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Improved Synthesis of Mononuclear Triphenylphosphine and Carbon Monoxide Complexes of Zerovalent Nickel, Palladium and Platinum, and of Bis(Triphenylphosphine)ethylenenickel(0)

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The synthesis of zerovalent derivatives of nickel, palladium and platinum has received considerable attention in recent years, mainly due to these elements' reactivity and catalytic properties in many reactions, such as oligomerization, polymerization and carbonylation reactions of unsaturated organic compounds [1].

The zerovalent derivatives of these metals are usually prepared by reduction of their salts by strong reducing agents such as sodium borohydride and aluminium alkyls or by hydrazine in presence of ligands [1]; however, some of these compounds can be obtained only through cumbersome and time-consuming techniques involving poisonous or dangerous substances, like nickel tetracarbonyl or the aluminium alkyls, or not easily accessible starting compounds.

Moreover, no general method of synthesis of compounds of formula $ML_n(PPh_3)_2$ (M = Ni, Pd, Pt; L = CO, PR_3, olefin; n = 1, 2) has been described; thus, for instance, while $Ni(PPh_3)_3$ and $Pt(PPh_3)_3$ can be obtained by several methods, the corresponding palladium compound has been prepared in moderate yields only by action of nucleophiles on the cationic π-allyl-complexes of palladium [2].

We have found that the $MCl_2(PPh_3)_2$ complexes, obtained *in situ* by reaction of nickel, palladium or platinum chloride with the stoichiometric amount of triphenylphosphine in THF, can be easily reduced with zinc dust in presence of the ligand L (namely carbon monoxide or tertiary phosphine or olefin) to give, under very mild conditions and in good yields, the compounds of formula $ML_n(PPh_3)_2$:

$$MCl_2 + 2PPh_3 + nL = ML_n(PPh_3)_2 + ZnCl_2$$

This method, which has been previously described only for the preparation of the toluene-solvated $Ni(PPh_3)_3$ [3], is more rapid and simple than the other method described in the literature and generally gives better yields.

The method described here is particularly useful for the synthesis of pure $Ni(CO)_2(PPh_3)_2$, $Ni(C_2H_4)(PPh_3)_2$, $Pd(PPh_3)_3$ and $Pt(PPh_3)_3$. However, while bis(triphenylphosphine)ethylenenickel is obtained in very good yields, the corresponding palladium and platinum complexes cannot be obtained by this method. The reason why these latter metals behave differently from the nickel resides in the different reactivity of $Ni(PPh_3)_2$ on one side, and of $Pd(PPh_3)_2$ and $Pt(PPh_3)_2$ on the other, towards a Lewis acid such as $ZnCl_2$: in fact, we have found that $Pt(PPh_3)_2$, prepared from *trans*-$PtHCl(PPh_3)_2$ and butyl lithium [4], reacts easily with ethylene in ethanol in absence, but not in presence, of $ZnCl_2$.

Experimental

Bis(triphenylphosphine)dicarbonylnickel

a) 0.100 g (1.53 mmol) of zinc dust was added to a suspension of 0.700 g (1.07 mmol) of $NiCl_2(PPh_3)$ in 10 ml THF and the mixture was stirred at room temperature under carbon monoxide. After one hour the pale yellow solution obtained was filtered and 10 ml of a 50% mixture of ethanol–water added to the filtrate. The white crystals precipitated were washed with the ethanol–water mixture and dried under vacuum: 0.57 g (83%), ν_{CO} 1932, 1998 cm^{-1} (nujol). *Anal.* Found: P, 9.4; Ni, 9.1. Calcd. for $Ni(CO)_2(PPh_3)_2$: P, 9.7; Ni 9.2%.

b) A mixture of 0.259 g (2 mmol) of anhydrous nickel chloride, 1.047 g (4 mmol) of triphenylphosphine and 0.196 g (3 mmol) of zinc dust in 10 ml THF was stirred at room temperature under carbon monoxide for 3 hours. Then the filtered solution was treated as above. 0.90 g (70%) of $Ni(CO)_2(PPh_3)_2$ was obtained.

Bis(triphenylphosphine)ethylenenickel

a) A mixture of 1.00 g (1.53 mmol) of $NiCl_2(PPh_3)_2$ and 0.150 g (2.3 mmol) of zinc dust in 10 ml THF was stirred at room temperature under ethylene for one hour. The yellow solution was filtered under nitrogen, the filtrate was partially evaporated under vacuum, added to 20 ml of 95% ethanol and kept under ethylene overnight. The yellow crystals precipitated were washed with ethanol and dried under vacuum: 0.75 g (80%) of $Ni(C_2H_4)(PPh_3)_2$, identified by elemental analysis and by comparison of its I.R. spectrum with that of an authentic sample [5], was obtained. *Anal.* Found: P, 10.3; Ni, 9.6. Calcd. for $Ni(C_2H_4(PPh_3)_2$: P, 10.1; Ni, 9.6%.

b) A mixture of 0.259 g (2 mmol) of anhydrous nickel chloride, 1.047 g (4 mmol) of triphenylphosphine and 0.196 g (3 mmol) of zinc dust in 10 ml THF was stirred at room temperature under ethylene

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for 3 hours. Then the filtered solution was treated as above. 0.91 g (71%) of $Ni(C_2H_4)(PPh_3)_2$ was obtained.

Tris(triphenylphosphine)palladium

A mixture of 0.090 g (0.51 mmol) of $PdCl_2$ and 0.400 g (1.53 mmol) of triphenylphosphine in 5 ml THF plus 5 ml CH_3CN was refluxed for one hour under nitrogen. 0.080 g of zinc dust was then added and the mixture was refluxed for 5 hours. Filtration of the hot solution gave, after standing at room temperature, yellow crystals, which were washed with ethanol and dried under vacuum: 0.35 g (77%) of $Pd(PPh_3)_3$ was obtained. *Anal.* Found: P, 10.4; Pd, 11.7. Calcd. for $Pd(PPh_3)_3$: P, 10.4; Pd, 11.9%. All operations were carried out under a nitrogen atmosphere.

Tris(triphenylphosphine)platinum

A mixture of 0.067 g (0.253 mmol) of $PtCl_2$ and 0.200 g (0.762 mmol) of triphenylphosphine in 5 ml THF was refluxed for one hour under nitrogen. 0.040 g of zinc dust was then added and the mixture refluxed for 3 hours. The solution was filtered, the filtrate evaporated to dryness under vacuum and the residue washed with ethanol: 0.16 g (65%) of $Pt(PPh_3)_3$ was obtained. *Anal.* Found: P, 9.4; Pt, 20.0. Calcd. for $Pt(PPh_3)_3$: P, 9.5; Pt, 19.9%. All operations were carried out under a nitrogen atmosphere.

Bis(triphenylphosphine)dicarbonylplatinum

A mixture of 0.079 g (0.297 mmol) of $PtCl_2$ and 0.156 g (0.595 mmol) of triphenylphosphine in 5 ml THF was refluxed for one hour under nitrogen. 0.030 g of zinc dust was then added and the mixture was kept under a carbon monoxide atmosphere and under stirring at room temperature till complete dissolution of the white precipitate of $PtCl_2(PPh_3)_2$ (about six hours). The solution was then filtered from the zinc in excess and the filtrate, added with 15 ml of 95% ethanol, was kept under carbon monoxide for three hours at -10 °C. The pale cream crystals precipitated were washed with ethanol and dried: 0.17 g (74%) of $Pt(CO)_2(PPh_3)_2$, identified by elemental analysis and by comparison of its I.R. spectrum with that of an authentic sample [6], was obtained. *Anal.* Found: P, 8.0; Pt, 25.0. Calcd. for $Pt(CO)_2(PPh_3)_2$: P, 8.0; Pt, 25.1%.

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