Pergamon

Tetrahedron Letters 42 (2001) 5697–5700

TETRAHEDRON
LETTERS

Efficient silylformylation of alkynes catalyzed by rhodium complexes with P,N donor ligands

M. Aránzazu Alonso, Juan A. Casares, Pablo Espinet,* Elena Vallés and Katerina Soulantica

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain

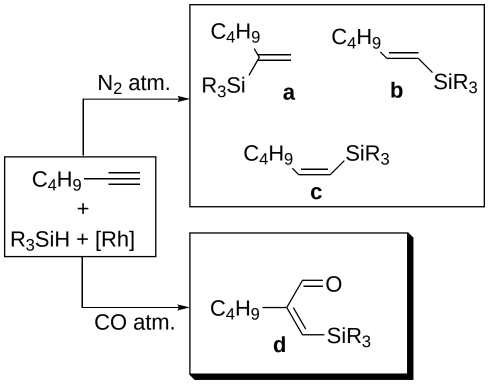
Received 30 May 2001; revised 19 June 2001; accepted 20 June 2001

Abstract—The complexes [Rh(diene)(L-L′)](BF_4), and [RhCl(CO)(L-L′)] (diene = COD 1,5-cyclooctadiene; L-L′ = P(bzN)Ph_2, P$(bzN)_2$Ph, P$(bzN)_3$, PePy, or PePy_2, bzN = 2-(dimethylaminomethyl)phenyl, PePy_n = P$(CH_2CH_2Py)_nPh_{3-n}$; Py = 2-pyridyl; n = 1,2) are poor catalysts for the hydrosilylation of 1-hexyne, but excellent catalysts for the silylformylation of 1-hexyne in tetrahydrofurane at atmospheric pressure and room temperature. © 2001 Elsevier Science Ltd. All rights reserved.

---

1. Introduction

The silylformylation of alkynes as a method of regio- and stereoselective synthesis of (*Z*)-3-silyl-2-alkenals in high yields was independently reported by the Ojima and Matsuda groups.[1,2] Recent advances include studies on the reaction mechanism,[3,4] the application of this reaction to the synthesis of 4-silylated 1-aza-1,3-butadienes, β-substituted (*E*)-crotylsilanes and pyrrolizidine alkaloids,[5] the extension of the reaction to silylcarbocyclization and silylcarbotricyclization of triynes[6] and silylhydroformylation reactions.[7] The catalysts usually employed are $Rh_4(CO)_{12}$,[2,3] or $Rh_2Co_2(CO)_{12}$.[2] The zwitterionic Rh(COD)($PhBPh_3$) has also been used,[8] but the best results under very mild conditions have been obtained with [$Rh_2(pfb)_4$] (pfb = perfluorobutyrate), while rhodium acetate is much less efficient.[9] Several catalysts for the reaction, as well as its use in the synthesis of optically active propionic acids, have been patented.[10]



Scheme 1.

Despite such significant progress, very little is known about the possible role of the ligands in determining the properties of the catalysts. Here we report the behavior of several neutral and cationic rhodium(I) complexes with P,N donor ligands as catalysts for the silylformylation of 1-hexyne. The P,N ligands have shown to be an interesting class of auxiliary ligands in different types of transition-metal catalyzed processes, including hydrosilylation and carbonylation.[11–13] The small energy differences between the situations with the N groups coordinated or uncoordinated can provide an accessible route for single reaction steps such as coordination of small molecules or reductive elimination.[12]

The selected catalysts are neutral and cationic rhodium(I) complexes of the type [RhCl(CO)(PePy)], $[Rh(PePy_n)(COD)]^+$, $[RhCl(CO)\{P(bzN)_n\}]$ and $[Rh\{P(bzN)_n\}(COD)]^+$ ($PePy_n = P(CH_2CH_2Py)_nPh_{3-n}$; Py = 2-pyridyl; n = 1,2; $P(bzN)_n = P(bzN)_nPh_{3-n}$; bzN = 2-[dimethylaminomethyl]phenyl); n = 1, 2, 3).[14–16] The complexes selected have two kinds of N donor groups: pyridyl in the PePy_n ligands, or amino in the P$(bzN)_n$ ligands. Both complexes form a non-planar six-membered metallacycle upon chelation.[14–17]

All the complexes employed turned out to be poor catalysts for the hydrosilylation of alkynes, giving mix-

---

Keywords: rhodium; P,N ligand; pyridylphosphine; silylformylation; carbonylation.

* Corresponding author. Tel.: +34/983423231; fax: +34/983423013; e-mail: espinet@qi.uva.es

PII: S0040-4039(01)01086-3

tures of the vinylsilanes **a**, **b** and **c** as shown in Scheme 1, which were identified by ^1H NMR and GC.[6] For instance, complex $[Rh(PePy_2)(COD)](BF_4)$ (1 mmol in dichloromethane) catalyzed the reaction of 43 mmol of Et_3SiH and 43 mmol of 1-hexyne in 72 h at rt to give a 35:30:35 **a**:**b**:**c** mixture.

More interesting was their behavior towards silylformylation: in THF as solvent, and under atmospheric pressure of CO, only the silyl-alkenal **d** was produced at room temperature.[†] By using only 0.1% of catalyst, yields higher than 95% in 24 h were obtained with four of the catalysts tested (Table 1).

All the tested compounds catalyzed the reaction. The cationic compounds exhibited lower catalytic activity than the neutral ones (entries 6–10 versus entries 1–5), while the number or the kind (Py or amine) of the nitrogen chelating atoms does not have a relevant effect on the catalytic activity. Neither hydrosilylation products nor the formation of other isomers of silylformylation were detected.

Table 1. Silylformylation of 1-hexyne with Et_3SiH[a] in THF to give **d**

Entry	Catalyst	% Conversion after		
		90 min	6 h	24 h
1	$[RhCl(CO)(PePy)]$ (**1**)	9	49	99
2	$[RhCl(CO)(PePy_2)]$ (**2**)	14	49	95
3	$[RhCl(CO)\{P(bzN)\}]$ (**3**)	29	60	100
4	$[RhCl(CO)\{P(bzN)_2\}]$ (**4**)	21	52	100
5	$[RhCl(CO)\{P(bzN)_3\}]$ (**5**)	19	40	91
6	$[Rh(PePy)(COD)](BF_4)$ (**6**)	0	5	11
7	$[Rh(PePy_2)(COD)](BF_4)$ (**7**)	9	14	53
8	$[Rh\{P(bzN)\}(COD)](BF_4)$ (**8**)	11	39	–
9	$[Rh\{P(bzN)_2\}(COD)](BF_4)$ (**9**)	11	31	44
10	$[Rh\{P(bzN)_3\}(COD)](BF_4)$ (**10**)	0	20	33
11	$[RhCl(CO)\{P(bzN)_2\}]$ (**4**)[b]	14	26	–

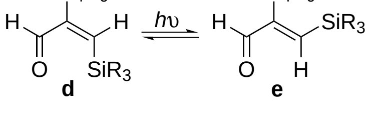
[a] 30 mL of a solution in THF containing 1-hexyne 592 μL (5.0 mmol) and Et_3SiH 806 μL (5.0 mmol). CO (atm.). Catalyst = 0.1% molar (5.0 μmol).

[b] The same general conditions but using $(EtO)_3SiH$ instead of Et_3SiH.

Table 2. Effect of the light and the air in the silylformylation reactions catalyzed by **3**

Reaction conditions[a]	% Conversion after 2.5 h	Products
Exclusion of air and light	24	**d**
Exclusion of light, non-deoxygenated Schlenk	36	**d**
Exclusion of air, exposed to sunlight.	59	**d** + **e** (85:15)

[a] 30 mL of a solution in THF containing 1-hexyne 592 μL (5.0 mmol) and Et_3SiH 806 μL (5.0 mmol). CO (atm.). Catalyst = 0.1% molar (5.0 μmol). $T = 0°C$ (ice bath).

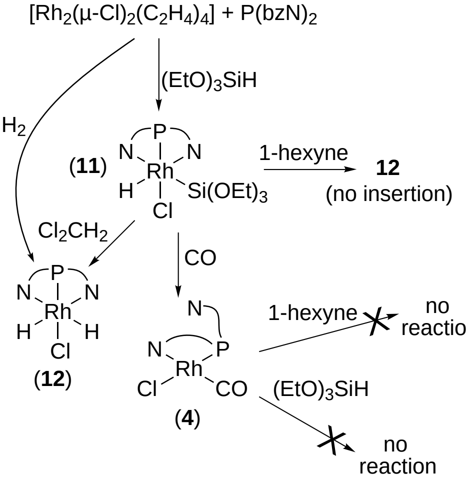


Scheme 2.

The effect of oxygen and of daylight was also tested (Table 2). The presence of oxygen slightly increases the yield after 2.5 h. The effect of light is particularly marked, doubling the yield in 2.5 h and leading to complete consumption of the reactants after 7 h. It must be noted, however, that in this experiment light produces a second effect, the isomerization of the product to the (*E*) isomer **e** (Scheme 2).[‡]

Since **e** has not been detected in the experiments carried out in the absence of light, its presence can be assigned to a photochemical isomerization rather than to a lack of selectivity of the reaction. In fact, **e** could be obtained in the absence of any rhodium catalyst, by irradiating **d** with a UV lamp.

We have also tried to obtain some mechanistic information about the rhodium species involved in the catalytic cycle. In the presence of P,N donor ligands $[Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4]$ reacts with a large excess of Et_3SiH, but the expected hydridotriethylsilylrhodium complexes were too unstable to be isolated. We could prepare and isolate $[RhClH\{(EtO)_3Si\}\{P(bzN)_2\}]$ (**11**) by reacting $[Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4]$ with the stoichiometric amount of $\{P(bzN)_2\}$ and $(EtO)_3SiH$ in THF (Scheme 3). The silyl derivative **11** reacts immediately with CO to give $[RhCl(CO)\{P(bzN)_2\}]$ (**4**) by reductive elimination of silane. Complex **4** does not react with silane or with



Scheme 3.

[†] The products were characterized by comparison of spectral data with the published values. See Refs. 2, 9b and 18.

[‡] The formation of (*E*) isomers in silylformylation reactions has been reported by Doyle et al., who also reported the *Z*-*E* isomerization of 3-silyl-2-alkenals derived from arylacetylenes catalyzed with iodine.[9] Panek and co-workers have reported the isomerization of the analogous 3-(dimethylphenylsilyl)-2-heptenal, also catalyzed by I_2, and established the greater thermodynamic stability of the *E* isomer based on theoretical calculations.[5b]

1-hexyne under nitrogen. Complex **11** does not react with a five-fold excess of 1-hexyne; rather than giving insertion of hexyne or reductive elimination of the silane, the only product formed is **12**, which was also prepared by an alternative route. So it seems that the multidentate ability of most of the P,N ligands saturates the Rh(III) centers and it is very unlikely that the catalytic cycle operates through Rhodium(III).

Thus, we favor an alternative route through Rh(I) metal centers which is one of the pathways proposed by Matsuda et al.[4] In fact, when the reactions catalyzed with **3**–**5** in THF were monitored by NMR under silylformylation conditions, only [RhCl(CO){P(bzN)$_n$}] complexes were detected in the ^{31}P NMR spectra. Hence, the starting complex seems to be also the resting state of the metal center in the catalytic cycle.

In summary, chlorocarbonyl Rhodium complexes with P,N ligands are excellent catalysts for the selective silylformylation of 1-hexyne under atmospheric pressure of CO in THF as solvent. The exposure of the reactants to the daylight increases the reaction rate, but leads to mixtures of isomers. Most of the rhodium remains during the reaction as a rhodium(I) carbonyl complex, a resting state from which the actual active species is formed in undetectable amount during the catalytic process.

2. Experimental

2.1. Synthesis of [RhClH{P(bzN)$_2$}{Si(OEt)$_3$}] (11)

To a solution of P(bzN)$_2$ (387 mg, 1.03 mmol) in THF (30 mL) under nitrogen, cooled to −78°C, was added [RhCl(C_2H_4)$_2$]$_2$ (200 mg, 0.510 mmol). The mixture was allowed to warm slowly until the rhodium compound dissolved. At that moment (EtO)$_3$SiH (195 μL, 1.03 mmol) was added. The solution was stirred for 5 h and filtered to remove some brown precipitate. After concentration of the clear solution and addition of *n*-hexane (12 mL) orange crystals were formed, which were filtered, washed with ether and vacuum dried. Yield 69% (482 mg). Anal. calcd for $C_{30}H_{45}ClN_2O_3PRhSi$: C, 53.06; H, 6.68; N, 4.12. Found: C, 52.93; H, 6.50; N 4.01. IR (Nujol mull, cm^{-1}): 2093 s, ν(Rh–H). ^{31}P NMR (C_6D_6, 293 K): δ 54.0 (d, $^1J_{\text{Rh-P}}=161.7$ Hz). ^{1}H NMR (C_6D_6, 293 K): δ −17.82 (t, $J_{\text{P-H}}=J_{\text{Rh-H}}=22$ Hz, 1H); δ 0.96 (t, $J=7.0$ Hz, 9H); δ 2.13 (broad 9H); δ 2.38 (broad, 4H); δ 3.29 (d, $J=13$ Hz, 2H); δ 3.65 (d, $J=13$ Hz, 2H); δ 3.94 (m, 6H); δ 6.41 (broad 1H); δ 6.53 (t, 1H); δ 6.66 (m, 2H); δ 6.85 (m, 6H); δ 7.03 (m, 1H); δ 7.81 (broad 2H). ^{1}H NMR (CD_2Cl_2, 205 K): δ −17.76 (t, $J_{\text{P-H}}=J_{\text{Rh-H}}=21$ Hz); δ 0.65 (t, 9H); δ 1.9 (s, 3H); δ 2.17 (s, 3H); δ 2.29 (s, 3H); δ 2.67 (s, 3H); δ 2.70 (s, 1H); δ 2.83 (d, 1H); δ 3.45 (m, 6H); δ 3.46 (m, 1H); δ 3.70 (d, 1H); δ 6.91 (t, 1H); δ 6.97 (m, 1H); δ 7.10 (m, 3H); δ 7.17 (m, 2H); δ 7.24 (m, 3H); δ 7.36 (t, 2H); δ 8.14 (q, 1H).

2.2. Synthesis of [RhClH$_2${P(bzN)$_2$}] (12)

To a solution of P(bzN)$_2$ (0.146 g, 0.387 mmol) in THF (15 mL) under nitrogen, cooled to −78°C, was added [RhCl(C_2H_4)$_2$]$_2$ (75.0 mg, 0.193 mmol). The mixture was allowed to warm slowly until the rhodium compound dissolved. At that moment the solution was saturated with hydrogen and stirred for 16 h more. The resulting brown solution was filtered and concentrated to 5 mL. After addition of *n*-hexane (5 mL) the compound precipitated as a yellow solid, which was filtered, washed with hexane and vacuum dried. The compound slowly decomposes at room temperature, and must be stored under inert atmosphere. Yield 74% (147 mg). Anal. calcd for $C_{24}H_{31}ClN_2PRh$: C, 55.77; H, 6.05; N, 5.42. Found: C, 55.88; H, 6.39; N 5.33. IR (Nujol mull, cm^{-1}): 2028, 2056 s, ν(Rh—H). ^{31}P NMR (CD_2Cl_2, 213 K): 53.21 (d, $^1J_{\text{Rh-P}}=159$ Hz). ^{1}H NMR (CD_2Cl_2, 213 K): δ −19.45 (td, 1 H, $^2J_{\text{H-H}}=10$ Hz, $^2J_{\text{P-H}}=22$ Hz, $^1J_{\text{Rh-H}}=32$ Hz); δ −20.08 (t.d., 1 H, $^2J_{\text{H-H}}=10$ Hz, $^2J_{\text{H-P}}=22$ Hz, $^1J_{\text{Rh-H}}=32$ Hz); δ 2.15 (s, 3H); δ 2.17 (s, 3H); δ 2.53 (s, 3H); δ 2.78 (s, 3H); δ 3.01 (d, $J=12.2$ Hz, 1H); δ 3.12 (d, $J=11.8$ Hz, 1H); δ 3.52 (d, $J=12.2$ Hz, 1H); δ 3.96 (d, $J=11.8$ Hz, 1H); δ 6.47 (m, 1H); δ 6.87 (m, 2H); δ 7.21–7.87 (m, 9H); δ 8.11 (m, 1H).

2.3. General procedure for the silylformylation of 1-hexyne

A stock solution 0.16 M in 1-hexyne, 0.16 M in triethylsilane and 0.08 M in *n*-decane was prepared in 480 mL of freshly distilled and deoxygenated tetrahydrofurane. The solution was saturated with CO at atmospheric pressure and stored at room temperature protected from the light. In each catalytic experiment a 30 mL aliquot of the stock solution was placed in a 100 mL Schlenk tube containing a magnetic bar, under CO, and protected from light. 5 μmol of the catalyst was added to obtain solutions 1.6×10^{-4} M in the rhodium complex. A balloon containing CO was connected to the gas inlet of the Schlenk and the solution was stirred during the reaction. The course of the reaction was followed by GC. When the reaction was finished, the products **d** and **e** were purified by evaporation of the volatiles followed by liquid chromatography on silica gel using *n*-hexane/AcOEt (90/10) as eluent.

Acknowledgements

We thank Professor M. A. Esteruelas for helpful discussions. Financial support by the Dirección General de Enseñanza Superior (Project No. PB96-0363) and the Junta de Castilla y León (Projects No. VA80-99 and No.VA120-01).

References

1. Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38.

2. (a) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332–2333; (b) Matsuda, I.; Ogiso, A.; Sato, S. *J. Am. Chem. Soc.* **1990**, *112*, 6120–6121.
3. Ojima, I.; Li, Z.; Donovan, R. J.; Ingallina, P. *Inorg. Chim. Acta* **1998**, *270*, 279–284.
4. Matsuda, I.; Fukuta, I.; Tsuchihashi, T.; Nagashima, H.; Itoh, K. *Organometallics* **1997**, *16*, 4327–4345.
5. (a) Bärfacker, L.; Hollmann, C.; Eilbracht, P. *Tetrahedron* **1998**, *54*, 4493–4506; (b) Jain, N. F.; Cirillo, P. F.; Schaus, J. V.; Panek, J. S. *Tetrahedron Lett.* **1995**, *36*, 8723–8726; (c) Eguchi, M.; Zeng, Q.; Korda, A.; Ojima, I. *Tetrahedron Lett.* **1993**, *34*, 915–918.
6. (a) Ojima, I.; Vu, A. T.; McCullagh, J. V.; Kinoshita, A. *J. Am. Chem. Soc.* **1999**, *121*, 3230–3231; (b) Ojima, I.; Zhu, J.; Vidal, E. S.; Kass, D. F. *J. Am. Chem. Soc.* **1998**, *120*, 6690–6697 and references cited therein.
7. Zhou, J. Q.; Alper, H. *Organometallics* **1994**, *13*, 1586–1591.
8. Monteil, F.; Matsuda, I.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4419–4420.
9. (a) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1993**, *12*, 11–12; (b) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1994**, *13*, 1081–1088.
10. (a) Doyle, M. P.; Shanklin, M. S., US Patent 5,302,737; (b) Krafft, T. E.; Rich, J. D.; Burnell, T. D. US Patent 5,124,468; (c) Tafesh, A. M.; Kotha, S.; Davenport, K. G. US Patent 5,223,640.
11. Espinet, P.; Soulantica, K. *Coord. Chem. Rev.* **1999**, *193–195*, 499–556.
12. Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680–699.
13. Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233–350.
14. Alonso, M. A.; Casares, J. A.; Espinet, P.; Soulantica, K.; Charmant, J. P.; Orpen, A. G. *Inorg. Chem.* **2000**, *39*, 705–711.
15. Alonso, M. A.; Casares, J. A.; Espinet, P.; Soulantica, K. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 533–535.
16. Rauchfuss, T. B.; Patino, F. T.; Roudhill, D. M. *Inorg. Chem.* **1975**, *14*, 652.
17. (a) Casares, J. A.; Espinet, P.; Soulantica, K.; Pascual, I.; Orpen, A. G. *Inorg. Chem.* **1997**, *36*, 5251; (b) Kapteijn, G. M.; Spee, M. P. R.; Grove, D. M.; Kooijman, H.; Spek, A.; van Koten, G. *Organometallics* **1996**, *15*, 1405–1413.
18. Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127–3133.