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A New Method for the Synthesis of Bis(triphenylphosphine)dicarbonylnickel

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One of the basic methods for preparing transition metal carbonyls consists in the carbonylation of metal salts with carbon monoxide in the presence of a reducing agent [1]. When preparing tungsten and molybdenum hexacarbonyls, Nesmeyanov and Anisimov with co-workers used iron pentacarbonyl as the reducing and carbonylation agent [2]. Later these abilities of $Fe(CO)_5$ were exploited for the synthesis of cobalt and rhodium carbonyls [3].

While studying the reactivity of ethyl(acetylacetonato) (triphenylphosphine)nickel, we showed quite recently that the action of iron carbonyl derivatives, such as $NaFe(CO)_2Cp$ and $Fe(CO)_5$, on this compound produces bis(triphenylphosphine)dicarbonylnickel [4].

In the present work we have investigated the reductive carbonylation of nickel(II) compounds with the aim of developing a new, more convenient procedure to obtain bis(triphenylphosphine)dicarbonylnickel. This phosphinic nickel carbonyl derivative is an efficient catalyst for polymerization of unsaturated hydrocarbons [5]. It is usually prepared either by reacting the notoriously poisonous nickel tetracarbonyl with triphenylphosphine [6], or by the treatment of freshly reduced metallic nickel and triphenylphosphine with carbon monoxide under pressure [7].

We have found that the reaction of bistriphenylphosphinenickel dibromide with a tenfold excess of iron pentacarbonyl at room temperature and atmospheric pressure in the presence of triphenylphosphine leads to the formation of bis(triphenylphosphine)dicarbonylnickel with 90% yield. By chromatographic separation of the reaction products on alumina we also isolated the diphosphinic iron carbonyl derivative, $Fe(CO)_2(PPh_3)_2Br_2$:

$$Ni(PPh_3)_2Br_2 + Fe(CO)_5 + 2PPh_3 \longrightarrow Ni(CO)_2(PPh_3)_2 + Fe(CO)_2(PPh_3)_2Br_2 + [CO] \qquad (1)$$

Similarly, the action of iron pentacarbonyl on the mixture containing anhydrous $NiBr_2$ and triphenylphosphine produces $Ni(CO)_2(PPh_3)_2$ and $Fe(CO)_2(PPh_3)_2Br_2$:

$$NiBr_2 + Fe(CO)_5 + 4PPh_3 \longrightarrow Ni(CO)_2(PPh_3)_2 + Fe(CO)_2(PPh_3)_2Br_2 + [CO] \qquad (2)$$

In this case the yield of bis(triphenylphosphine)dicarbonylnickel amounts to 45%. In the reaction considered above iron pentacarbonyl acts as a donor of electrons and CO groups simultaneously. Probably the carbonyl ligand transfer proceeds via an unstable intermediate complex containing both nickel and iron.

In 1977 a paper appeared according to which the authors failed to prepare the same bimetallic complex by reacting $Ni(PPh_3)_2X_2$ with $[Fe(CO)_4]^{2-}$ [8]. However, they succeeded in obtaining the compound (NO) $(PPh_3)Ni{-}Fe(CO)_3(NO)$ containing nitric oxide as one of the ligands.

Experimental

Bis(triphenylphosphine)dicarbonylnickel

4 ml (30 mmol) of $Fe(CO)_5$ was added to a solution of 2.22 g (3 mmol) of $Ni(PPh_3)_2Br_2$ and 0.78 g (3 mmol) of PPh_3 in 30 ml THF. The reaction mixture was stirred at 22 °C for 18–20 h, then evaporated to dryness and the residue chromatographed on an alumina column (2 × 20 cm). Elution with petroleum ether/benzene mixture (1:1) gave 1.72 g (90%) of $Ni(CO)_2(PPh_3)_2$, m.p. 208–210 °C, ν_{CO} 1955, 2010 cm^{-1} (hexane) [9]. Thereafter 0.90 g of $Fe(CO)_2(PPh_3)_2Br_2$ was eluted with benzene, ν_{CO} 1989, 2039 cm^{-1} (KBr) [10].

4 ml (30 mmol) of $Fe(CO)_5$ was added to a mixture of 0.66 g (3 mmol) of anhydrous $NiBr_2$ and 2.34 g (9 mmol) PPh_3 in 30 ml THF. Then the reaction mixture was treated as in the preceding experiment. 0.89 g (45%) of $Ni(CO)_2(PPH_3)_2$, m.p. 208–210 °C and 1.13 g of $Fe(CO)_2(PPH_3)_2Br_2$, ν_{CO} 1989, 2039 cm^{-1} (KBr), were obtained.

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