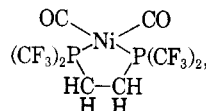


### A Volatile Chelated-Nickel Dicarbonyl<sup>1</sup>

Sir:

Chelation of nickel by bis-phosphines or bis-arsines, forming heterocyclonickel dicarbonyls, has been accomplished by Chatt and Hart<sup>2</sup>; however, no compound in this class was reported to be volatile without decomposition, whereas volatility often would be advantageous for the further study of such substances. Accordingly, we have used high-vacuum methods to make the study of a new volatile compound presumed to have the structure



hereinafter designated as "D." D was attacked by  $\text{PF}_3$  to form another volatile derivative of the same ring, with comparable small yields of the known  $(\text{PF}_3)_2\text{Ni}(\text{CO})_2$  and  $(\text{PF}_3)_3\text{NiCO}$ , and major yields of nonvolatiles having infrared bands for Ni-CO-Ni bridging.

**Synthesis.**—An equimolar mixture of  $\text{Ni}(\text{CO})_4$  and the bis-phosphine  $(\text{CF}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CF}_3)_2$ <sup>3</sup> (hereinafter designated as "B") liberated CO bubbles immediately upon warming to 25° and was allowed to stand for a few days to complete the process. However, the yield of D was only 25%; repetition at 40° gave only an 8% yield. Actually, a polymer might be expected if some units encounter others faster than each can cyclize. Dilution favors single-unit cyclization; thus in benzene under dry nitrogen at 60° the yield rose to 50%, augmented further by boiling the benzene solution of the nonvolatile by-product. This was partly converted to the monomer in the manner of the presumed dimer  $[(\text{C}_2\text{H}_5)_2\text{PC}_2\text{H}_4\text{P}(\text{C}_2\text{H}_5)_2\text{Ni}(\text{CO})_2]_2$ .<sup>2</sup>

**Physical Properties.**—The colorless crystals of D melted in the range 4.5–6.0°. Its molecular weight (vapor, 8 mm. and 90°) was 485 (calcd. 481). Its regionally averaged vapor tensions (Table I) agree with an equation from which  $\Delta S_{\text{vap}} = 21.00$  e.u. and b.p. 203°, suggesting acceptable purity.

TABLE I

VAPOR TENSIONS OF  $(\text{CF}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CF}_3)_2\text{Ni}(\text{CO})_2$

( $\log P_{\text{mm.}} = 6.6902 + 1.75 \log T - 0.004912 T - 2931/T$ )

<i>t</i> , °C.	30.0	36.3	41.2	46.3	51.2	60.4
<i>P</i> mm. (obsd.)	0.75	1.13	1.56	2.14	2.82	4.82
<i>P</i> mm. (calcd.)	0.75	1.14	1.56	2.13	2.86	4.79

**Chemical Behavior.**—D decomposes slowly to CO and nonvolatiles at 70°, so that physical measurements at higher temperatures must be made rapidly. Its reaction with iodine in  $\text{CCl}_4$  at 25° yielded all of the CO (11.5% by wt.; calcd. 11.6%); then nickel was determined as 12.0% (calcd. 12.2%) by the dimethylglyoxime method. The B content is estimated by difference as 76.5% (calcd. 76.2%). Its major presence in the  $\text{CCl}_4$  solution was confirmed by its infrared spectrum. With the molecular weight, these results prove the formula of D.

One D with 10  $\text{PF}_3$ , in a closed tube at 70°, consumed 1.81  $\text{PF}_3$  during 18 days, liberating an unmeasured amount of CO. One fraction of the product (trapped *in vacuo* at –120° to remove  $\text{PF}_3$ ) showed infrared

peaks at 2085, 2102, and 2064  $\text{cm}^{-1}$ , as reported for  $(\text{PF}_3)_3\text{NiCO}$  (2082) and for  $(\text{PF}_3)_2\text{Ni}(\text{CO})_2$  (2099 and 2061).<sup>4</sup> The P–F stretching bands appeared at 931, 903, and 864  $\text{cm}^{-1}$ . A less volatile fraction, not easily separable from D, showed (by the Infracord instrument) a single C–O stretching band at 2066, one P–F band at 883  $\text{cm}^{-1}$ , and C–F stretching just like that of D. The formula  $(\text{CF}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CF}_3)_2\text{NiPF}_3\text{CO}$  seems probable.

The major D– $\text{PF}_3$  reaction product was a nonvolatile oil showing C–H stretching (Infracord) at 2933, C–O stretching at 2053, typical C–F and P–F stretchings, and a strong peak at 1727  $\text{cm}^{-1}$ , indicating Ni–Co–Ni bridging. A nonvolatile white-solid final product has not been examined.

Triphenylphosphine (large excess) also attacked D, liberating 30% of its CO during 12 hr. in benzene at 70°. Some of the ligand B also was displaced; there was no other volatile product. The benzene solution of the nonvolatiles showed C–O absorption at 2016 and 1946  $\text{cm}^{-1}$  and a C–F stretching spectrum just like that of D.

**Infrared Study of D and B.**—The infrared spectra of the vapors of D and B were compared, using path lengths near 100 mm. and respective pressures of 1.44 and 18 mm. The relative intensity of each band maximum was calculated as  $k = (100/PL) \log I_0/I$  (path *L* and pressure *P* both in cm.) and shown in parentheses after the frequency in  $\text{cm}^{-1}$ ; however, very intense bands had to be recorded at unknown pressures too low for useful calculations of intensity.

Bands unique for D are C–O stretchings 2090 (vvs), 2057 (vvs), and 2018 (4.9); and ring- $\text{CH}_2$  motions 1089 (4.9) and 1054 (1.5). B showed C–H stretchings 2984 (0.03), 2961 (0.02), 2941 (0.05), 2931 (0.04), 2854 (0.10), 2730 (0.05); and C–F stretching overtones appeared at 2290 (0.7), 2256 (0.4), 2244 (0.4). For D the pressure was too low to show any of these modes.

Corresponding bands for D and B are the  $\text{CH}_2$  deformations D1420 (2.4) vs. B1431 (1.6) and D1310 (5.1), 1259 (3.5) vs. B1282 (1.9); C–F stretchings D1195, 1174, 1158, 1122 vs. B1197, 1169, 1147, 1114 (all vvs);  $\text{CH}_2$  motions D878 (3.8), 811 (4.6) vs. B877 (0.3), 797 (0.1);  $\text{CF}_3$  asymmetrical deformation D734 (21) vs. B748 (1.0), 726 (0.8); P– $\text{CH}_2$  stretchings D683 (2.4), 655 (2.3) vs. B691 (1.3), 657 (0.3);  $\text{CF}_3$  symmetrical deformation D562 (3.2) vs. B558 (2.3); and P– $\text{CF}_3$  stretchings D481 (13) vs. B486 (1.0). Bands D534 (11), D522 (2.4), and B542 (0.7) might correspond, but D507 (3.8), 506 (5.4) are not easily assigned. Also uncertain of assignment are D464 (18), 437 (6.4), 399 (4.6), and B446 (4.0), 444 (4.0), 361 (3.0), 1889 (0.7), 1853 (0.2).

(4) M. Bigorgne and A. Zelner, *Bull. soc. chim. France*, 1986 (1960).

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF SOUTHERN CALIFORNIA  
LOS ANGELES, CALIFORNIA 90007

ANTON B. BURG  
G. BRYAN STREET

RECEIVED SEPTEMBER 3, 1963

### Alkylidenecarbenes<sup>1</sup>

Sir:

The addition of carbenes to olefins is used as a criterion to establish the intermediate formation of these reactive species.<sup>2</sup> When 1-chloro-2-methylpropene-1 (I, 0.25 mole) was treated with potassium *t*-butoxide

(1) This investigation was supported by Public Health Service Research Grant AM-05183 from the National Institute of Arthritis and Metabolic Diseases.

(2) (a) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6182 (1954); (b) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (c) H. O. Hartzler, *ibid.*, **83**, 4990 (1961).

(1) It is a pleasure to acknowledge the support of this research through National Science Foundation Grant No. GP-199. Except as otherwise specified, all infrared spectra were recorded within 1  $\text{cm}^{-1}$  by a Beckman IR7 spectrophotometer with NaCl and CsI optics, provided by National Science Foundation Grants G-14465 and GP-199.

(2) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

(3) First made by L. R. Grant, Ph.D. Dissertation, University of Southern California Libraries, 1960; cf. also A. B. Burg, *J. Am. Chem. Soc.*, **83**, 2226 (1961).