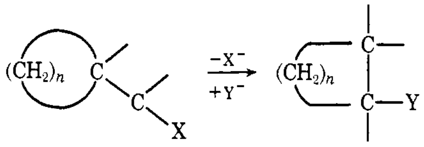
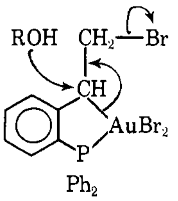
the Pt–Br distance trans to the σ-bonded carbon atom is significantly (Δ/σ = 13.2) greater than this. This is ascribed to the well-documented trans bond weakening, σ-inductive effect of carbon as a ligand atom which operates in planar and octahedral complexes.[6,7]

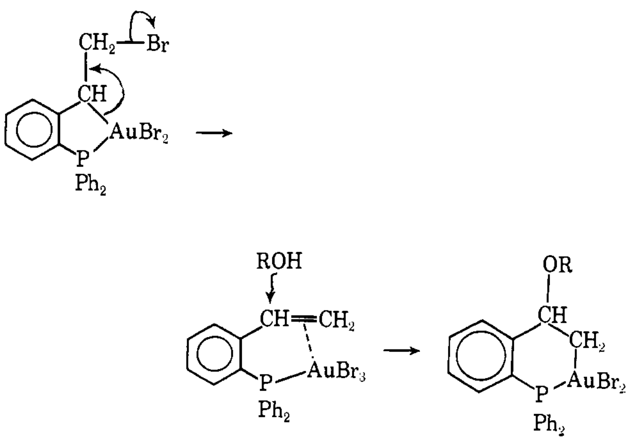
The ring expansion accompanying nucleophilic substitution of Br by OCH_3, OC_2H_5, or OH (**1** → **3**; **2** → **4**, **5**, or **6**) bears an obvious resemblance to the Wagner–Meerwein rearrangements occurring in ring expansions of cycloalkanecarbinyl systems,[8] *i.e.*



A similar mechanism involving a Wagner–Meerwein shift of the metal atom could be operative in the present case, *e.g.*



An alternative possibility[9] involves initial cis elimination of $AuBr_3$, followed by nucleophilic attack on the resulting coordinated double bond, *e.g.*



V

Experiments are in progress in an effort to distinguish between these possibilities.

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[6] R. Mason and A. D. C. Towl, *J. Chem. Soc. A*, 1601 (1970), and references cited therein; J. J. Daly and R. P. A. Sneeden, *ibid.*, 736 (1967).

[7] R. McWeeney, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, No. 47, 20 (1969).

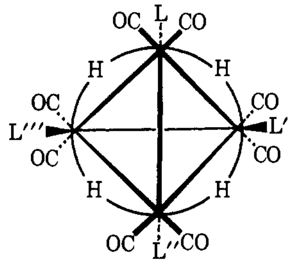
[8] C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968, Chapter 2.

[9] We are indebted to a referee for calling our attention to this mechanism, which nevertheless seems to us unlikely. There is no precedent for five-coordinate gold(III)–olefin complexes such as V. If the double bond were not coordinated so that gold(III) retained its normal planar coordination, there seems to be no reason why the olefin should be susceptible to nucleophilic attack by an alcohol.

Intramolecular Tautomerism of Hydrogen in Hydrido Carbonylmetal Clusters[1]

Sir:

The spin coupling of magnetically active nuclei with hydrogen atoms is potentially useful in determining their relative position in hydrido carbonylmetal clusters. A face-bridging position for hydrogen has been postulated[2] for $H_4Re_4(CO)_{12}$ (I) on the basis of the high symmetry (T_d) required by the two observed carbonyl stretching modes. A structure of lower symmetry is indicated from the infrared spectrum for $H_4Ru_4(CO)_{12}$ (II), and several possible isomers have been discussed.[3] More recently, the report[4] of a simplified spectrum containing five carbonyl stretching bands for a sample of II of improved purity favors the D_{2d} structure shown,



II, (D_{2d}), L = L′ = L″ = L‴ = CO
III, L = $P(OCH_3)_3$; L′ = L″ = L‴ = CO
IV, L = L′ = $P(OCH_3)_3$; L″ = L‴ = CO
V, L = L′ = L″ = $P(OCH_3)_3$; L‴ = CO
VI, L = L′ = L″ = L‴ = $P(OCH_3)_3$

for which this number of bands is predicted. Hydrogen modes have been observed in the laser-Raman spectrum of II (at 1585 and 1290 cm^{-1}, and for the tetradeuterated derivative at 1153 and 909 cm^{-1}), confirming a bridging position for the hydrogen atoms. To gain some additional information on the location of these atoms, we have prepared derivatives substituted with $P(OCH_3)_3$ (L) to follow the coupling of metal-bonded H with ^{31}P. We chose this ligand because ^{31}P–CH_3 coupling might also be used to provide information on its relative

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[1] Work supported by National Science Foundation Grant No. 2367X. Departmental instruments used in this work were supported as follows: Varian A-60 nmr spectrometer, E. I. du Pont de Nemours and Co. and National Science Foundation Grant No. G 20207; Beckman IR-4, E. I. du Pont de Nemours and Co.; AEI MS9 mass spectrometer, National Science Foundation Grant No. GP 3672.

[2] R. B. Saillant, G. Barcelo, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **92**, 5739 (1970).

[3] B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc. A*, 2856 (1968).

[4] H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, *Chem. Commun.*, 477 (1971).

Table I. Nmr Data[a]

Compound	CH_3				Ru-H			
	τ, ppm	Multiplicity	Rel int	J_{PH}, Hz	τ, ppm	Multiplicity	Rel int	J_{PH}, Hz
III	6.31	2	1:1	12.2	27.72	2	1:1	2.65
IV	6.31	2	1:1	12.0	27.61	3	1:2:1	6.63
V	6.23[b]	c[b]	1:1.35:1	12.0[b]	27.84	4	1:3:3:1	7.70
VI	6.26	c[b]	1:2.2:1	12.2[c]	27.83	5	1:4:6:4:1	7.95

[a] $CDCl_3$ solution, tetramethylsilane internal standard, Varian A-60 spectrometer, 60 MHz. [b] See Figure 1 and text for discussion; c = complex. [c] Separation of outer doublet = $|J_{HP} + J_{HP'}|$.[6]

position to other ligands in multiple substituted derivatives.[5]

II (0.19 g, 0.256 mmol) was treated gradually with L (0.075 g, 0.604 mmol) in refluxing heptane (97°) until infrared spectra indicated that it had been consumed (5 hr). Chromatography (silica gel column) with a 50:50 dichloromethane–hexane solvent mixture as eluent developed five well-separated bands, which proved to be due to a trace of unreacted II and the four members of the series $H_4Ru_4(CO)_{12-n}L_n$ (III, $n = 1$; IV, $n = 2$; V, $n = 3$; VI, $n = 4$). The major products of this reaction were the bis- and tris-substituted derivatives IV and V, but the conditions can be varied so as to optimize the yields of each of the four. Thus, VI is obtained in 61% yield with only traces of V when II (0.10 g, 0.135 mmol) is heated (97°) in heptane with excess L (0.10 g, 0.806 mmol) for 1 hr. By ir monitoring during reflux, optimization of the less substituted complexes can be achieved in yields of 20–50% each.

All of the complexes III–VI[6] are air stable, orange crystalline solids readily soluble in hydro- and halocarbons. The infrared spectra show only terminal carbonyl absorptions as follows (cyclohexane solution, cm^{-1}): III, 2097 (m), 2068 (vs), 2060 (s, br), 2032 (vs), 2030 (vs), 2017 (s), 2008 (s), 1974 (w); IV, 2080 (m), 2059 (s), 2039 (w), 2023 (vs, br), 2001 (s), 1967 (w); V, 2067 (m), 2033 (vs, br), 2014 (s), 1998 (s), 1985 (m, br), 1976 (m), 1962 (w); VI, 2025 (vs), 1970 (s).

Proton nmr spectra for the complexes are summarized in Table I, and those for V and VI are shown in Figure 1. It is apparent from these data, and from the simplicity of the chromatographic development, that only one of the many isomers possible for each of IV, V, and VI has been formed. Some simplifying factors must play a role in this as for other substituted polynuclear metal clusters.[7] We assume mainly for steric but possibly also for electronic considerations that the ligands are bonded each to a different metal atom in the multiple-substituted clusters. From these considerations and from the pattern of the methyl proton resonances as discussed below, we propose the structures for the substituted derivatives III, IV, V, and VI as shown. Molecular models confirm that the positions indicated are those for low steric interactions between the bulky ligands.

Thus, the structure assigned to VI is of the D_{2d} symmetry required by the observation of only three carbonyl stretching bands. The methoxy resonance (lower spectrum, Figure 1) appears as a virtual triplet arising from a system $X_nAA'X'_n$, where $J_{AA'}$ is large with respect to $|J_{AX} - J_{AX'}|$ as discussed by Harris[5a] and others.[5b] We can exclude from consideration a more complex spin coupling such as $AA'A''A'''$-$X_nX'_nX''_nX'''_n$, that is, ^{31}P coupling between the two pairs of mutually pseudotrans phosphite ligands, through interpretation of the methoxy resonance of IV, discussed below. From the separation of the sharp doublet we infer $|J_{HP} + J_{HP'}| = 12.2$ Hz. This is the first observation of virtual coupling effects in metal clusters, where the P–P interaction must be transmitted through a metal–metal bond.[8]

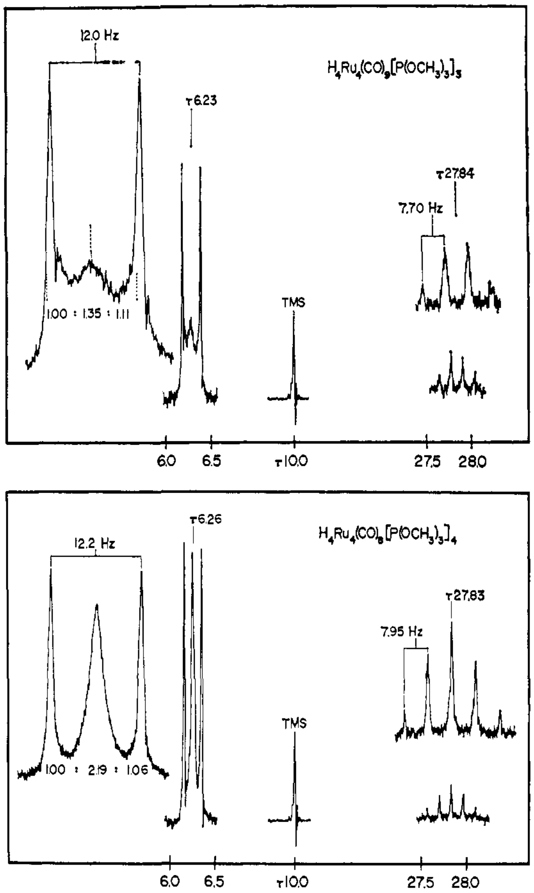

Figure 1. Proton magnetic resonance spectra for $H_4Ru_4(CO)_9$-$[P(OCH_3)_3]_3$ (V) (upper spectrum) and $H_4Ru_4(CO)_8[P(OCH_3)_3]_4$ (VI) (lower spectrum). The lower traces in each spectrum were obtained at spectrum amplitudes of 80 and 32, respectively, at sweep width of 500 cps, which corresponds to the given scale. The expanded signals for V were recorded at spectrum amplitude of 100 and sweep widths of 100 cps (methoxy protons) and 250 cps (metal protons). The expanded signals for VI were similarly recorded at amplitudes of 32 and 100, respectively.

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(5) (a) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964); (b) P. R. Brookes and B. L. Shaw, *J. Chem. Soc. A*, 1079 (1967).

(6) Elemental C and H and mass spectrometric analyses confirm the formulations indicated. For VI, the isotope pattern of the molecular ion is identical with that calculated for the formula.

(7) (a) V. Albano, P. Bellon, and V. Scatturin, *Chem. Commun.*, 730 (1967); (b) P. J. Pollick and A. Wojcicki, *J. Organometal. Chem.*, **14**, 469 (1968); (c) W. S. McDonald, J. R. Moss, G. Raper, B. L. Shaw, R. Greatrex, and N. N. Greenwood, *Chem. Commun.*, 1295 (1969).

(8) A virtual triplet has been noted for the CF_3 resonance in the compound *cis*-$(CF_3)(Ph_3PAu)C{=}C(Ph_3PAu)(CF_3)$ where the phosphorus nuclei, though on different metals, are strongly coupled: C. M. Mitchell and F. G. A. Stone, *ibid.*, 1263 (1970).

Both III and IV exhibit only a sharp doublet for the methoxy protons, and for IV this requires that the phosphite ligands adopt the unambiguous pseudocis configuration indicated, with essentially zero P–P coupling. This also provides the basis for the simplifying assumptions in the interpretation of the spectrum of VI, discussed above.

In the spectrum for V, Figure 1, we see a virtual triplet whose central band is of lower relative intensity than that of VI and whose maximum is displaced somewhat to lower field (τ 6.22) from the midpoint (τ 6.23) of the two outer peaks. This is the result of near coincidence in what we assign as a doublet for the phosphite (L′) trans to CO and a virtual triplet of the two phosphites trans to each other (L and L′′). The near superposition of an outer 1:1 doublet and a virtual 1:2:1 triplet requires that the apparent triplet have peaks of relative intensity 1:1.33:1, close to that observed.

The most prominent feature to be noted in the nmr spectra of III–VI is the single chemical shift for metal–hydrogen in all the derivatives. Each hydrogen appears also to be equivalently spin coupled to all the phosphorus nuclei in any particular complex. Whatever else may be said about the structures of these substituted clusters, it is clear that some form of intramolecular tautomerism is occurring in which the chemical shift of hydrogen and its coupling to phosphorus becomes averaged. The increase in averaged coupling constant from III through VI is interpretable as due to an increase in average proximity of H to P as ligand substitution is increased.

The observed equivalence of the environment of the hydrogen atoms could come about from their rapid exchange of positions along the edges and in part from an intramolecular rotation of the $Ru(CO)_2L$ groups about the C_3 axes of the tetrahedron. The second of these two possibilities can be eliminated on two grounds. In IV, rotation of the $Ru(CO)_2L$ groups would bring the phosphite ligands into trans positions where P–P coupling would occur, as it does in V and VI, and a time-averaged virtual triplet should result, which is *not* the case. In addition, low-temperature studies of VI in dichlorofluoromethane showed no change in the nmr spectrum on cooling to −100°. This suggests a very low activation energy for the tautomeric process, consonant with exchange of hydrogen atoms,[9] parallel to hydrogen exchange in boron hydrides.[10]

We believe similar degenerate tautomerism very likely is occurring in the unsubstituted carbonyl hydride II and could be ascertained from the ^{13}C satellites of the metal hydrogen resonance; solubility problems, however, have thus far prevented us from observing these. Hydrogen tautomerism in the edge-bridged H_4Ru_4 group might well involve face bridging in the transition state. It is interesting to note in this connection that the face-bridged hydrogen atoms of I are easily converted[2] to what is most certainly edge bridging in tetrahedral $[H_6Re_4(CO)_{12}]^{2-}$. Tautomerism in I is therefore also possible, as it is in any cluster with unoccupied polyhedral sites lying energetically close to the sites occupied by the bridging hydrogen in the ground-state structure.

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[9] Time-averaged equivalence of ligands has been observed in $C_4H_6Fe(CO)(PF_3)_2$ and $C_4H_6Fe(PF_3)_3$ at room temperature, but rotational motion was effectively frozen out at about −100°; see J. D. Warren and R. J. Clark, *Inorg. Chem.*, **9**, 373 (1970), and references cited therein.

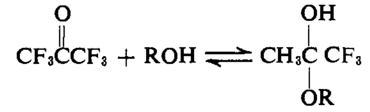
[10] (a) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961); (b) W. N. Lipscomb, *Science*, **153**, 377 (1966).

Thermochemistry of Carbonyl Addition Reactions. I. Addition of Water and Methanol to Hexafluoroacetone

Sir:

While the thermochemistry of water and methanol addition to carbonyl compounds has been of significant interest, the studies have been limited to the solution phase[1] and little thermochemical data are available on the formation of carbonyl hydrates or hemiacetals in other phases where solvation and intermolecular interactions play a smaller role. We wish to report the heat of addition of methanol and water to a ketone in the solution, "standard state," and gas phases at 25°.

Hexafluoroacetone (HFA) reacts rapidly and completely with water and methanol to form the stable hydrate[2] **1**, mp 43–45° and hemiacetal[3] **2**, bp 95°, respectively.



$$\mathrm{CF_3\overset{\overset{O}{\|}}{C}CF_3 + ROH \rightleftharpoons CH_3\overset{OH}{\underset{OR}{C}}\,CF_3}$$

1, R = H
2, R = CH_3

The heats of addition in solution were determined by adding a known quantity of HFA gas to distilled water or anhydrous methanol in a solution calorimeter described elsewhere.[4] The heats of solution and vaporization of the hydrate and hemiacetal were determined by direct calorimetry and the data were treated according to the enthalpy cycle. Since

$$\begin{tikzcd}
\mathrm{HFA(g)} & +\ \mathrm{ROH(g)} & \rightleftharpoons & \mathrm{HFA\cdot ROH(g)} & \Delta H_r{}^\circ{}_{(g)} \\
\mathrm{HFA(g)} \arrow[d, "\Delta H_{(soln)}"] & +\ \mathrm{ROH(l)} \arrow[u, "\Delta H_v"'] \arrow[d, "\Delta H_{(soln)}"] & \rightleftharpoons & \mathrm{HFA\cdot ROH(l\ or\ c)} \arrow[u, "\Delta H_v"'] \arrow[d, "\Delta H_{(soln)}"] & \Delta H_r{}^\circ \\
\mathrm{HFA(soln)} & +\ \mathrm{ROH(soln)} & \rightleftharpoons & \mathrm{HFA\cdot ROH(soln)} & \Delta H_r{}^\circ{}_{(soln)}
\end{tikzcd}$$

HFA is added to the solvent $\Delta H_{exptl} = \Delta H_{soln}(HFA) + \Delta H_r{}^\circ{}_{(soln)}$ so that $\Delta H_r{}^\circ = \Delta H_{exptl} + \Delta H_{soln}(ROH) - \Delta H_{soln}(adduct)$ and $\Delta H_r{}^\circ{}_{(g)} = \Delta H_r{}^\circ + \Delta H_v(adduct) - \Delta H_v(ROH)$. These expressions can be simplified further since dilute solutions are involved (*ca.* 4×10^{-3} *M* in adduct), $\Delta H_{soln}(ROH) \cong 0$. The experimental quantities are given in Table I.

The data clearly show that the heat of hydration and hemiacetal formation of HFA are reasonably close in any one phase. The methanol addition is slightly more exothermic in the "standard state" and slightly less in the gas phase. Presumably, the same trend will obtain

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[1] (a) R. P. Bell, *Advan. Phys. Org. Chem.*, **4**, 1 (1966); (b) J. Kurz, *J. Amer. Chem. Soc.*, **89**, 3524 (1969); J. M. Bell, D. G. Kubler, P. Sartwell, and R. G. Zepp, *J. Org. Chem.*, **30**, 4284 (1965).

[2] W. J. Middleton and R. V. Lindsey, *J. Amer. Chem. Soc.*, **86**, 4948 (1964).

[3] I. L. Knunyanto, T.-Y. Chen, and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **686** (1960).

[4] F. E. Rogers, *J. Phys. Chem.*, **75**, 1734 (1971).