Journal of Organometallic Chemistry, 467 (1994) 231-234

Some remarks on the Pd^0/Cu^I-catalysed alkynylation reaction of tricarbonyl(η^6-chlorobenzene)chromium

Adam Gryff-Keller, Jan Prejzner, Joanna Szewczyk and Krzysztof Wiśniewski

Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa (Poland)

(Received November 20, 1993)

Abstract

Alkynylation of tricarbonyl(η^6-chlorobenzene)chromium (**I**) in the presence of tetrakistriphenylphosphinepalladium and cuprous iodide in triethylamine only gave good yields with the freshly prepared palladium catalyst. On prolonged standing, particularly in air, the catalyst (which still worked well in the analogous reaction with iodobenzene instead of **I**) gave low yields of tricarbonyl (η^6-diphenylacetylene)chromium (**2**) [or tricarbonyl(phenylethynyltrimethylsilane)chromium (**5**)] and generally promoted a side reaction resulting in the formation of tricarbonyl(η^6-benzene)chromium (**3**) and diphenylbutydiyne (**4**) [or bistrimethylsilylbutydiyne (**6**)]. The latter process became predominant as the ratio of Pd^0 to Cu^1 was decreased from 1:1 to 1:5.

Key words: Palladium; Copper; Chromium

1. Introduction

In the course of our NMR studies on tricarbonyl (η^6-arene)chromium complexes, samples of tricarbonyl(η^6-phenylethenyltrimethylsilane)chromium (**5**) and tricarbonyl(η^6-diphenylacetylene)chromium (**2**) were needed [1]. The first syntheses of complexes of this type reported in the literature, involving reactions of alkenylarenes with hexacarbonylchromium or its derivatives, resulted in low yields of the products [1,2]. A more promising approach to the synthesis of these compounds was based on the alkynylation of tricarbonyl(η^6-chlorobenzene)chromium (**1**) with terminal alkynes run in triethylamine in the presence of 5 mol% catalyst consisting of tetrakistriphenylphosphinepalladium(0), or bistriphosphinepalladium(II) chloride, and cuprous iodide used in a 1:1 ratio, yielding complexes **2** and **5** in good yield [3]. Our initial attempts to use this reaction for the preparation of **2** and **5** were not very successful, resulting in wide variations in both yield and variety of product. In particular, the phenylethynylation of **1** did not generally go to completion even with concentrations of the catalyst as high as 30 mol% and 50 mol% excess of phenylacetylene, but was usually accompanied by a side reaction which gave tricarbonyl(η^6-benzene)chromium (**3**) and 1,4-diphenylbutadiyne (**4**).

The Pd^0-catalysed alkynylation reactions of haloarenes are believed to proceed according to a generally accepted mechanism involving initial oxidative addition of the aryl halide to palladium(0), followed by the formation of an intermediate arylalkenylpalladium(II). Reductive elimination of the alkynylarene regenerates the Pd^0 species, thus maintaining the catalytic cycle [4–6]. The introduction of cuprous iodide as a cocatalyst allowed the use of a lower reaction temperature probably due to a catalytic cycle facilating the generation of alkenylide anions [3,7,8]. In the light of this mechanism it might be deemed that the alkynylation of iodobenzene or the alkynylation of **1** in the presence of a Pd^0/Cu^I catalyst are closely related reactions. However, we found that some batches of tetrakistriphenylphosphinepalladium which worked very well as a catalyst in the former reaction did not function at all or gave very poor results in the latter. The purpose of the work described in this paper was to attract the attention of the potential user of this procedure to some problems which may arise in running this reaction.

Correspondence to: Prof. A. Gryff-Keller.

0022-328X/94/$7.00
SSDI 0022-328X(93)24360-H

2. Results and discussion

In order to account for the observed discrepencies, we ran a series of tetrakistriphenylphosphinepalladium/cuprous iodide-catalysed alkynylation reactions using phenylacetylene and trimethylsilylacetylene as substrates. During the course of our investigations, we found that a distinct increase in yield was observed for the phenylethynylation reaction of **1** when the concentration of the Pd^0/Cu^I catalyst was increased to 30 mol% in contrast to the 5 mol% recommended [3]. Although there is no doubt, in the light of our work, that the proportion of the catalyst needed depends in the first place on its quality, it is likely to depend also on the nature of the alkyne substrate. For the sake of comparison, we ran a series of reactions (Table 1) using 1.5 equiv. of alkyne substrate and 0.3 equiv. of the palladium catalyst per mole of **1**.

The small scale of our experiments (50–100 mg) required that, unlike the original procedure [3], cuprous iodide and the acetylene derivative were injected as triethylamine solutions into a slurry of **1** and the Pd^0 catalyst. Once the reaction was complete and the solvent removed *in vacuo*, the resulting solid residue was extracted with a mixture of hexane and ether. The solid remaining after extraction consisted of the catalyst, triethylamine hydrochloride and, occasionally, some acetylene derivative as evidenced by a band at 2180 cm^{-1} in its IR spectrum. The soluble fractions consisted mainly of the chromium complexes **1**, **2** (or **5**) and occasionally **3** and **4** (or **6**), and small amounts of undefined aromatic material.

TABLE 1. Results of the phenylethynylation of tricarbonyl(η^6-chlorobenzene)chromium (**1**) in the presence of Pd(PPh$_3$)$_4$ and CuI [a]

Entry No.	CuI (equiv.)	Reaction time (h)	Molar ratio of chromium complexes (PhC≡C)$_2$ [g]			
			1	**2**	**3**	**4**
1 [b]	0.3	21	53	15	32	+
2 [c]	0.3	7	6	88	6	–
3 [c,f]	0.3	20	23	77	0	–
4 [d]	0.3	24	18	78	4	–
5 [d]	1.5	24	0	28	72	+
6 [e]	0.15	20	68	32	0	–

[a] Approximate molar ratio of **1**/phenylacetylene/Pd(PPh$_3$)$_4$ was 1:1.5:0.3.

[b] Catalyst, (PdPPh$_3$)$_4$, stored in a dessicator for 2 months.

[c] Catalyst freshly prepared.

[d] Catalyst freshly prepared (second batch).

[e] Catalyst (footnoted) stored in air for 1 week.

[f] 1 equiv. of deuterium oxide added.

[g] The presence of **4**, denoted by '+', detected on the basis of the corresponding signals in the ^{13}C NMR spectrum (CDCl$_3$): 74.0; 81.6; 128.5; 129.1; and 132.5 ppm.

This mixture, after removal of the solvents, was analysed without further purification by means of ^{1}H and ^{13}C NMR spectroscopy. The ratios of the chromium complexes **1**, **2** and **3** were determined on the basis of the relative intensities of their ^{13}C NMR carbonyl signals at δ 231.5, 232.1 and 232.8 ppm, respectively. This method was assumed to give a fair estimate of their relative amounts since the longitudinal relaxation times of the ^{13}C nuclei in carbonyl groups of different tricarbonyl(η^6-arene)chromium compounds do not differ to any great extent [9]. Additionally, the composition of the products could be supported by information derived from the ^{1}H NMR spectra and the regions of acetylenic and aromatic ring carbons in the ^{13}C NMR spectra.

All the reactions were run under argon, which was taken from a tank without further deoxygenation (oxygen content 10 ppm). The absence of any green decomposition products of the chromium complexes and high yields of products in some runs indicated that a sufficiently non-oxidative atmosphere had been preserved during these reactions.

Our initial highly irreproducible results for the phenylethynylation of **1** (see, for example, Table 1, entry 1) were undoubtedly due to some changes in the structure of the palladium catalyst on storage for prolonged periods of time. The nature of this change is unclear as no differences between particular batches of the catalyst could be spotted by means of their IR spectra taken over the 4000–600 cm^{-1} spectral region and the fact that their activity was preserved in the analogous reaction with iodobenzene instead of **1**. The only feature associated with some deactivation observed might be a colour change from bright yellow for the freshly prepared catalyst [10] to orange–red or brown for a stored sample. However, even when the freshly prepared catalyst was used, we found that the phenylethynylation of **1** was generally accompanied by the formation of small amounts of **3** and **4** (Table 1, entries 2 and 4). In contrast, trimethylsilylation of **1** carried out in the presence of the freshly prepared catalyst represented a 'clean' reaction which went to completion at 50°C within 2 h, without the formation of by-products **3** and **6** (Experimental details). Trimethylsilylethynylation of the tricarbonylchromium complexes of methyl 4-chlorobenzoate, 4-chloro-*N*,*N*-dimethylaniline, bromobenzene and fluorobenzene showed that the first of these complexes was more reactive than the others and that tricarbonyl(η^6-fluorobenzene)chromium did not react at all under these conditions. The first two complexes gave 4-trimethylsilylethynyl derivatives, indicating an *ipso*-type substitution reaction.

In an attempt to seek possible factors influencing the reaction discussed, we examined the phenylethynylation reaction to which 1 equiv. of deuterium oxide had been added. The formation of small amounts of **3** in the presence of methanol had already been found in related reaction systems [11]. The added deuterium oxide seemed to decrease the reactivity somewhat without essentially affecting the yield of **2**. However, somewhat surprisingly, this addition suppressed the side reaction as no **3** and **4** were observed in the crude product (Table 1, entry 3).

The formation of considerable amounts of **3** was always accompanied by the formation of significant quantities of **4** (or **6**) (Table 1, entries 1 and 5). This side reaction usually (but not always) occurred with the deactivated catalyst, but its occurrence seemed to depend not only on the state of the palladium catalyst but also on the ratio of an 'active' catalyst to cuprous iodide. The following experiments seem to support this suggestion:

1. The phenylethynylation of **1** in the presence of tetrakistriphenylphosphinepalladium stored in air for 1 week, and cuprous iodide used in a molar ratio of 2:1 instead of the usual 1:1, gave **2** in only one-third of the average yield but no **3** and **4** was observed in the product (Table 1, entry 6).
2. In contrast, the same reaction with the freshly prepared palladium catalyst, and cuprous iodide used in a molar ratio of 1:5, gave **3** as the main product (Table 1, entry 5).

When the reaction with PhC ≡ CD was run under conditions that favour hydrodechlorination, we observed the substitution of the chlorine atom by deuterium as evidenced by the characteristic 0.1 ppm upfield isotope shift of the *ortho* carbons of deuterated **3** [12]. In the reaction with tricarbonyl(η^6-chlorotoluene)chromium, deuterium appeared exclusively at position 4. Although the extent of deuteration of the two reactions was no greater than 50%, the result of the latter reaction points to an *ipso*-type substitution and excludes both participation of benzyne-type intermediates and accidental deuterium exchange under the reaction conditions.

The available data do not allow us to postulate the mechanism of the hydrodechlorination reaction. One may assume, however, that both the alkynylation and the hydrodechlorination reactions are catalysed by a Pd^0/Cu^I-catalytic system and both proceed via the same initial step(s). According to the above-mentioned generally accepted mechanism, the alkynylarylpalladium intermediate formed in a catalytic cycle may react under proper conditions with excess cuprous acetylide leading to the formation of the acetylenic dimer and the hydrodechlorinated complex as the main products (Table 1, entry 5). In order to account for the formation of these products, we could invoke a scheme rationalising the dimerisation of the nucleophile $[CpFe(CO)_2]^-$ and the hydrodechlorination of **1** accompanying substitution of the nucleophile by these reagents [13]. The similarity of both reactions is only apparent, however, because a palladium intermediate rather than **1** is likely to be involved in the formation of **3** in the title reaction. Moreover, it is the acetylenic substrate rather than **1** which seems to deliver the hydrogen needed for substitution of the chlorine.

It is worth remembering that the hydrodechlorination reaction has been reported as a side reaction in the complexation of chlorobenzene with hexacarbonylchromium in dibutyl ether [14]. We observed the same process during the preparation of tricarbonylchromium complexes of methyl 4-chlorobenzoate, 4-chloro-*N*,*N*-dimethylaniline and 4-chlorotoluene. Hydrodechlorination of η^6-chloroarenetricarbonylchromium complexes was performed by nucleophilic tele–metha substitution of the chlorine by a hydride ion using lithium triethylborohydride [15]. However, when account is taken of the completely different conditions employed in the two above-mentioned reactions and the hydrodechlorination reaction reported in this paper, there is no doubt that their mechanisms must be different.

3. Conclusions

We confirm that a chlorine atom in η^6-chloroarenetricarbonylchromium complexes can be substituted by an alkenyl moiety in the reaction with terminal alkynes in the presence of a tetrakistriphenylphosphinepalladium/cuprous iodide catalyst. It should be stressed, however, that in order to obtain good results only the freshly prepared palladium catalyst should be used in the reaction. The presence of water in the reaction medium seems to be a secondary factor. On the other hand, an excess of cuprous iodide relative to the palladium catalyst retards the alkynylation reaction and favours the side reaction involving substitution of chlorine by hydrogen and the formation of the dimer of the terminal alkyne. With a large excess of cuprous iodide, the hydrodechlorination process prevails. The preference for one direction or the other in the investigated reaction also probably depends on the properties of both reagents. However, this particular point demands further investigation.

Results of experiments are presented which show that both the alkynylation and hydrodechlorination reactions occur exclusively at a chlorine-bonded carbon atom of tricarbonyl(η^6-chloroarene)chromium complexes.

4. Experimental details

All reactions were run under argon using dry triethylamine as the solvent, the latter having been deoxygenated by distillation over benzophenone ketyl. Chloroform-*d* was deoxygenated by distillation in an argon atmosphere. The $CDCl_3$ solutions of the tricarbonylchromium complexes contained in 5-mm i.d. NMR tubes were additionally deoxygenated by repeated freeze–pump–thaw cycles before being sealed.

^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer under standard measurement conditions. Chemical shifts were referenced to signals of residual $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.0 ppm) in the ^1H and ^{13}C NMR spectra, respectively.

All η^6-chloroarenetricarbonylchromium complexes [16] and tetrakistriphenylphosphinepalladium [10] were prepared according to published procedures.

4.1. General procedure for the phenylethynylation of 1

To a stirred slurry of tricarbonyl(η^6-chlorobenzene)-chromium (0.2 mmol) and tetrakistriphenylphosphinepalladium (0.06 mmol) in triethylamine (1.5 ml) was added a colourless, homogeneous solution of cuprous iodide (0.06 mmol) in triethylamine (0.4 ml) by means of a syringe. After a few minutes a solution of phenylacetylene (0.3 mmol) in triethylamine (0.6 ml) was injected. The mixture was stirred for 7–24 h. After removal of the solvent *in vacuo*, the residue was extracted three times with a mixture of hexane and ether (4:1 v/v, 3 × 1.5 ml), being centrifuged each time with the resulting yellow solution transferred via a syringe to another weighed vessel. The third extract was practically colorless. After removal of the solvents *in vacuo* at room temperature, the crude product was weighed, dissolved in $CDCl_3$ and subjected to ^1H and ^{13}C NMR analysis. The solid residue was dried, weighed and its IR spectrum recorded.

4.2. Trimethylsilylethynylation of 1

The reaction of **1** (49.7 mg, 0.2 mmol) was undertaken using a procedure similar to that described above. After stirring at room temperature for 0.5 h, the mixture was warmed to 50°C and stirred at this temperature for 1.5 h. After removal of the solvents *in vacuo*, the crude product was obtained almost quantitatively (61.4 mg). The NMR spectra indicated that it consisted almost exclusively of **5**. ^1H NMR ($CDCl_3$) δ: 0.23 (s, 6H, $SiMe_3$); 5.20–5.45 (m, 5H, C_6H_5Cr) ppm. ^{13}C NMR ($CDCl_3$) δ: 0.30; 90.27; 90.53; 92.66; 94.75; 100.58 ppm [1].

Acknowledgment

We express our appreciation to the State Committee of Scientific Research for supporting this work via project PB185/2/91.

References

1 J. Szewczyk and A. Gryff-Keller, *J. Chem. Res.*, (1992) 25.
2 G.R. Knox, D.G. Leppard, P.L. Pauson and W.E. Watts, *J. Organomet. Chem.*, *34* (1972) 347.
3 D. Villemin and E. Schigeko, *J. Organomet. Chem.*, *293* (1985) 347.
4 H.A. Dieck and T.R. Heck, *J. Organomet. Chem.*, *93* (1975) 259.
5 L. Cassar, *J. Organomet. Chem.*, *93* (1975) 253.
6 W.B. Austin, N. Bilow, W.J. Kelleghan and K.S. Ylan, *J. Organomet. Chem.*, *46* (1981) 2280.
7 K. Songashira, Y. Tohoda and N. Hagihara, *Tetrahedron Lett.*, *50* (1975) 4467.
8 S. Takohashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, (1980) 627.
9 A. Gryff-Keller, P. Szczeciński and H. Kozieł, *Magn. Reson. Chem.*, *28* (1990) 25.
10 P.R. Culson, *Inorg. Synth.*, *13* (1972) 121.
11 V. Dufaud, J. Thivolle-Cazat, J.-M. Basset, R. Mathieu, J. Jaud and J. Waissermann, *Organometallics*, *10* (1991) 4005.
12 Y. Nakashima, A. Yoshino and K. Takahashi, *Bull. Chem. Soc. Jpn.*, *62* (1989) 1401.
13 J.A. Heppert, M.A. Morgenstern, D.M. Scherubel, F. Takusagawa and M.R. Shaker, *Organometallics*, *7* (1988) 1715.
14 M. Hudecek and S. Toma, *J. Organomet. Chem.*, *393* (1990) 115.
15 J.P. Djukic, P. Geysermans, F. Rose-Munch and E. Rose, *Tetrahedron Lett.*, *32* (1991) 6703.
16 M. Ghavshou and D.A. Widdowson, *J. Chem. Soc.*, *Perkin Trans. 1*, (1983) 3065.