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NOTE

COORDINATING PROPERTIES OF [BIS(TRIFLUOROMETHYL)AMINO]-BIS(TRIFLUOROMETHYL)PHOSPHINE WITH NICKEL CARBONYL

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In 1958 Emeleus and Smith[1] isolated [tris(trifluoromethyl)phosphine]nickel tricarbonyl and bis[tris(trifluoromethyl)phosphine]nickel dicarbonyl from the reaction of tris(trifluoromethyl)phosphine with nickel carbonyl. Attempts to prepare the tri- and tetra-substituted nickel(0) complexes were unsuccessful, although Wilkinson's method involving the use of tetrakis(phosphorus trichloride)nickel(0) was employed. In the same year, Burg and Mahler[2] found that certain (perfluoromethyl)phosphines, $(CF_3)_2PP(CF_3)_2$ and $(CF_3P)_4$, afforded polynuclear substitution products of nickel, *viz.* $(CO)_3Ni(CF_3)_2PP(CF_3)_2Ni(CO)_3$ and $Ni_{1.77}(CO)_{4.45}$-$[(CF_3P)_4]_x$ respectively. It seemed of interest to investigate reactions of [bis(trifluoromethyl)amino]bis(trifluoromethyl)phosphine, $(CF_3)_2NP(CF_3)_2$, with nickel carbonyl in order to ascertain whether complexes can be formed without involving intramolecular fluorination; and, if so, to what extent can the substitution reaction proceed.

An equimolar quantity of nickel carbonyl and [bis(trifluoromethyl)amino]bis(trifluoromethyl)phosphine reacted at room temperature to give $(CF_3)_2NP(CF_3)_2$-$Ni(CO)_3$, (I), where the phosphorus atom is assumed to be bonded to nickel. It does not appear likely that the nitrogen atom in the bis(trifluoromethyl)amino group would have sufficiently strong donor properties to form complexes containing N–metal bonds. Use of a 1/2 molar ratio at room temperature also gave the same product (I), indicating that no further substitution occurred.

The vapour spectrum in the infrared region of the complex (I) gave bands at 1495 m, 1350 sh, 1350 sh, 1315 vs, 1280 sh, 1260 vs, 1220 vs, 1200 sh, 1145 vs, 1120 s ν(C–F), 973 m, 950 w, 718 w ν(C–N), and 745 w ν(P–C), thus confirming the presence of the ligand. Peaks located at 2117 w, 2059 vs and 2021 vw are due to the C–O stretching vibrations. The position and relative intensities of the peaks indicate that the complex carries three carbon monoxide groups.

Compound (I) is a colourless liquid which is unstable in high vacuum. A purple residue was often formed in the traps during vacuum fractionations. This property is similar to that observed by Burg and Mahler[3] for the complex $[(CF_3)_2P]_2$-$[Ni(CO)_3]_2$.

Reactions of [bis(trifluoromethyl)amino]bis(trifluoromethyl)phosphine with manganese and cobalt carbonyls proceeded differently[4]. With manganese carbonyl at 140° for 4 days, an orange crystalline complex, corresponding to $[Mn(CO)_4P(CF_3)_2]_2$ was formed, together with perfluoro-2-azapropene (50%), manganese fluoride and unreacted manganese carbonyl. Reaction with cobalt carbonyl at 70° for 3 days also gave a similar bridged complex, $[Co(CO)_3P(CF_3)_2]_2$. Perfluoro-2-azapropene and $Co_4(CO)_{12}$ were also formed. In both these reactions, no carbonyl complexes containing fluorine or bis(trifluoromethyl)amino bridging groups were produced.

EXPERIMENTAL

A conventional vacuum line was employed in handling the compounds. All reactions were carried out in evacuated sealed ampoules carrying break seals. The infrared spectra were recorded on a Perkin–Elmer Infracord spectrometer using sodium bromide optics. [Bis(trifluoromethyl)amino]bis(trifluoromethyl)phosphine was prepared and purified according to the method reported elsewhere[3].

Reaction of [bis(trifluoromethyl)amino]bis(trifluoromethyl)phosphine with nickel carbonyl

A mixture of nickel carbonyl (0.852 g, 4.99 mmole) and [bis(trifluoromethyl)-amino]bis(trifluoromethyl)phosphine (0.966 g, 3.01 mmole) was allowed to react in 5 ml ether (sodium dried) in a sealed ampoule at room temperature. A colourless gas was evolved. The colourless solution was fractionated the next day to give the required complex, $(CF_3)_2NP(CF_3)_2Ni(CO)_3$, trapped out at $-50°$. (Found: Ni, 12.1. $C_7F_{12}NNiO_3P$ calcd.: Ni, 12.6%.)

In another experiment, nickel carbonyl (0.481 g, 2.81 mmole) and the phosphine (1.83 g, 5.70 mmole) were used. Fractionation gave only one product, $(CF_3)_2NP(CF_3)$-$Ni(CO)_3$. No disubstituted complex was isolated.

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