there is a substantial variation in the chemical shifts. A few representative values are +3.9 for Co(III), 8.2 for Ni(II), and 12.9 for Cd(II) (ppm, with reference to $CFCl_3$). These are to be compared with the value of 15.8 for the anhydrous acid. Cobalt–fluorine coupling is evident in the spectrum of the Co(III) derivative; however, the relatively large line width precluded assignment of a meaningful value to the $Co^{59}F^{19}$ coupling. Long-range FF or PF coupling ($\sim$5 cps) was evident in the palladium compound.

Singularly, $Mn(S_2PF_2)_2$ in warm benzene solution absorbs oxygen with a change in color from a very light yellow characteristic of tetrahedral Mn(II) to a deep red. A nitrogen purge of the warm solution does not regenerate the original Mn(II) complex. There is some degradation of the ligand, but the decomposition reaction has not been completely defined. Most of the bis chelates react readily with donor molecules to yield five- and six-coordinate complexes. Of particular note is the reaction of $Co(S_2PF_2)_2$ with nitric oxide. There is a fast process which leads to the formation of $(NO)_2CoS_2PF_2$ and $(S_2PF_2)_2$. In a concurrent reaction the bis chelate is oxidized by the disulfide, $(S_2PF_2)_2$, to form the trisdithiophosphato derivative of Co(III). The tris chelate is also attacked by nitric oxide although the reaction is slow, and this attack leads to the formation of the nitrosyl derivative as well as the disulfide. The nitrosyl derivative is diamagnetic and volatile (bp 64° (12 mm)). Nitrosyl stretching frequencies are at 1797 and 1869 cm^{-1}. The position of the nitrosyl bands suggests function of the nitrosyl ligand as NO$^+$ implicating the relatively unusual *formal* −1 oxidation state for cobalt.

Full experimental details, as well as a more complete chemical characterization, of these unusual chelates will be presented shortly. We wish to acknowledge the assistance of Mr. D. Hall and Dr. M. O'Connor in the Gouy measurements.

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Organogallium Compounds. V. The Gallium–Carbon–Gallium Bridge Bond in Trivinylgallium[1,2]

Sir:

The trialkyl compounds of group III have been studied intensively in order to characterize electron-deficient bridge bonds and the exchange phenomena associated with them. In contrast, little is known about the corresponding vinyl systems: $B(C_2H_3)_3$ is monomeric,[3] uncoordinated $Al(C_2H_3)_3$ polymerizes too readily to study,[4] the synthesis of $In(C_2H_3)_3$ has not been reported,[5] and attempts to prepare $Tl(C_2H_3)_3$ have

(1) Presented in part at the 3rd International Symposium on Organometallic Chemistry, Munich, Aug 1967.

(2) Supported in part by National Science Foundation Grant GP 6762.

(3) T. D. Parsons, M. B. Silverman, and D. M. Ritter, *J. Am. Chem. Soc.*, **79**, 5091 (1957); F. E. Brinckman and F. G. A. Stone, *ibid.*, **82**, 6218 (1960).

(4) B. Bartocha, A. J. Bilbo, D. E. Bublitz, and M. Y. Gray, *Z. Naturforsch.*, **14b**, 357 (1961).
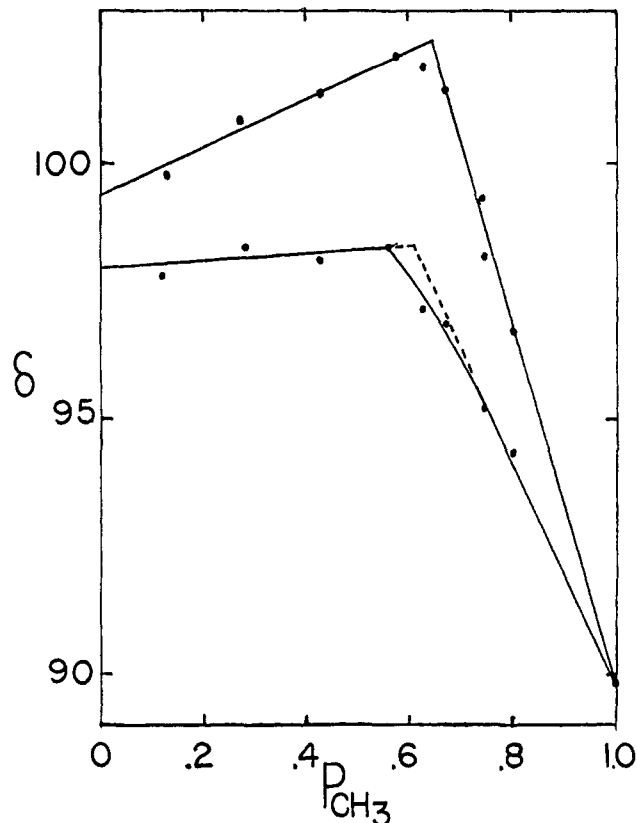

Figure 1. The chemical shift (in cps, 60 MHz) upfield from cyclopentane of the methyl protons *vs.* the mole ratio $(CH_3)/((CH_3) + (C_2H_3))$. The lower curve was obtained at +40°, while the upper one was obtained at −50°.

failed.[6] $Ga(C_2H_3)_3$ and the three isomeric propenyl derivatives have been isolated and shown to be dimeric in noncoordinating solvents,[7] unlike the saturated alkyl derivatives which are known to be monomeric.[8]

A structure similar[9] to that of $Al_2(CH_3)_6$ has been proposed for $Ga_2(C_2H_3)_6$ in which the vinyl groups occupy both bridge and terminal positions.[7a] Attempts to directly observe the groups in these positions by low-temperature nmr studies (−100°, 100 MHz) have failed since a single sharp vinyl spectrum is observed under all conditions. This implies the vinyl groups are still undergoing rapid exchange.

In order to gain further insight into the nature of the vinyl bridge bond, we undertook a study of the $Ga(CH_3)_3$–$Ga(C_2H_3)_3$ system. Rapid exchange between all sites also occurs in this system. Only a single methyl resonance and a single vinyl spectrum were observed for all relative CH_3:C_2H_3 ratios and all temperatures; however, marked changes occur in the spectrum with variation of these parameters. Figure 1 shows the effect of relative concentration and temperature on the methyl resonance while Figure 2 portrays these effects on chemical shifts, obtained from exact analyses of the vinyl spectrum, of the proton *trans* to the metal. Iden-

(5) $In(C_2H_3)_3$ has been synthesized in this laboratory and will be reported at a later date.

(6) J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 5534 (1963).

(7) (a) J. P. Oliver and L. G. Stevens, *J. Inorg. Nucl. Chem.*, **24**, 953 (1962); (b) D. Moy, J. P. Oliver, and M. T. Emerson, *J. Am. Chem. Soc.*, **86**, 371 (1964).

(8) M. Muller and A. L. Otermat, *Inorg. Chem.*, **4**, 296 (1965).

(9) R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.*, **89**, 3121 (1967); P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

Table I. Chemical Shifts and Coupling Constants Calculated for the Vinyl Group in $Ga_2(C_2H_3)_6$ and in $Ga_2(C_2H_3)_2(CH_3)_4$

Compd	δ_a, ppm[a]	δ_b, ppm	δ_c, ppm	J_{ab}, cps	J_{ac}, cps	J_{bc}, cps
$Ga_2(C_2H_3)_6$[b] (average)	4.983	4.757	4.427	14.49	21.30	4.07
$Ga_2(C_2H_3)_2(CH_3)_4$[c] (bridge)	5.007	5.073	4.663	14.14	21.39	4.68
Terminal C_2H_3[d]	4.972	4.598	4.308			

[a] Protons are defined by $\frac{H_a}{X}{>}C{=}C{<}\frac{H_b}{H_c}$; all samples were run in Freon 11 solvent. Chemical shifts are negative (downfield) from the internal cyclopentane standard. [b] The nmr analysis is temperature independent. [c] The nmr analysis was obtained at $-55°$. [d] Calculated by assuming that the spectrum of $Ga_2(C_2H_3)_6$ is an average of bridge and terminal groups and that $Ga_2(C_2H_3)_2(CH_3)_4$ contains only bridging vinyl groups, and neglecting CH_3 group interaction in $Ga_2(C_2H_3)_2(CH_3)_4$.

tical behavior was observed for the *cis* proton. The chemical shift of the geminal proton is essentially independent of these quantities. In both figures, a sharp break occurs at a $CH_3:C_2H_3$ ratio of 2:1 which is accentuated at lower temperatures. These results are
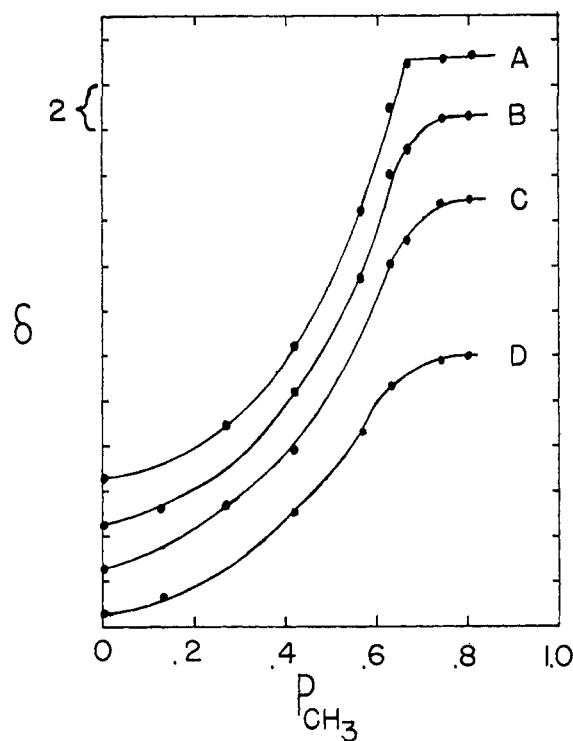
CH_3 groups on free $Ga(CH_3)_3$, δ_a is 1.495 ppm, P_b = the mole ratio of CH_3 groups on $Ga_2(CH_3)_4(C_2H_3)_2$, and δ_b is 1.69 ppm. A simple relationship of this type does not exist for $CH_3:C_2H_3 < 2$ because of the variety of species which may exist.

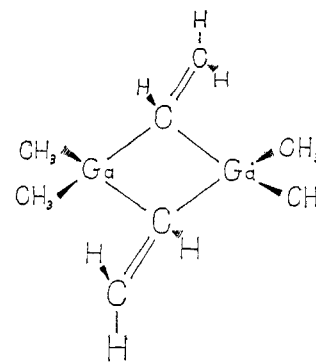Figure 2. The chemical shift of the *trans* proton *vs.* the mole ratio $(CH_3)/((CH_3) + (C_2H_3))$ at various temperatures: A = $-50°$, B = $-30°$, C = $-4°$, and D = $+36°$. Each curve is offset by 2 cps (one unit on the graph) on the chemical shift scale (in cps, 60 MHz).

Figure 3. Proposed structure for dimeric $Ga_2(C_2H_3)_2(CH_3)_4$.

consistent with the structure shown in Figure 3 in which the vinyl groups are preferentially located in the bridge position. For all $CH_3:C_2H_3$ ratios greater than 2, the chemical shifts of the vinyl protons remain constant, which implies that they are all located in the bridge positions while the methyl groups in excess of the 2:1 ratio are in the form of $Ga(CH_3)_3$. This excess free $Ga(CH_3)_3$ exchanges with the terminal methyl groups on the dimeric species (Figure 3), as shown by the linear dependence of the chemical shift of the methyl resonance on concentration. This dependence is given by $\delta_{exptl} = P_a\delta_a + P_b\delta_b$, where P_a = the mole ratio[10] of

Some additional results from the exact analysis of the vinyl portion of the spectrum are presented in Table I. The coupling constants obtained from these analyses show only a very small dependence on temperature and concentration. This implies that the electronic structure of the vinyl group has not undergone a major disruption. The changes in chemical shift are consistent with the formation of a bridge bond through the sp^2 orbital of the vinyl group. The major effect of this should be a deshielding of the protons associated with this group, as is observed, due to the donation of electron density to the three-centered bridge bond.

With this visualization of the structure, one may now account for the enhanced stability of vinyl bridge bonds over alkyl bridge bonds. Upon examination of the molecular orbital description of the three-centered bridge-bonded systems, one finds that the nonbonding molecular orbital has appropriate symmetry to interact with the π orbitals of the vinyl groups. Interaction of this type may stabilize bridge bonds in the unsaturated derivatives, whereas in the saturated systems no interaction of this type can occur. We would emphasize that this interaction is not of sufficient strength to disrupt the carbon–carbon double bond since no isomerization has been observed between *cis-* and *trans*-propenylgallium.

(10) The mole ratio is defined as the concentration of exchange groups of a given type divided by the total concentration of all exchanging groups.

These arguments can be extended to account for the catalysis of methyl group exchanges in methylthallium systems due to the addition of a vinylthallium species if one assumes that the rate-determining step for exchange involves formation of a bridged species.[6]

(11) NASA Trainee, 1967–1968.
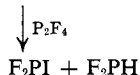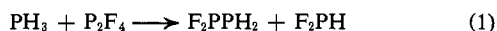
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The Preparation of Phosphinodifluorophosphine. A High-Yield Synthesis of Difluorophosphine

Sir:

Initial investigations of the reactions of PH_3 with fluorophosphines have shown that, with F_2PI in the presence of mercury, F_2PH is formed in high yield (90%), and that, with a $F_2PI-P_2F_4$ mixture, the new diphosphine H_2PPF_2 is formed along with F_2PH. Only a very small amount of H_2PPF_2 could be detected when pure P_2F_4 was treated with PH_3; the major products were F_2PH and PF_3.[1] The reaction of excess PH_3 with F_2PI gives *no* H_2PPF_2 but only PF_3[1] and a small amount of F_2PH. Apparently, small amounts of H_2PPF_2 are formed according to eq 1, while the scheme given by eq 2 might explain the reaction involving both F_2PI and P_2F_4.

$$PH_3 + P_2F_4 \longrightarrow F_2PPH_2 + F_2PH \qquad (1)$$

$$PH_3 + F_2PI \longrightarrow H_2PPF_2 + HI \qquad (2)$$

$$\downarrow P_2F_4$$

$$F_2PI + F_2PH$$

Phosphinodifluorophosphine, H_2PPF_2, was formed when a mixture of F_2PI (2.17 mmoles) and P_2F_4 (2.00 mmoles) was treated with PH_3 (8.36 mmoles) in a 500-cc bulb, the tip of which was held at $-78°$ for 1 week. Complete separation of the reaction mixture could not be effected by trap-to-trap distillation, but an incomplete separation was obtained by fractional condensation at -130 and $-196°$. A mixture of F_2PI and H_2PPF_2 was held at $-130°$ while F_2PH, PF_3, and unreacted PH_3 were retained at $-196°$. Large amounts of phosphinodifluorophosphine could not be obtained free from F_2PI. However, a $-112°$ trap was used to hold the majority of the F_2PI, while 0.84 mmole of H_2PPF_2 (87% pure as demonstrated by a vapor-density molecular weight of 114 g/mole and the ir spectrum) slowly passed through the $-112°$ trap. A pure sample large enough for a mass spectrum (70 eV) was obtained. In the range m/e 32–200 the spectrum displayed peaks (relative intensities and assignment in parentheses) at m/e 102 (2.0 $H_2PPF_2^+$), 101 (0.3 $HPPF_2^+$), 100 (0.2 PPF_2^+), 88 (25.7 PF_3^+), 70 (13.0 F_2PH^+), 69 (45.2 PF_2^+), 51 (9.2 (FPH^+), 50 (6.2 PF^+), 34.5 (0.2 F_2P^{2+}), 34 (68.8 PH_3^+), 33 (22.9 PH_2^+), and 32 (100.0 PH^+).

The infrared spectrum of gaseous H_2PPF_2 shows absorptions at 2317 (sh, w), 2302 (w), 1065 (br, w), 986 (br, w), 830 (vs), 823 (vs), 727 (m), and 719 (m) in the 4000–650-cm^{-1} region.

(1) Disproportionation was evidenced not only by the presence of PF_3 but also by the formation of yellow solids.
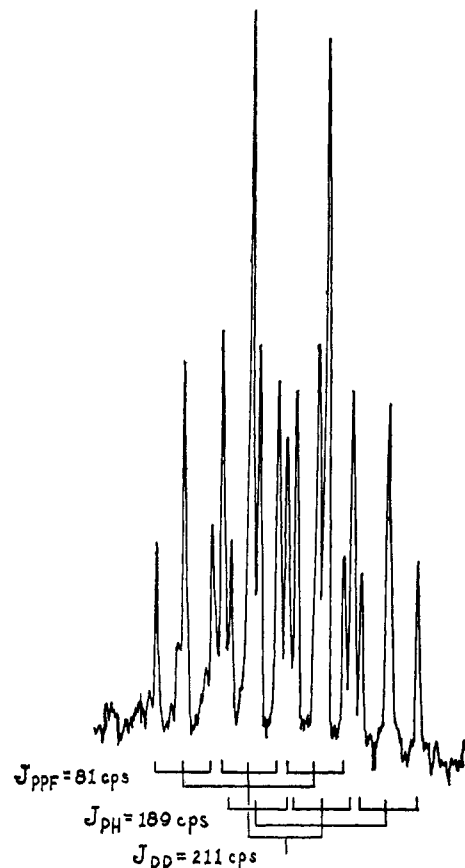

Figure 1. The [$-PH_2$] portion of the ^{31}P nmr spectrum of H_2PPF_2.

Because of the difficulties encountered with purification, analytical and vapor pressure data were not obtained. Nevertheless, unequivocal characterization of phosphinodifluorophosphine was obtained from the ^1H (60 Mc), ^{19}F (94.1 Mc), and ^{31}P (40.5 Mc) nmr spectra.

The proton spectrum at 37° consists of a doublet (J_{PH} = 191 cps) centered -2.75 ± 0.03 ppm from TMS internal standard; each member of the basic doublet displays a doublet of overlapping 1:2:1 triplets (J_{HPPF} = 22, J_{PPH} = 17 cps).

The fluorine spectrum ($-40°$) displays the same basic pattern as the proton spectrum (doublet of doublets of 1:2:1 triplets) centered $+43.2 \pm 1.0$ ppm from F_2PI internal standard.[2] The coupling constants derived from the ^{19}F spectrum were J_{PF} = 1203, J_{PPF} = 82, and J_{HPPF} = 22 cps.

The phosphorus spectrum ($-40°$) of H_2PPF_2 gave two signals of equal integrated area, corresponding to the [$-PF_2$] and [$-PH_2$] environments, centered at -51.5 ± 1.0 and $+379.8 \pm 1.0$ ppm from F_2PI internal standard, respectively.[2] The [$-PF_2$] portion of the spectrum consisted of a 1:2:1 triplet of doubled 1:2:1 triplets from which the coupling constants J_{PF} = 1189, J_{PP} = 211, and J_{PPH} = 17 cps were directly measured. As shown in Figure 1, the [$-PH_2$] portion of the spectrum displays a multiplet composed of a basic doublet (J_{PP}

(2) F_2PI resonance appears at -31.9 ppm relative to trifluoroacetic acid (TFA) and at -242.2 ppm relative to 85% orthophosphoric acid (OPA): R. W. Rudolph, J. G. Morse, and R. W. Parry, *Inorg. Chem.*, **5**, 1464 (1966). Therefore, the value in the text when stated relative to external TFA is $+11.3$ ppm; adjusted to external OPA, the values are -293.7 and $+137.6$ ppm, respectively.

Communications to the Editor