

New Approach to the Polymerization of Disubstituted Acetylenes by Bulky Monophosphine-Ligated Palladium Catalysts

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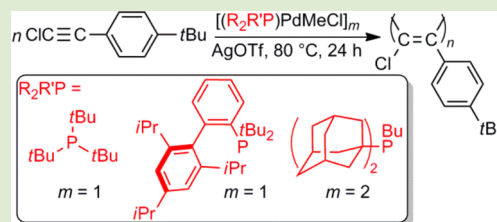
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Supporting Information

ABSTRACT: Bulky monophosphine-ligated Pd complexes served as unprecedented admirable catalysts for the polymerization of a disubstituted acetylene. The moderately high polymer yields and cis content of the formed polyacetylene contrasted with those observed for traditional Mo catalyst-based polymer. These Pd catalysts are strong tools to promote the understanding of the structure–property relationships of disubstituted acetylenes.



Application of well-defined transition metal catalysts to polymerization reactions has contributed in numerous cases to develop controlled polymerization systems and in some cases to even gain some insight into the polymerization mechanism.^{1–10} For the polymerization of substituted acetylenes, a great deal of effort has been devoted to develop controlled systems since the polymerization reaction directly impacts the unparalleled properties of these materials. Their higher stability, selective gas permeability, and superior luminescent properties make disubstituted polyacetylenes more suitable for practical applications than their monosubstituted counterparts. This has fostered the development of metal catalysts applicable to a wide range of monomers.^{4–12} Although initial investigations of substituted polyacetylenes focused on early transition metal catalysts, in recent years the utilization of late transition metal catalysts has proven to be more attractive because their lower oxophilicity allows them to polymerize acetylenes containing highly polar functional groups that cannot be handled by early transition metals.^{4–10} However, late transition metal catalysts have not generally shown polymerization activity for disubstituted acetylenes, presumably due to the higher steric hindrance of these monomers compared to monosubstituted acetylenes.^{7–11}

In recent years, introduction of bulky alkyl monophosphines to palladium-catalyzed reactions has shown to yield high activities.^{1,13–16} In particular, employment of bulky monophosphine-ligated Pd catalysts has allowed synthesis of polymers that are hardly accessible through other Pd catalysts.^{1,17–19} Bulky monophosphine-containing [(R₃P)-PdR'X]-type complexes feature a T-shape tricoordinated Pd structure having a vacant site partially stabilized by weak interactions with the surrounding ligands.^{19–23} It is likely that

the presence of a vacant site in the Pd structure favors reactions involving bulky substrates since the vacant site potentially allows the sterically hindered substrate to be accommodated in the coordination sphere of the Pd center. Herein, we report the synthesis of bulky monophosphine-ligated [(R₂R'P)PdMeCl]-type complexes (1–3) to investigate the polymerization of a disubstituted acetylene, 1-chloro-2-(4-*tert*-butyl)phenylacetylene (4). Application of the bulky monophosphine-ligated Pd catalysts for the polymerization of disubstituted acetylenes is an exciting topic since it potentially allows the synthesis of copolymers consisting of conjugated and nonconjugated blocks, i.e., polyacetylene and polyolefin blocks.

Bulky monophosphine-ligated Pd complexes 2 and 3 were synthesized by replacing the 1,5-cyclooctadiene (cod) in [(cod)PdMeCl] with 2-di-*tert*-butylphosphino-2',4',6'-tri-isopropylbiphenyl (*t*BuXPhos) or di-1-adamantyl-*n*-butylphosphine (cataCXium A) in a manner similar to the reported synthetic method for 1 (Scheme 1).¹⁹ The ¹H and ³¹P NMR together with X-ray crystal structure analysis revealed a mononuclear structure for complex 2 and a dinuclear structure for 3, both of which are in agreement with structures for other Pd complexes bearing adamantyl and biaryldialkylphosphine ligands (Figure S1, Supporting Information).^{21–25}

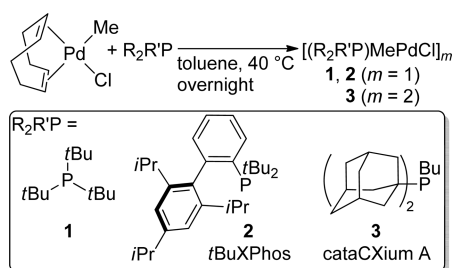
Next, we examined the polymerization of acetylene monomer 4 using Pd complexes 1–3 (Scheme 2),²⁶ wherein the complexes were dehalogenated with silver trifluoromethanesulfonate (AgOTf) in situ; the Cl atom was replaced by OTf, an anion having a weaker coordinating ability. Complexes 1–3

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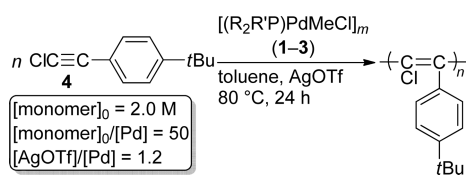
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Scheme 1. Synthesis of Bulky Monophosphine-Ligated Palladium Complexes



Scheme 2. Polymerization of 1-Chloro-2-(4-*tert*-butyl)phenylacetylene (**4**) by $(R_2R'P)PdMeCl$ (1–3)/AgOTf



successfully polymerized **4** (Table 1, entries 1–3) to give the corresponding polymers in yields higher than 76%.²⁷ In

Table 1. Polymerization of **4 by 1–3/AgOTf^a**

entry	catalyst	yield, % ^b	M_w ^c	PDI ^c	DP
1	1	77	37600	2.01	195
2	2	76	17000	3.51	88
3	3	76	24400	1.58	127
4 ^d	MoCl ₅ /SnBu ₄	58	350000	3.13	1816

^a[**4**]₀ = 2.0 M, [**4**]₀/[Pd] = 50, [AgOTf]/[Pd] = 1.2. ^bMeOH-insoluble part. ^cEstimated by SEC of the THF-soluble part, THF as eluent (calibrated by polystyrene standards). ^d[**4**]₀ = 1.0 M, [**4**]₀/[Mo] = 50, [SnBu₄]/[Mo] = 1.0 in toluene at rt for 24 h.

contrast, highly active Rh catalysts for the polymerization of monosubstituted acetylenes, [(nbd)Rh[(η^6 -C₆H₅)B(C₆H₅)₃]] (nbd = 1,5-norbornadiene) and [(nbd)RhCl]₂/NEt₃, only yielded products with M_w 's < 800 from the analysis of the crude reaction mixture (Table S1, Supporting Information).

Approximately 60% of the 1–3-based poly(**4**) (entries 1–3) were insoluble in common organic solvents including CHCl₃, THF, and DMF. It is reasonable to assume that the solvent-insoluble parts are high molecular weight fractions featuring high cis contents as reported regarding cis–cisoidal stereoisomers of some other substituted polyacetylenes that are poorly soluble in common organic solvents.^{8,28,29} SEC analysis of the THF-soluble parts revealed that the M_w and PDI of 1-based poly(**4**) [poly(**4**)-1] (entry 1) were 37 600 and 2.01. Catalysts 2 and 3 gave polymers [poly(**4**)-2 and poly(**4**)-3] both in 76% yield. The comparatively low M_w and broad PDI of poly(**4**)-2 may be explained by the occurrence of some termination reactions, which may be promoted by the presence of the *t*BuXPhos ligand through dearomative rearrangement of Pd species, as reported for Pd-catalyzed reactions involving biaryldialkylphosphine ligands.^{22,30,31} The polymerization of other monomers is being performed, and the preliminary results indicate that a bulky substituent is necessary in the monomer to obtain polymers. The results will be disclosed in the near future.²⁶

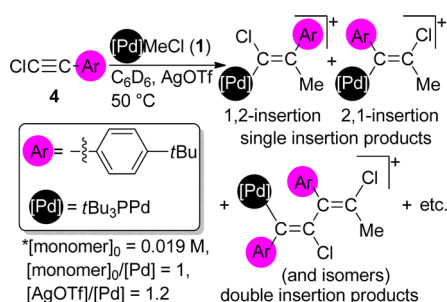
To compare the activity of the Pd catalysts presented in this work to the activities of the well-known Mo catalytic systems,^{5,32–36} we performed the polymerization of **4** by MoCl₅/SnBu₄ under conditions similar to those employed for the Pd catalytic systems ([**4**]₀ = 2.0 M, [**4**]₀/[Pd] = 50). The yield of the Mo-based polymer [poly(**4**)-Mo] was lower than those featured by the Pd catalytic systems (58% vs 76–77%). Poly(**4**)-Mo was completely soluble in CHCl₃ and THF. We compared the structure of poly(**4**)-Mo with that of poly(**4**)-1 to obtain further information about the differences of both catalytic systems. The IR spectroscopic analysis confirmed the complete transformation of the monomer to poly(**4**)-1 and poly(**4**)-Mo since the polymers displayed C=C stretching bands around 1608 cm⁻¹ but no C≡C stretching band around 2221 cm⁻¹ (Figure S2, Supporting Information). Moreover, no loss of Cl atoms was confirmed by the appearance of intense C–Cl stretching bands in the region of 828–834 cm⁻¹.^{35,36}

Since the *cis*-/*trans*-geometries of main chains of substituted polyacetylenes significantly influence the properties,^{4,8,37} it is important to develop polymerization methods that can yield substituted acetylene polymers containing highly *cis*- or *trans*-stereoregulated double bonds. The Raman spectra of poly(**4**)-1 and poly(**4**)-Mo were measured to examine the stereoregularity.

As shown in Figure S3 (Supporting Information), poly(**4**)-1 displayed a Raman spectroscopic signal assignable to *cis* structure around 1573 cm⁻¹, while poly(**4**)-Mo displayed a signal assignable to *trans* structure around 1605 cm⁻¹ together with a shoulder signal of *cis* structure.^{38–41} The Raman spectra simulated for the *cis*- and *trans*-hexamers of **4** supported the above-mentioned assignments (Figure S4, Supporting Information). The ¹H and ¹³C NMR spectra of poly(**4**)-1 and poly(**4**)-Mo also confirmed the different structures for both polymers (Figures S5 and S6, Supporting Information). In particular, comparison of the experimental (Figure S7, Supporting Information) and calculated (Chart S1, Supporting Information) ¹³C NMR spectra gave further support to the high *trans* content for poly(**4**)-Mo compared with that of poly(**4**)-1.

Rh catalysts efficiently polymerize monosubstituted acetylenes to give the corresponding polymers featuring a high *cis* double bond content, which is associated with the coordination–insertion mechanism.^{4,5,7,8,42} A large body of evidence demonstrates that Pd catalysts also yield *cis*-stereoregulated monosubstituted acetylene polymers through the coordination–insertion mechanism.^{43–47} Together with the background for the polymerization of monosubstituted acetylenes by Pd and Rh catalysts, the high *cis* content of poly(**4**)-1 suggests that the Pd catalysts in the present work follow the coordination–insertion mechanism, in contrast to the metathesis mechanism featured representatively by Mo catalysts.^{4,8} We attempted to give further support to this proposal by analyzing a mixture of a stoichiometric reaction between **4** and 1/AgOTf using mass spectrometry, as well as ³¹P and ¹H NMR spectroscopies (Scheme 3).

The ¹H and ³¹P NMR spectra of the reaction mixture were measured at *t* = 25 min, 40 min, and 12 h (Figures S8, S9, and S10, Supporting Information). During the initial 40 min of the reaction, only a small amount of products was formed, as indicated by the appearance of small singlets at 2.57 and 2.17 ppm in the ¹H NMR, which potentially correspond to =CMe species formed from the insertion of a monomer into the Pd–Me bond (Scheme 3). New signals assignable to *t*Bu₃P and *t*Bu–*p*-C₆H₄ appeared between 1.19–1.26 ppm and 0.93–1.05 ppm

Scheme 3. Stoichiometric Reaction Between 1/AgOTf and 4 (1:1)^a

^aThe counteranion (OTf⁻) was omitted for clarity.

after 25 min, and the intensities increased slightly after 40 min in the ¹H NMR spectra. After 12 h at 50 °C, the monomer was quantitatively consumed as indicated by the disappearance of an aromatic proton signal assignable to the unreacted monomer at 7.29 ppm and concomitant appearance of new aromatic proton signals at 7.36, 7.19, 6.90, and 6.75 ppm (Figure S9, Supporting Information). In addition, the =CMe signals at 2.15 ppm broadened, and the number of signals for tBu₃P and tBu-*p*-C₆H₄ further increased (Figure S9, Supporting Information). The final reaction mixture was analyzed by ESI-mass spectrometry as shown in Figure 1 and Figure S11 (Supporting

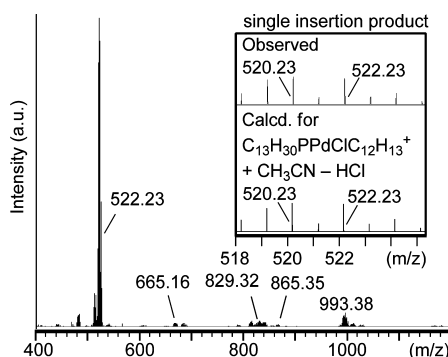


Figure 1. ESI-mass spectrum of a mixture of 1/AgOTf and 4 (1:1). Inset: expanded experimental and calculated isotope patterns of a peak.

Information). We could observe signals corresponding to the products of single, double, and triple insertion of monomer 4 into the Pd–Me bond of 1 as supported by comparison of the observed and calculated isotope patterns (Figure S11, Supporting Information).⁴⁸ The low intensity of some signals made it difficult to match perfectly the height of the observed and calculated isotope patterns, but the remarkable agreement of the *m/z* values between the calculated and observed patterns together with the number of observed signals supported the above-mentioned assignment. Therefore, the identification of the species in the mass spectrometry strongly supports the coordination–insertion mechanism featured by the Pd catalytic system 1/AgOTf in the polymerization of disubstituted acetylene 4. It is reasonable to conclude that the structure difference between the Pd- and Mo-based polymers arises from the different mechanisms in agreement with theoretical studies.⁴²

In summary, we have presented the polymerization of a disubstituted acetylene 4 by Pd catalytic system 1/AgOTf for

the first time. The Pd-based disubstituted polyacetylenes featured cis double bond content higher than the conventional Mo-based polymer according to the ¹³C NMR and Raman spectroscopies. The stoichiometric reaction between 4 and 1/AgOTf strongly supported the coordination–insertion mechanism for the polymerization. The Pd catalysts represent a key tool to understand the structure–property relation of disubstituted polyacetylenes. Even though the present research is limited to the polymerization of 4, we are confident that bulky monophosphine-based Pd catalysts can be utilized for the polymerization of other disubstituted acetylenes, including monomers bearing polar groups, thereby expanding and simplifying the synthesis of a wide variety of disubstituted polyacetylenes. Moreover, due to the versatility of the Pd catalysts for the synthesis of many other polymers, we can foresee the combination of our method with already existing synthetic methodologies to yield new classes of materials. Research for the polymerization of other disubstituted monomers is ongoing.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental procedures, synthesis of catalysts and monomer, IR, Raman, ¹H and ¹³C NMR spectra of polymers, Pd complex X-ray crystal structure analyses, DFT calculation details, stoichiometric reaction procedures, ¹H NMR, and mass spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Yokozawa, T. In *Conjugated Polymer Synthesis*; Chujo, Y., Ed.; WILEY-VCH: Weinheim, 2010; pp 35–58.
- (2) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30.
- (3) Breen, D.; Curran, K.; Risse, W. In *Stereoselective Polymerization with Single-Site Catalysts*; Baugh, L. S., Canich, J. A. M., Eds.; CRC Press: Boca Raton, 2008; pp 509–551.
- (4) Liu, J. Z.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2009**, *109*, 5799.
- (5) Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 165.
- (6) Masuda, T.; Sanda, F. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Vol. 3, pp 375–406.
- (7) Shiotsuki, M.; Sanda, F.; Masuda, T. *Polym. Chem.* **2011**, *2*, 1044.
- (8) Masuda, T.; Sanda, F.; Shiotsuki, M. In *Comprehensive Organometallic Chemistry III*; Crabtree, R., Mingos, M., Eds.; Elsevier: Oxford, 2007; Vol. 11, pp 557–593.

- (9) Sanda, F.; Shiotsuki, M.; Masuda, T. In *Polymer Science: A Comprehensive Reference*; Matyjaszewski, K., Möller, M., Eds.; Elsevier: Amsterdam, 2012; Vol. 3, pp 875–954.
- (10) Masuda, T.; Shiotsuki, M.; Tabei, J. In *Stereoselective Polymerization with Single-Site Catalysts*; Baugh, L. S., Canich, J. A. M., Eds.; CRC Press: Boca Raton, 2008; pp 553–573.
- (11) (e) Lam, J. W. Y.; Luo, J.; Dong, Y.; Cheuk, K. K. L.; Tang, B. Z. *Macromolecules* **2002**, *35*, 8288.
- (12) Masuda, T.; Nagai, K. *Materials Science of Membranes*; Yampolskii, Y., Pinnau, I., Freeman, B. D., Eds.; Wiley: Chichester, 2006; Chapter 8, pp 231–250.
- (13) Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 12527.
- (14) Roy, A. H.; Hartwig, J. F. *Organometallics* **2004**, *23*, 1533.
- (15) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176.
- (16) Anderson, K. W.; Tundel, R. E.; Ikawa, T.; Altman, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 6523.
- (17) Nanashima, Y.; Shibata, R.; Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 3628.
- (18) Kuwabara, J.; Mori, H.; Teratani, T.; Akita, M.; Kanbara, T. *Macromol. Rapid Commun.* **2009**, *30*, 997.
- (19) Yamashita, M.; Takamiya, I.; Jin, K.; Nozaki, K. *Organometallics* **2006**, *25*, 4588.
- (20) Yamashita, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 5344.
- (21) Hayashi, Y.; Wada, S.; Yamashita, M.; Nozaki, K. *Organometallics* **2012**, *31*, 1073.
- (22) Milner, P. J.; Maimone, T. J.; Su, M.; Chen, J.; Muller, P.; Buchwald, S. L. *J. Am. Chem. Soc.* **2012**, *134*, 19922.
- (23) Watson, D. A.; Su, M.; Teverovskiy, G.; Zhang, Y.; Garcia-Fortanet, J.; Kinzel, T.; Buchwald, S. L. *Science* **2009**, *325*, 1661.
- (24) Sergeev, A. G.; Zapf, A.; Spannenberg, A.; Beller, M. *Organometallics* **2008**, *27*, 297.
- (25) Sergeev, A. G.; Spannenberg, A.; Beller, M. *J. Am. Chem. Soc.* **2008**, *130*, 15549.
- (26) We have examined the polymerization of various disubstituted acetylenes including MeC≡CC₆H₅, ClC≡CC₆H₅, ClC≡CC₆H₄-p-Me, ClC≡CC₆H₄-p-F, and ClC≡C(1-naphthyl) using the Pd catalysts to find no polymerization takes place. It is assumed that the size and electrical nature of the combination of chloro and 4-tert-butyl groups are suitable for the present Pd-catalyzed polymerization, but the concrete reason is unclear at the moment.
- (27) We attempted the polymerization of **4** with [(dppf)Pd(C₆H₄-p-CN)Br] [dppf = 1,1'-bis(diphenylphosphino)ferrocene] (references 43 and 44), which is active for the polymerization of monosubstituted acetylenes, to obtain only a trace amount of solvent-insoluble yellow powder that could not be characterized. The tetracoordinated Pd catalyst was inactive for the polymerization of **4**.
- (28) Mastrolli, P.; Nobile, C. F.; Rizzuti, A.; Suranna, G. P.; Acierno, D.; Amendola, E. *J. Mol. Catal. A: Chem.* **2002**, *178*, 35.
- (29) Masuda, T.; Karim, S. M. A.; Nomura, R. *J. Mol. Catal. A* **2000**, *160*, 125.
- (30) Maimone, T. J.; Milner, P. J.; Kinzel, T.; Zhang, Y.; Takase, M. *K. J. Am. Chem. Soc.* **2011**, *133*, 18106.
- (31) Allgeier, A. M.; Shaw, B. J.; Hwang, T.-L.; Milne, J. E.; Tedrow, J. S.; Wilde, C. N. *Organometallics* **2012**, *31*, 519.
- (32) Taniguchi, Y.; Sakaguchi, T.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* **2006**, *39*, 243.
- (33) Iwakaki, E.; Hayano, S.; Masuda, T. *Polymer* **2001**, *42*, 4055.
- (34) Masuda, T.; Yoshimura, T.; Tamura, K.; Higashimura, T. *Macromolecules* **1987**, *20*, 1734–1739.
- (35) Masuda, T.; Yamagata, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 126.
- (36) Masuda, T.; Kuwane, Y.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1043.
- (37) Matsunami, S.; Kakuchi, T.; Ishii, F. *Macromolecules* **1997**, *30*, 1074.
- (38) Tabata, M.; Takamura, H.; Yokata, K.; Nozaki, Y.; Hoshina, T.; Minakawa, H.; Kodaira, K. *Macromolecules* **1994**, *27*, 6234.
- (39) Kobayashi, S.; Itomi, K.; Morino, K.; Iida, H.; Yashima, E. *Chem. Commun.* **2008**, *0*, 3019.
- (40) Tabata, M.; Tanaka, Y.; Sadahiro, Y.; Sone, T.; Yokota, K.; Miura, I. *Macromolecules* **1997**, *30*, 5200.
- (41) Tabata, M.; Sone, T.; Sadahiro, Y.; Yokata, K. *Macromol. Chem. Phys.* **1998**, *199*, 1161.
- (42) Ke, Z.; Abe, S.; Ueno, T.; Morokuma, K. *J. Am. Chem. Soc.* **2011**, *133*, 7926.
- (43) Rodriguez Castanon, J.; Kuwata, K.; Shiotsuki, M.; Sanda, F. *Chem.—Eur. J.* **2012**, *18*, 14085.
- (44) Shiotsuki, M.; Nakagawa, A.; Rodriguez Castanon, J.; Onishi, N.; Kobayashi, T.; Sanda, F.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 5549.
- (45) Carfagna, C.; Gatti, G.; Mosca, L.; Paoli, P.; Guerri, A. *Organometallics* **2003**, *22*, 3967.
- (46) Yagyu, T.; Hamada, M.; Osakada, K.; Yamamoto, T. *Organometallics* **2001**, *20*, 1087.
- (47) LaPointe, A. M.; Brookhart, M. *Organometallics* **1998**, *17*, 1530.
- (48) The C–Cl bonds of the insertion products of **4** into the Pd–Me of 1/AgOTf (Scheme 3) were cloven during the mass spectrometric analysis. For instance, the product of the monoinsertion of **4** was detected as a CH₃CN adduct of [tBu₃PPdMe(C₁₂H₁₃Cl)–HCl]⁺ (Figure 1), while other species lacked Cl₂.