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NICKEL(0) COMPLEXES
II. THE REACTION OF NICKEL CONTAINING ZIEGLER SYSTEMS WITH CARBON MONOXIDE

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SUMMARY

The preparation of $[(PhO)_3P]_3NiCO$ by reaction of nickel acetylacetonate, triphenyl phosphite, triethylaluminium and carbon monoxide or by reaction of $[(PhO)_3P]_4Ni$ with carbon monoxide is described. The former procedure also served in the preparation of $[(PhO)_3P]_2Ni(CO)_2$.

The properties of various Ziegler systems, *i.e.* products obtained by reaction of transition metals and metal alkyls have been investigated in depth in recent years. The preparation of the metal carbonyls of Group VI and VII elements in the presence of aluminum alkyls is but one example of the reactivity of these systems[1]. Our interest in nickel(0) complexes[2], in particular in the utilization of routes circumventing the use of nickel carbonyl prompted us to investigate this method as a route to various substituted nickel carbonyl derivatives, in particular the Group V-A substituted derivatives of nickel carbonyl.

These particular carbonyl complexes have previously been prepared via the reaction of the free phosphine or phosphite with nickel tetracarbonyl, and in some instances the mono- and dicarbonyl complexes were separated only with difficulty, if at all[3,4]. We find that the method described below will give the mono-and dicarbonyl complexes in a high degree of purity and in excellent yield.

The reaction involves the reduction of a nickel(II) salt in the presence of a ligand from Group V-A and subsequent treatment of this mixture, containing tetrakis-(triphenyl phosphite)nickel(0) with the stoichiometric amount of carbon monoxide required to produce the carbonyl complex. This sequence was verified by independent synthesis of the tetrakis complex[2,5] and conversion of this complex to the carbonyl moiety in the presence of one molar equivalent of carbon monoxide. Treatment with two molar equivalents of carbon monoxide gave the bis(triphenyl phosphite)nickel dicarbonyl. The reaction sequence is as follows:

$$Ni^{II} + 2.5\ Et_3Al \rightarrow [Ni^0]$$
$$[Ni^0] + 4\ (RO)_3P \rightarrow [(RO)_3P]_4Ni$$
$$[(RO)_3P]_4Ni + CO \rightarrow [(RO)_3P]_3NiCO + (RO)_3P$$
$$[(RO)_3P]_4Ni + 2\ CO \rightarrow [(RO)_3P]_2Ni(CO)_2 + 2\ (RO)_3P$$

The use of less than 4 moles of ligand per mole of nickel did not produce the carbonyl complex in high yield. An excess of ligand is preferred. Investigations are in progress to extend this synthesis to other transition metals.

EXPERIMENTAL

Preparation of tris(triphenyl phosphite)nickel monocarbonyl

Into a clean, dry one-gallon autoclave was placed 257 g (1.0 mole) of anhydrous nickel acetylacetonate*, 1000 ml of n-hexane**, 1241 g (4.0 mole) of redistilled triphenylphosphite and 1410 g (2.5 mole) of a 20% solution of triethylaluminum in hexane. The temperature of the reactor was raised to 85° and 28 g (1.0 mole) of carbon monoxide was added. After the reaction was complete, (2 h) as evidenced by no residual pressure in the system, the contents were cooled to 0° and the tris(triphenyl phosphite) nickel monocarbonyl was allowed to settle from the system over a period of 1 h. The hexane was decanted and the residual complex was filtered. The hexane wet cake was then dried in a vacuum oven to give 990 g (85%) of the complex, m.p. 98–99° (reported[7] 98.5°) found to be 98% pure by IR analysis (see below). The remaining 2% was found to be tetrakis(triphenyl phosphite)nickel(0).

The reaction may be carried out in benzene as solvent to give a 65% yield of complex, m.p. 97–98°, or in 1,5-cyclooctadiene as solvent to give an 81% yield of complex, m.p. 98–99.5°. (Found C, 56.19; H, 3.58; Ni, 4.96; P, 7.47. $C_{55}H_{45}NiO_{10}P_3$ calcd.: C, 56.58; H, 3.86; Ni, 5.03; P, 7.95%.)

Preparation of tris(triphenyl phosphite)nickel monocarbonyl from tetrakis(triphenylphosphite)nickel(0)

Tetrakis(triphenyl phosphite)nickel(0) was prepared according to published methods[2]. Treatment of 129.8 g (0.1 mole) of the tetrakis complex in 1,5-cyclooctadiene with 2.8 g (0.1 mole) of carbon monoxide at 85° for 30 min gave the monocarbonyl complex in 97% yield, m.p. 97–98°.

Preparation of bis(triphenyl phosphite)nickel dicarbonyl

Into a clean dry one-gallon autoclave was placed 257 g (1.0 mole) of anhydrous nickel acetylacetonate, 1000 ml of dry hexane, 1241 g (4.0 mole) of redistilled triphenyl phosphite and 1410 g (2.5 mole) of a 20% solution of triethylaluminum in hexane. The temperature of the reactor was raised to 85° and 56 g (2.0 mole) of carbon monoxide was added. After completion of the reaction (2 h) as evidenced by no residual pressure in the system, the contents were cooled to 0° and the bis(triphenyl phosphite)nickel dicarbonyl was allowed to settle from the system over a period of 1 h. The complex was recovered by filtration to give 588 g (80%) m.p. 95° (reported[6] 95°) found to be at least 98% pure by IR analysis (see below). The reaction may also be carried out in either benzene or 1,5-cyclooctadiene with similar results. (Found C, 61.86; H, 4.05; Ni, 7.57; P, 8.20. $C_{38}H_{30}NiO_8P_2$ calcd.: C, 62.07; H, 4.11; Ni, 7.98; P, 8.43%.)

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* The naphthenate or other organonickel salt may be employed with no observable decrease in yield or purity.

** Hexane was employed to eliminate a precipitation step with methanol when benzene was employed as the solvent. Also the highest yield of *tris*-complex was obtained with this system.

TABLE 1

CARBONYL FREQUENCIES FOR THE TRIS- AND BIS-PHOSPHITE-NICKEL CARBONYL COMPLEXES IN SOLUTION

Complex	ν(CO) (cm^{-1})[a,b]	
	Cyclohexane	Carbon tetrachloride
$Ni(CO)[P(OC_6H_5)_3]_3$	1996	2020
$Ni(CO)_2[P(OC_6H_5)_3]_2$	2043, 1996	2053, 2016

[a] Frequency assignments are accurate to ±3–5 cm^{-1}. [b] The higher frequency is due to asymmetric stretching, the lower frequency is due to symmetric stretching.

Attempts to introduce three moles of carbon monoxide were not successful.

Identification and characterization of the complexes

Spectra were taken with a Perkin–Elmer Model 21 double-beam recording spectrophotometer with NaCl optics programmed for maximum resolution (expanded scale and slow scanning) which was in a constant temperature, constant humidity room. Table 1 lists the IR carbonyl frequencies for the nickel carbonyl phosphite complexes in solution.

The optical densities at each wave length were corrected for background and the purity of the complexes was calculated from the linear relationship between optical density and concentration. The extinction coefficients of the pure complexes were calculated from standard solutions of the pure carbonyls prepared by known methods[6,7] and purified by repeated recrystallization from petroleum ether, until their theoretical and found nickel contents agreed within 0.1%.

At this time the purity of both complexes could be determined by this method within 1.0% of the actual purity.

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