CO)_{10}$, has so far been examined crystallographically,[5] although attempts have been made to study $H_3Re_3(CO)_{12}$.[6] We now wish to report the structure of $HRe_2Mn(CO)_{14}$,[4b] which no doubt will be closely related to $HRe_3(CO)_{14}$.[7]

$HRe_2Mn(CO)_{14}$ crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a = 9.31$, $b = 15.82$, $c = 14.38$ A, $\beta = 106.4°$, $V = 2032$ A^3; $\rho_{obsd} = 2.64$ g cm^{-3} ($\rho_{calcd} = 2.68$ g cm^{-3} for $Z = 4$, $M = 820$). A single-crystal X-ray crystallographic analysis, based on complete three-dimensional data (Mo Kα; sin $\theta_{max} = 0.38$) 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 Re···Re–Mn angle being 98.1°. The Re–Mn bond length of 2.960 A is in good agreement with the value of 2.97 A predicted from the M–M distances in $M_2(CO)_{10}$ (Mn–Mn = 2.923 A,[8] Re–Re = 3.02 A[9]). However, the Re···Re distance of 3.39 A in $HRe_2Mn(CO)_{14}$ is ~0.37 A longer than a normal Re–Re single bond. It is proposed that the hydrogen atom known[10] to be present in $HRe_2Mn(CO)_{14}$ occupies a bridging position between the two rhenium atoms. The otherwise normal octahedral coordination of the rhenium atoms leads us to believe that the Re–H–Re bridge is probably linear [a similar scheme has been suggested for the $HCr_2(CO)_{10}^-$ ion[11]]. If a symmetrical, linear Re–H–Re linkage is assumed, then the resulting Re–H distance of 1.695 A is in remarkably good agreement with the Re–H distance of 1.68 ± 0.01 A determined by a neutron-diffraction study[12] of K_2ReH_9.

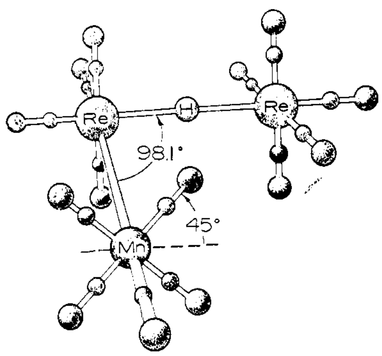

Figure 1. The stereochemistry of $HRe_2Mn(CO)_{14}$.

An interesting observation in the present study is that the carbonyls in the $(OC)_4Re–Mn(CO)_5$ portion of the molecule are in a strictly staggered conformation (as are those in $Mn_2(CO)_{10}$,[8] $Tc_2(CO)_{10}$,[13] and, presumably, the isomorphous[9] $Re_2(CO)_{10}$), whereas the carbonyl groups in the hydrogen-bridged portion of the molecule are in an eclipsed configuration. (The author's drawing of the $HCr_2(CO)_{10}^-$ ion[11] indicates that this too adopts an eclipsed configuration.) Furthermore, the sets of radial carbonyl groups in the $(OC)_5Mn–Re(CO)_4$ moiety bend slightly toward each other, a feature noted also for $Mn_2(CO)_{10}$[8] and $Tc_2(CO)_{10}$.[13]

The structure of $HRe_2Mn(CO)_{14}$ taken together with the chemistry (treatment of this compound with CO gives $HRe(CO)_5$ and $MnRe(CO)_{10}$)[4] suggests a description of the bonding which correlates the two. The $HRe(CO)_5$ unit might be regarded as a neutral ligand in a radial position on $LMnRe(CO)_9$ held through hydrogen bridging *via* a two-electron three-center bond.[14] More extensive studies on $HRe_3(CO)_{14}$ strengthen this idea: ^{13}CO-enriched CO reacts with $HRe_3(CO)_{14}$ to produce $Re_2(^{12}CO)_9(^{13}CO)$, with the ^{13}CO group in the *radial* position.[15] CH_3CN and $(C_6H_5)_3P$ similarly give monosubstituted derivatives $LRe_2(CO)_9$ but with $(C_6H_5)_3P$ *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: $(OC)_5ReH \cdot M(CO)_5$ and $(\pi\text{-}C_5H_5)_2ReH \cdot M(CO)_5$ (M = Cr, Mo, W), $(OC)_4CoH \cdot Fe(CO)_4$, or $L_2(X)PtH \cdot M(CO)_{n-1}$ [where $M(CO)_n$ is any of a number of known carbonyls]. These compounds would be

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[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) $HRe_2Mn(CO)_{14}$ is obtained in 10% yield by acidification of a dry mixture of $NaMn(CO)_5$ and a salt containing lower carbonyl anions of rhenium (obtained from the treatment of $Re_2(CO)_{10}$ with $NaBH_4$ in tetrahydrofuran[2]).

[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 $H_3Re_3(CO)_{12}$, 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 $H_3Re_3(CO)_{12}$ and $H_3Mn_3(CO)_{12}$.

[7] The structure of $HRe_3(CO)_{14}$ 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).

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

[12] S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).

[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.