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A one-pot method for the preparation of $(R_3P)_2Ni^0L$ complexes [†]

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Abstract

A new, general, one-pot method for the preparation of $(R_3P)_2Ni^0L$ complexes is described. The method is based on the reductive elimination of $(R_3P)_2NiMe_2$ [which is prepared *in situ* from the corresponding $(R_3P)_2NiCl_2$ and MeLi] in the presence of a free ligand. The elimination can be induced thermally (at r.t. or higher) or photochemically. A comparison between the thermal and photochemical methods was made with several phosphine-nickel complexes.

1. Introduction

Ni^0 complexes are important compounds in academic research and in industry [1]. These complexes are usually very sensitive to air, and sometimes also to heat, and so when used in catalysis they are usually prepared *in situ* [2]. This, however, means that the "catalysts" are undefined, and in some cases it is unclear which of the species present in the reaction mixture is the reactant (or catalyst), although there is no doubt that the desired products are obtained [3*]. It is desirable in some cases to work with clean and defined catalysts prepared separately, especially in cases in which the reaction (and not only the product) is of interest.

When Ni^0 complexes are needed in pure form there are two main routes that can be used for their preparation. One is from Ni^0 complexes, by replacement of labile ligand(s). This route usually starts from the reaction of Ni(CDT) with ethene to yield tris(ethene)nickel, which is then substituted (stepwise) by the relevant ligand to yield the desired complex. Ni(CDT) is prepared by the reduction of $Ni(acac)_2$ in the presence of CDT [4,5] and so this route requires several synthetic steps, involving air sensitive (sometimes pyrophoric) complexes, and is expensive [6a]. There are numerous methods of preparing $(R_3P)_2Ni$(ethene) in a one-pot procedure, but these apply only to a limited range of phosphines and sometimes give unsatisfactory yields [7]. However, even when these methods can be used, they involve two steps and the need to manipulate air sensitive compounds. Thus, it is desirable to have a one-pot procedure that gives the target complexes in high yields.

The second route to Ni^0 complexes starts from Ni^{II} [or Ni^I] complexes (which are usually much less sensitive than the corresponding Ni^0 complexes), which are subjected to reduction or reductive elimination in the presence of the desired ligand(s).

2. Results and discussion

In the course of our investigations of $(R_3P)_2Ni$-arene complexes [8] we needed a general method for the preparation of these compounds. The reductive olefination route that works well for unsubstituted anthracenes [*e.g.* $(R_3P)_2NiCl_2$ and magnesium-anthracene$(THF)_3$ as a (formally doubly) negatively charged ligand] [8a] failed for all the substituted arenes because the relevant arene-magnesium complex was not formed. Thus, attempts to prepare several substituted-anthracenes magnesium complexes either by direct reaction

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[*] Reference number with an asterisk indicates a note in the list of references.

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[9] or by exchange with magnesium-anthracene$(THF)_3$ [10] failed. Nevertheless, we attempted to find a method based on Ni^{II} complexes (preferably $NiCl_2$ complexes, because of their low cost) [6], which can be handled much more easily than Ni^0 complexes. Our initial attempts in this direction involved the reduction of $(R_3P)_2NiCl_2$ by "traditional" reducing agents (Mg, Zn, K, Na/K and C_8K) in the presence of an arene as the ligand. Most of these experiments failed to give the respective $(R_3P)_2Ni$-arene complexes, except when unsubstituted anthracene was used; in this latter case the reactions yielded the desired complex (*i.e.*, $(R_3P)_2Ni$-anthracene) in varying yields (usually low, except when Mg was used) [11]. It became clear that this type of reaction could not provide the general synthetic route that we were looking for. Probably all these reduction reactions involve an electron transfer step, which destroys the ligand (unless it is the unsubstituted anthracene) or leads to other processes.

An alternative route which has been examined is based on reductive elimination. First we attempted to prepare the dihydride complex $(R_3P)_2NiH_2$ by the reduction of $(R_3P)_2NiCl_2$ with $LiAlH_4$ or DIBAL-H in the presence of the arene. The nickel dihydride was probably formed, but its reductive elimination was too fast and so the reactions yielded only "black nickel" and none of the desired product. The ligand was quantitatively recovered from these reactions, but no remaining $(R_3P)_2NiCl_2$ was observed. These results, however, suggested to us that this approach should work, provided that the appropriate R groups in the $(R_3P)_2NiR_2$ complexes could be found (clearly R could not be H), so that the complex would be stable enough at the preparation step but undergo elimination of RR where required.

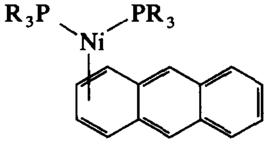
We have found the appropriate type of complex, namely $(R_3P)_2NiMe_2$. The preparation of $(R_3P)_2NiL$ involves reductive elimination from $(R_3P)_2NiMe_2$ in the presence of free ligand and the overall process is summarized in eqn. (1). The preparation of **1** is straightforward [8a] and involves refluxing anhydrous $NiCl_2$ with 2.2 equivalents of the desired phosphine in THF. A solution of **1** in THF or ether is treated with two equivalents of **2** at −78°C to yield **3** quantitatively [12]. This solution is transferred by a cannula to a cold suspension (or solution) of the desired ligand in the reaction solvent. It is not necessary to isolate **3**, since its formation is quantitative, and the only by-product present in the reaction mixture is LiCl, which is inert. (In contrast, the formation of an $(R_3P)_2Ni(alkyl)_2$ from a Ni^{II} complex and $Al(alkyl)_3$, rather than MeLi [1a] gives as a by-product a strong Lewis acid that might catalyze or inhibit the reaction.) Although the preparation described formally involves two-steps, it can be carried out in a one-pot fashion without the need to isolate the intermediates.

$$\underset{\mathbf{1}}{(R_3P)_2NiCl_2} + \underset{\mathbf{2}}{2\,MeLi} \longrightarrow \underset{\mathbf{3}}{(R_3P)_2NiMe_2} \xrightarrow[\Delta \text{ or } h\nu]{L} \underset{\mathbf{4}}{(R_3P)_2NiL} \quad (1)$$

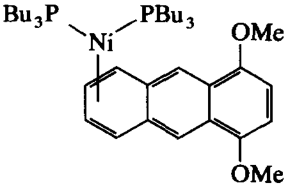
The last step (*i.e.*, **3** → **4**) can be carried out thermally or photochemically. If the reaction mixture is allowed to warm to 25–50°C and stirred at such a temperature for 24–96 h (depending on the ligand), the product can be isolated by removal of the THF, addition of pentane or toluene, filtration, and crystallization.

Alternatively, irradiation of the reaction mixture (*i.e.*, the solution of **3** with the ligand) with a slide projector lamp [13] for several hours yields the required product, which can be isolated by work-up identical with that described for the thermal procedure. The photochemical procedure can be carried out at low temperatures (some reactions were carried out at −85°C), and thus has the advantage of allowing preparation of thermally unstable $(R_3P)_2Ni^0L$ complexes.

A variety of $(R_3P)NiL$ complexes has been prepared by the new method (thermal and photochemical), and in all the cases tried it proved satisfactory.



5 R = Et, Bu, Ph



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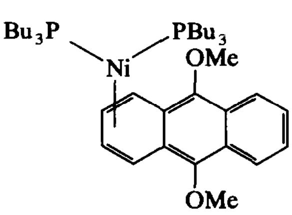

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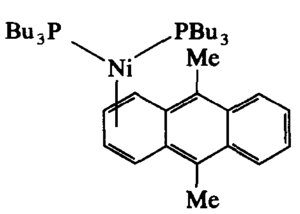

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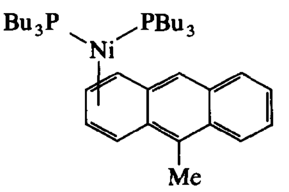

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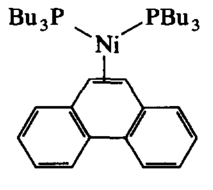

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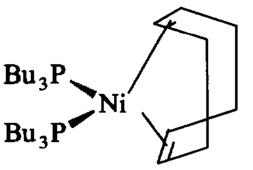

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$(R_3P)_3Ni$

12 R = Et, Bu

In order to compare the thermal and the photochemical routes, some compounds were made by both methods. The reaction was stopped before completion, and the degree of conversion of the $(R_3P)_2NiMe_2$ to the desired complexes was measured. The results are summarized in Table 1, and suggest that the thermal and the photochemical routes in general give comparable yields. However, the bridged derivative (Table 1, entries 7,8) does not yield any of the corresponding Ni^0-anthracene complex, and the (depe)NiMe$_2$ remains intact. A possible explanation for this is that a T-shaped intermediate (or transition state) is involved in the reductive elimination of the methyls. We are currently developing a NiCl$_2$-based method for the preparation of similar complexes with bridged phosphine.

In addition to the simplicity and low cost of the new method described here, the photochemical route has the advantage of opening up an opportunity to learn more about Ni^0 chemistry. For example, $(R_3P)_2Ni^0$ inserts into strained organic unsaturated rings to form the corresponding nickelacycle [14]. It has been postulated [15] that the first interaction of the $(R_3P)_2Ni$ moiety is with the π-system of the substrate. Since the photochemical synthesis can be carried out at very low temperatures there is a possibility of studying this type of intermediate.

TABLE 1. Reactions of $(R_3P)_2NiMe_2$ with anthracene [a]

	Phosphine	T/P [b]	Time (min)	% convergence [c]
1	Bu$_3$P	T	45	40.5
2	Bu$_3$P	P	45 [d]	37.8
3	Ph$_3$P [e]	T	180	49.7
4	Ph$_3$P [e]	P	180 [f]	74.5
5	Et$_3$P	T	150	24.9
6	Et$_3$P	P	150 [g]	13.9 [h]
7	depe [i]	T	300 [j]	N.R.
8	depe [i]	P	300 [k]	N.R.

[a] A solution of $(R_3P)_2NiMe_2$ and the relevant ligand was prepared at −78°C (see Experimental section). Half of the solution was transferred by cannula to the double-jacketed Schlenk flask in which the photochemical reaction was carried out. The remaining solution was heated to the indicated temperature. [b] Thermal (r.t.) or photochemical. [c] Determined by ^{1}H NMR at *ca.* −30°C, %convergence = 100×[complex]/{[complex]+[free anthracene]}. [d] At −45°C. [e] In diethylether. [f] At −50°C. [g] At −40°C. [h] At low temperature the $(Et_3P)_2NiMe_2$ solution is light yellow, and thus its absorbance is small and the photochemical reaction is less effective. [i] 1,2-bis(diethylphosphino)ethane. [j] At room temperature, 40°C and 60°C. [k] At −60°C and at room temperature.

3. Experimental section

All manipulations were carried out under Ar by Schlenk techniques. The THF, ether and pentane were freshly distilled from potassium-benzophenone ketyl, Na/K, or CaH$_2$, respectively, prior to use.

3.1. Preparation of 11

The preparation of **11** [1a] is described as a typical thermal procedure. MeLi (4.8 ml of 1.6 M solution in Et$_2$O, 7.7 mmol) was added to a stirred cold (−78°C) solution of $(Bu_3P)_2NiCl_2$ (2.238 g, 4.19 mmol) in THF (10 ml). The solution was stirred for 0.5 h during which the colour changed from purple to brown. This solution was transferred by cannula into a solution of 1,5-cyclooctadiene (0.47 ml, 0.41 g, 3.83 mmol) in THF (10 ml) at −78°C, and the mixture was allowed to warm to room temperature and stirred for 3 days. The volatiles were removed (*in vacuo*), pentane was added, and the slurry filtered. the precipitate was washed with pentane until the washings were colourless (in total about 25 ml of pentane was used). The pentane solution was allowed to stand overnight at −85°C, and the mother liquor was removed by cannula from the yellow crystals which had formed. The crystals were dried *in vacuo*, to give 2.092 g (3.66 mmol, 95% yield) of **11** [1a].

3.2. Preparation of 7

This is a typical photochemical preparation. The synthesis of $(Bu_3P)_2NiMe_2$ was identical to that described above for the preparation of 11. Quantities: $(Bu_3P)_2NiCl_2$; 1.49 g, 2.79 mmol. THF; 4 ml. MeLi; 3.9 ml of 1.5 M ether solution, 5.8 mmol. The solution of $(Bu_3P)_2NiMe_2$ was transferred by cannula into a suspension of 9,10-dimethoxyanthracene (0.46 g, 1.93 mmol) in THF (7 ml) at −85°C in a double jacketed Schlenk flask (inner jacket with two inlets for the circulation of the coolant, outer vacuum jacket to prevent icing). The stirred suspension was irradiated for 2.5 h, during which the colour changed from yellowish brown to red. The ^{1}H and ^{31}P NMR of the crude mixture revealed that no free ligand remained. During work-up (similar to that in the case of **11**) about 25% of the complex decomposed and the crystals obtained (after the pentane solution was allowed to stand for 2 days at −85°C) consisted of 75% of **7** and 25% of 9,10-dimethoxyanthracene. No attempt was made to isolate the pure complex since a pure sample was obtained from the thermal preparation) [11].

3.3. Selected spectral data for 5–11

5; identical with literature data [8a]. **6**: ^{1}H (−52°C); 7.80 [s, 2H, H(9,10)], 6.43, [s, 2H, H(2,3)], 5.37 [m, 2H, H(6,7)], 5.27 [m, 2H, H(5,8)], 3.86 (s, 6H, O*Me*), 0.7–1.7 (m, 54H, P*Bu*$_3$). ^{31}P{^{1}H} (−52°C): 10.6 (d), 2.6 (d), *J*(P–P) = 54.7. ^{13}C{^{1}H} (−51°C) 137.1, 115.9, 100.0, 97.2 (d, *J*(P–C) = 25.2), 90.6, 86.4 (d, *J*(P,C) = 9.3), 55.2, 14.7–28.0 [P–$(CH_2)_3CH_3$, partly buried under the solvent resonances] [11]. **7**: ^{1}H (−52°C); 7.86 [AA′BB′, 2H, H(5,8)], 7.22 [AA′BB′, 2H, H(6,7)], 5.61 [m, 2H, H(1,4)], 5.30 [m, 2H, H(2,3)], 3.82 (s, 6H, O*Me*), 0.7–1.7 (m, 54H, P*Bu*$_3$). ^{31}P{^{1}H} (−52°C) 13.5 (d), 3.9 (d), *J*(P–P) = 50.7. ^{13}C{^{1}H} (−62°C) 144.9, 129.2, 125.8, 123.9, 121.7, 90.2 (br), 79.3 (br) 61.0, 14.7–27.8 [P–$(CH_2)_3CH_3$, partly buried under the solvent resonances] [11]. **8**: ^{1}H (r.t) 7.67 [m, 2H, H(5,8)], 7.01 [m, 2H, H(6,7)], 5.58 [m, 2H, H(1,4)], 5.19 [m, 2H, H(2,3)], 2.45 (s, 6H, 9,10 dimethyl), 1.25 and 0.81 [two multiplets, 54H, (P*Bu*$_3$)$_2$] [16]. **9**; (−23°C) ^{1}H; 7.82 [ps.d., 1H, H(8)], 7.52 [ps.d., 1H, H(5)], 7.37 [s, 1H, H(10)], 7.15 [m, 2H, H(6,7)], 6.20 (ps.d., 1H, H(1)], 5.95 [m, 1H, H(2)], 4.83 [m, 1H, H(4)], 4.68 [m, 1H, H(3)], 2.52 (s, 3H, 9-methyl), 1.43, 1.13 (m, 36H, $[P[(CH_2)_3CH_3]_3]_2$), 0.96, 0.82 (ps.t., 18H, $[P[(CH_2)_3CH_3]_3]_2$). ^{31}P{^{1}H}; 12.5 (d), 1.9 (d), *J*(P–P) = 51.6 Hz [15,17]. **10**; (r.t); ^{1}H; 7.87 [d, 2H, H(1,8)], 7.36 [d, 2H, H(2,7)], 6.98–7.06 [m, 4H, H(3,4,5,6)], 4.26 [s, 2H, H(9,10)], 1.47 (m, 36H, $[P[(CH_2)_3CH_3]_3]_2$, 0.90 (m, 18H, $[P[(CH_2)_3CH_3]_3]_2$). ^{31}P{^{1}H}; 8.2 (s) [18].

Acknowledgments

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