

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

A. N. NESMEYNOV, L. S. ISAEVA and L. N. MOROZOVA

Institute of Organo-Element Compounds, Academy of Sciences, Moscow, USSR

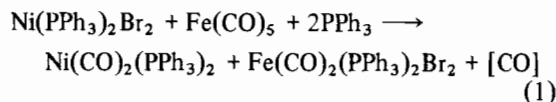
Received May 4, 1978

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 $\text{Fe}(\text{CO})_5$ were exploited for the synthesis of cobalt and rhodium carbonyls [3].

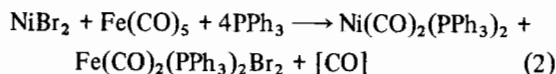
While studying the reactivity of ethyl(acetylacetonato) (triphenylphosphine)nickel, we showed quite recently that the action of iron carbonyl derivatives, such as $\text{NaFe}(\text{CO})_2\text{Cp}$ and $\text{Fe}(\text{CO})_5$, on this compound produces bis(triphenylphosphine)dicarbonylnickel [4].

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, $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{Br}_2$:



Similarly, the action of iron pentacarbonyl on the mixture containing anhydrous NiBr_2 and triphenylphosphine produces $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ and $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{Br}_2$:



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 $\text{Ni}(\text{PPh}_3)_2\text{X}_2$ with $[\text{Fe}(\text{CO})_4]^{2-}$ [8]. However, they succeeded in obtaining the compound $(\text{NO})(\text{PPh}_3)\text{Ni}-\text{Fe}(\text{CO})_3(\text{NO})$ containing nitric oxide as one of the ligands.

Experimental

Bis(triphenylphosphine)dicarbonylnickel

4 ml (30 mmol) of $\text{Fe}(\text{CO})_5$ was added to a solution of 2.22 g (3 mmol) of $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ 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 $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$, m.p. 208–210 °C, ν_{CO} 1955, 2010 cm^{-1} (hexane) [9]. Thereafter 0.90 g of $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{Br}_2$ was eluted with benzene, ν_{CO} 1989, 2039 cm^{-1} (KBr) [10].

4 ml (30 mmol) of $\text{Fe}(\text{CO})_5$ 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 $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$, m.p. 208–210 °C and 1.13 g of $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{Br}_2$, ν_{CO} 1989, 2039 cm^{-1} (KBr), were obtained.

References

- 1 R. A. Sokolik, in A. N. Nesmeyanov, K. A. Kocheshkov (Eds), "Methods of Organo-Element Chemistry. The Types of Organo-metallic Compounds of Transition Metals", v.1, Nauka, Moscow, (1975) p.35.
- 2 A. N. Nesmeyanov, K. N. Anisimov, E. P. Mikheev, V. L. Volkov, Z. P. Valueva, *Zh. Neorg. Khim.*, **4**, 249 (1959), *ibid.*, **4**, 503 (1959).
- 3 B. L. Booth, M. J. Else, R. Fields, H. Goldwhite, R. N. Haszeldine, *J. Organomet. Chem.*, **14**, 417 (1968).
- 4 A. N. Nesmeyanov, L. S. Isaeva, L. N. Lorens, *Dokl. Akad. Nauk SSSR*, **229**, 634 (1976).
- 5 L. S. Meriwether, E. C. Colthup *et al.*, *J. Org. Chem.*, **26**, 5155, (1961); *ibid.*, **27**, 3930 (1962).
- 6 W. Reppe, W. J. Sweckendiek, *Ann.*, **560**, 104 (1948); J. D. Rose, F. S. Statham, *J. Chem. Soc.*, 69 (1950).
- 7 K. Yamamoto, *Bull. Chem. Soc. Japan*, **27**, 491 (1954).
- 8 P. Braunstein, J. Dehand, B. Munchenbach, *J. Organometal. Chem.*, **124**, 71 (1977).
- 9 M. Bigorgne, A. Zelwer, *Bull. Soc. Chim. Fr.*, 1986 (1960).
- 10 I. A. Cohen, F. Basolo, *J. Inorg. Nucl. Chem.*, **28**, 511 (1966).