(phenyl), 6.93, 7.08 and 7.21 (C–H) and 8.01 μ (aryl ether).[23]

Anal. Calcd. for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.31. Found: C, 69.99; H, 6.03; N, 4.25.

Catalytic Hydrogenation of 3-(3,4-Methylenedioxyphenyl)-4-nitro-1-phenyl-1-butanone (I).—A slurry of nitro ketone (10.63 g.), Raney nickel[24] (4 g.) and absolute methanol (233 ml.) was subjected to hydrogenation for 35 hours at an initial pressure of 48 p.s.i. Concentration of the filtered solution yielded a faintly-green oil which was dissolved in anhydrous ether and treated with ethereal hydrogen chloride in the aforedescribed manner. The crystalline hydrochloride precipitated immediately; yield 6.35 g. (62%), m.p. 205–220° dec.

The corresponding picrate formed readily when an ethanol solution of picric acid was added to an ethanol solution of the hydrochloride; m.p. 165–167° and undepressed when mixed with picrate of the pyrroline VI obtained from reduction of I by zinc and aqueous ammonium chloride.

Essentially the same results were obtained when hydrogenation of I was effected over platinum black.

LOS ANGELES, CALIFORNIA

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[23] The infrared spectrum (obtained with a Leitz recording spectrophotometer equipped with a sodium chloride prism) and microanalytical data for this compound were kindly determined by W. M. Hazenberg, Laboratory for Organic Chemistry, The University, Groningen, The Netherlands.

[24] Catalyst 113 days old; prepared according to R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

COMMUNICATIONS TO THE EDITOR

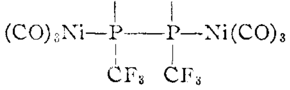
FLUOROCARBON-PHOSPHORUS-NICKEL CARBONYLS[1]

Sir:

The recent publication by Emeléus and Smith on the new compounds $(CF_3)_3PNi(CO)_3$ and $[(CF_3)_3P]_2Ni(CO)_2$[2] prompts us to report our independent (Aug. 1957) information on the latter, along with our earlier discovery of analogous materials derived from trifluoromethyl-polyphosphines.

The compound $[(CF_3)_3P]_2Ni(CO)_2$ formed from $Ni(CO)_4$ and $(CF_3)_3P$, but failed to react with excess $(CF_3)_3P$ even at 100°. It melted at −31° and its roughly measured vapor tensions (1 mm. at 0°; 3 mm. at 20°) indicated the b.p. as near 190° (Trouton const. 19 cal./deg. mole). Intense ultraviolet illumination had no effect upon its vapor or 0.001 *M.* solution in cyclohexane, but the pure colorless liquid responded to sunlight by forming an intensely purple-red solute. This was not colloidal nickel,[2] for the color accompanied the $[(CF_3)_3P]_2Ni(CO)_2$ during distillation; and the shiny black residue was soluble in acetone or sublimable on mild warming *in vacuo.*

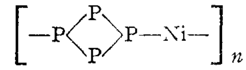
The diphosphine $P_2(CF_3)_4$ with $Ni(CO)_4$ at room temperature gave a product stoichiometrically shown to be



$$(CO)_3Ni-\underset{CF_3}{\overset{CF_3}{P}}-\underset{CF_3}{\overset{CF_3}{P}}-Ni(CO)_3$$

hereinafter designated as NiPPNi. Its slightly volatile (0.5 mm. at 20°) red-black crystals melted at 105°; no decomposition occurred during 100 hrs. at that temperature. NiPPNi is insoluble in water, but soluble in cyclohexane, benzene, ether, carbon tetrachloride, and methanol, with a permanganate-red color which was observed also for the vapor. Oxygen discharged the color of the solutions, but brief exposure of the solid to air was not harmful; a 12-hr. exposure converted it to a green powder.

The cyclo-tetraphosphine $(CF_3P)_4$[3] vigorously displaced CO from $Ni(CO)_4$ at 0°. In solution in toluene, the reaction gave a lively play of colors: green, gold, olive, brown, and finally an insoluble crimson. At the end, most of these colors were isolated by solvent extraction methods and filter-paper chromatography. The oily mixture of nonvolatile products (fairly stable in air) had the average composition $[Ni_{1.77}(CO)_{4.45}(CF_3P)_4]_x$, suggesting a mixture of compounds of the type $(CF_3P)_4[Ni(CO)_3]_n$ (n = 1, 2, or 3) and limited



chains with $Ni(CO)_3$ end groups and $Ni(CO)_2$ units cross-linking the chains through phosphorus. The reality of such bonding is supported by the existence of $[(CF_3)_3P]_2Ni(CO)_2$ and NiPPNi.

The absorption spectra of $[(CF_3)_3P]_2Ni(CO)_2$ and NiPPNi are shown in the table. In cyclohexane the 2370 peak of the former is only a shoulder. The vapor-phase spectrum of NiPPNi is like that in solution but shifted 50 Å. toward shorter wavelengths.

$[(CF_3)_3P]_2Ni(CO)_2$ (vapor)

λ, Å.	2,070	2,220	2,370
Shape	max.	min.	max.
Molar ext. coeff.	10,500	9,700	10,500

NiPPNi (in cyclohexane)

λ, Å.	2,470	3,100	3,490	4,050	5,300
Shape	max.	min.	max.	min.	max.
Molar ext. coeff.	14,600	1,000	11,100	570	2,850

The noumenological presence of d_π-d_π bonds in phosphine-nickel carbonyls has been mentioned.[4] We suggest that d orbitals provide a route for extensive delocalization of electrons along the angled hetero-chain O=C=Ni=P—P=Ni=C=O in NiPPNi and that this accounts for the dye-like color and relative stability of this compound.

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[2] H. J. Emeléus and J. D. Smith, *J. Chem. Soc.*, 527 (1958).

[3] W. Mahler and A. B. Burg, THIS JOURNAL, **79**, 251 (1957).

[4] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 345 (1954).