Journal of Organometallic Chemistry, 281 (1985) 213–220
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS OF POLYMER-ATTACHED NIOBIUM AND TANTALUM COMPLEXES AND THEIR APPLICATIONS TO THE CATALYSIS OF OLEFIN HYDROGENATION, ISOMERIZATION AND ETHYLENE DIMERIZATION

BIAU-HUNG CHANG, CHAK-PO LAU, ROBERT H. GRUBBS and CARL H. BRUBAKER, JR.
Department of Chemistry, Michigan State University, East Lansing, Michigan 48824 (U.S.A.)

(Received May 17th, 1984)

Summary

Polymer-attached $CpNbCl_4$, $CpNbCl_3$, $CpNbCl_2$, $Cp_2Nb(BH_4)$, $CpTaCl_4$, $(PhCH_2)NbCl_4$ and $(PhCH_2)TaCl_4$ have been prepared. The reduction products of supported niobium and tantalum chlorides are active hydrogenation catalysts for olefins and for diphenylacetylene which was hydrogenated to 1,2-diphenylethane through intermediate stilbene. The similar reduction products have also been employed in catalytic isomerization of allylbenzene which is converted into a mixture of *trans*- and *cis*-propenylbenzene. Polymer-attached $CpTaCl_4$, when treated with neopentyllithium, can effect dimerization of ethylene to give 1-butene.

We have previously demonstrated [1–3] that the attachment of titanocene-, zirconocene- and hafnocene-related catalysts to rigid polymers resulted in an increase in activity for olefin hydrogenation and isomerization which was the result of site isolation on the polymer [4]. The attachment of catalysts to the polymer also allows easy separation of catalysts from the reaction products.

In this work, niobium and tantalum complexes have been attached to polystyrene-divinylbenzene copolymer through cyclopentadienyl and benzyl ligands. Their catalytic activities in hydrogenation, olefin isomerization and ethylene dimerization have been examined.

Experimental

Because of the air and moisture sensitivity of the materials described, standard Schlenk-tube techniques were employed. An argon-filled glove-box was used for transfers.

Electron spin resonance (ESR) spectra were obtained by use of a Varian E-4 spectrometer. NMR spectra were obtained by using Varian T-60 and Varian

0022-328X/85/$03.30

A56/60D spectrometers. Tetramethylsilane (TMS) was used as reference. Gas chromatographic (GLC) analyses were performed by use of an F&M model 810-19 analytical gas chromatograph and a Varian 1400 analytical gas chromatograph. Infrared spectra were recorded by using Perkin–Elmer 457 or 237B spectrophotometers. Samples were prepared by crushing the polystyrene beads in a ball mill under anaerobic conditions and mulling the powder with dry Nujol in a dry glove-box. The samples were placed between NaCl plates.

Materials

The 20% cross-linked (600 Å pore size), macroreticular, polystyrenedivinylbenzene, copolymer beads were gifts from the Dow Chemical Company and were washed to remove impurities before use. They were washed with 10% HCl, 10% NaOH, H_2O, a 1/1 H_2O/CH_3OH mixture, CH_3OH, a 1/1 CH_3OH/CH_2Cl_2 mixture, and CH_2Cl_2 and benzene as recommended by Pittman [5] and were dried in a vacuum.

Reagent grade tetrahydrofuran (THF), benzene and mesitylene were distilled over sodium-benzophenone under argon. Hexane, cyclohexane, pentane and diethyl ether were refluxed over lithium aluminum hydride before distillation. Argon, hydrogen, carbon monoxide, ethylene and hydrogen chloride were Matheson purified grade. Organolithium reagents, 1-hexene, allylbenzene, 1,5-cyclooctadiene, cyclohexene, and chloromethyl ethyl ether * were obtained from the Aldrich Chemical Company. Niobium and tantalum pentachlorides were obtained from Alfa Products, Ventron Corp. Chloromethylated and cyclopentadiene-substituted copolymers were prepared by the previously published methods [1–3].

Analytical methods

Halide from the chloromethyl groups was removed from the copolymer by use of hot pyridine and was determined by the Volhard method [7]. Niobium and tantalum contents were determined by digesting the polymer-attached niobium and tantalum compounds with a few drops of concentrated sulfuric acid, ashing by use of a microburner, heating to 1000°C for 12 h, and weighing as Nb_2O_5 and Ta_2O_5, respectively. Niobium and tantalum complexed chloride was removed by digestion of polymer samples in 2 *N* KOH solution at 80°C for 24 h. Chloride was determined by the Volhard method, following acidification of the aqueous supernatant. Some elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of polymer-attached $CpNbCl_3$

A sample of 6 g cyclopentadiene substituted copolymer (1.41 mmol Cp/g of beads) was treated with a two-fold excess of methyllithium in THF, and the reaction mixture was stirred for 2 days under argon. The polymer turned deep purple-red. The solution was removed and the beads were washed four times with THF and then four times with benzene. The flask was cooled in an ice bath and a 30 ml portion of saturated niobium pentachloride solution in benzene was introduced by using a syringe. After the reaction mixture was stirred for about 20 minutes, the color of the

---

* Caution is advised in chloromethylation and in the handling of chloromethyl ethyl ether because the related compound bis(chloromethyl) ether is a carcinogen [6].

solution disappeared. The solution was removed and a second 30 ml portion of saturated niobium pentachloride solution in benzene was injected. The solution was again decolorized after being stirred for half an hour. Several 30 ml portions of saturated niobium pentachloride solution were added until the solution was no longer decolorized. The solution was removed and the black colored beads were washed with benzene in a Soxhlet extractor for 5 days and dried under vacuum. Anal. Calcd.: Cl/Nb, 3.00. Found: Nb, 0.941 mmol/g of beads; Cl, 2.913 mmol/g of beads; Cl/Nb, 3.10.

Preparation of polymer-attached Cp_2NbCl_2

A sample of 3 g of polymer-attached $CpNbCl_3$ (0.941 mmol Nb/g of beads) was treated with large excess of sodium cyclopentadienide solution in THF. The reaction mixture was stirred in darkness for 5 days. The solution, which had turned dark purple at the end of this period, was removed by using a syringe. The beads were washed several times with degassed THF. The brown beads, with attached niobium tetracyclopentadienyl, were suspended in THF and anhydrous hydrogen chloride was introduced. The beads turned black and after being washed with THF in a Soxhlet extractor for 3 days, they were greyish brown. Anal. Calcd.: Cl/Nb, 2.00. Found: Nb, 0.139 mmol/g of beads; Cl, 0.269 mmol/g of beads; Cl/Nb, 1.93.

Preparation of polymer-attached $CpNbCl_4$ and $CpTaCl_4$

In a typical reaction, 1 g of cyclopentadiene-substituted copolymer beads (1.41 mmol Cp/g of beads) was treated with excess n-BuLi in THF for 2 days under argon. The excess n-BuLi was removed and the beads were washed with THF, then dried under vacuum. The dried beads were suspended in benzene and R_3SnCl (R = n-Bu, or Me) was added. The reaction mixture was stirred for 3 days. The color of beads changed from red to pale yellow. The beads were then washed with benzene and dried. Treatment of pale yellow beads in toluene with MCl_5 (M = Nb, or Ta) gave red supported $CpNbCl_4$ beads and yellow supported $CpTaCl_4$ beads, respectively. Anal. Calcd. for supported $CpNbCl_4$: Cl/Nb, 4.00. Found: Nb, 0.810 mmol/g of beads; Cl, 3.081 mmol/g of beads Cl/Nb, 3.80. Anal. Calcd for supported $CpTaCl_4$: Cl/Ta, 4.00. Found: Ta, 0.792 mmol/g of beads; Cl, 3.052 mmol/g of beads; Cl/Ta, 3.85. No analysis for Sn was carried out.

Preparation of polymer-attached $(PhCH_2)MCl_4$ (M = Nb and Ta)

Typically, 2 g of chloromethylated polystyrene beads (1.57 mmol Cl/g of beads) were suspended in 10 ml of THF and the reaction flask was cooled in an ice bath. A two-fold excess of trimethylstannyllithium in THF, which was prepared by treatment of a tetrahydrofuran solution of hexamethyldistannane with methyllithium, was added slowly. After being stirred at room temperature for 36 h, the solution was removed and the beads were washed several times with THF, then dried. The polymer-attached benzyltrimethyltin beads were suspended in 20 ml toluene and treated with excess $TaCl_5$. After being stirred for 5 days, the beads were washed in a Soxhlet extractor with toluene for 3 days. The product, cream beads, was then dried under vacuum and gave chloride contents of 3.61 mmol/g of beads and tantalum contents of 0.93 mmol/g of beads.

Preparation of polymer-attached $NbCp_2(BH_4)$

To 2 g of polymer-supported niobocene dichloride (0.139 mmol Nb/g of beads) was added excess lithium borohydride. 10 ml of degassed THF was injected and the reaction mixture was stirred under argon at room temperature for 12 h. The color of the beads changed from greyish brown to dark green. Excess lithium borohydride was removed by washing the beads several times with THF. The product, which was very air and moisture sensitive, was stored in the argon filled glove-box. The IR spectrum showed ν(B–H) at 2380 cm^{-1}. No boron or chloride could be detected in the beads.

Catalytic hydrogenation of olefins and diphenylacetylene

The polymer-attached catalysts were weighed into a 100 ml round-bottomed flask with a side arm. The beads were suspended in 5 ml n-hexane and treated with 3 ml of 2.0 *M* n-butyllithium in n-hexane for 2 days. The excess of n-butyllithium was removed and the beads were washed with n-hexane several times. The 8.5 ml hexane was injected into the flask and 1.5 ml 1-hexene was added. The reaction mixture was stirred at a constant stirring rate, while the temperature was maintained at 25°C. The rate of hydrogen uptake was measured by using a 100 ml gas buret.

For the hydrogenation of diphenylacetylene, the catalyst was suspended in 5 ml toluene, then 0.267 g (1.5 mmol) of diphenylacetylene in 5 ml toluene was added into the flask. The rate of hydrogen uptake was measured at 100°C and at normal atmospheric pressure. A small amount of reaction mixture was drawn out periodically and then chromatographed by GLC on a 8 ft. × 1/8 in. 15% SE-30/Chromosorb P column.

Catalytic isomerization of allylbenzene and 1,5-cyclooctadiene

The reduction of polymer-attached niobium and tantalum chloride beads with excess n-butyllithium in hexane was carried out under hydrogen at room temperature for 2 days. The excess of n-butyllithium was removed and the beads were washed with hexane several times and dried under vacuum. Allylbenzene or 1,5-cyclooctadiene was then added and stirred under argon at 145°C. A small amount of reaction mixture was drawn out periodically and chromatographed by GLC on a 8 ft. × 1/8 in. 15% SE-30/Chromosorb P column. The relative amounts of allylbenzene, *cis*-propenylbenzene and *trans*-propenylbenzene were measured by integration. The relative amounts of 1,3-, 1,4- and 1,5-cyclooctadiene were measured by GLC integration and NMR integration.

Ethylene dimerization catalyzed by polymer-attached tantalum complexes

Typically, 0.50 g polymer-attached $CpTaCl_4$ beads (0.792 mmol/g of beads) was placed into a pressure bottle and suspended in 15 ml pentane. Two equivalents of neopentyllithium in pentane (0.80 mmol) was added slowly. The beads changed from yellow to brown. After being stirred for 2 days, the brown beads were washed several times with pentane. The brown beads were then suspended in 15 ml pentane. The pressure bottle was pressurized with 60 psi ethylene and the reaction mixture was stirred for 2 h. The brown color of the beads lightens to pale yellow. The solvent and ethylene were removed and the beads were dried under vacuum. After being stirred at 100°C under 80 psi of ethylene for 24 h; the gas sample was analyzed on a 20 ft. × 1/8 in. Durapak column.

When the pale yellow beads suspended in ether were treated with 90 psi of CO for 30 h, a supported dicarbonyl complex was formed. The IR spectrum shows two CO stretching bands at 2020 and 1940 cm^{-1}.

Results and discussion

Preparation of polymer-attached $CpNbCl_3$

It has been our initial intention to prepare the polymer-attached $CpNbCl_4$ by treating cyclopentadienide substituted copolymer with $NbCl_5$. Instead of $CpNbCl_4$, polymer-attached $CpNbCl_3$ is formed. The formation of supported $CpNbCl_3$ is not unexpected since the cyclopentadienide ion is a good reducing agent. During its reaction with $NbCl_5$, polymer-attached $CpNbCl_3$ is formed by reduction of Nb^{V} to Nb^{IV}.

The polymer-attached $CpNbCl_3$ has been confirmed by metal and chloride analyses, which gave a Cl/Nb ratio of 3.1. Brubaker and Kilmer have presented a computer simulated ESR spectrum of this compound [8]. Comparison of the experimental spectrum with the simulated one indicates that the two match very well.

Polymer-attached Cp_2NbCl_2

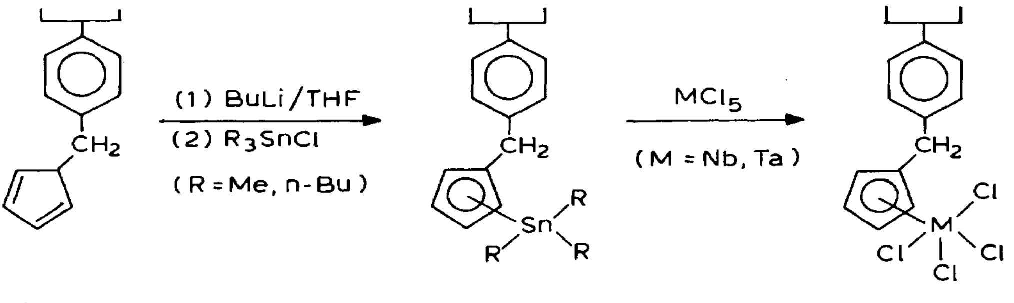
Polymer-attached Cp_2NbCl_2 was prepared by converting the corresponding $CpNbCl_3$ to Cp_4Nb with excess NaCp solution in THF, and then by treating the supported Cp_4Nb with a saturated solution of dry hydrogen chloride in THF [9,10]. The resin bound Cp_2NbCl_2 is confirmed by metal and chloride analyses. ESR spectrum of the supported Cp_2NbCl_2 is very similar to the frozen glass spectrum of the homogeneous Cp_2NbCl_2 [11] and the computer simulated one [8].

Loading in the polymer-attached $CpNbCl_3$ is 0.94 mmol Nb/g of beads, but in subsequent Cp_2NbCl_2 substituted polymer, it has decreased to 0.14 mmol Nb/g of beads. The large decrease in loading can be explained by the η^5-C_5H_5/η^1-C_5H_5 exchange mechanism reported earlier [12].

Preparation of polymer-attached $CpMCl_4$ ($M = Nb$ and Ta)

The complexes $CpMCl_4$ ($M = Nb$ and Ta) were prepared recently from the reaction of MCl_5 with $CpSnR_3$ ($R = CH_3$ or n-Bu) or $MgCp_2$ [13,14]. The attachment of $CpMCl_4$ species to the polymer is illustrated by Scheme 1.

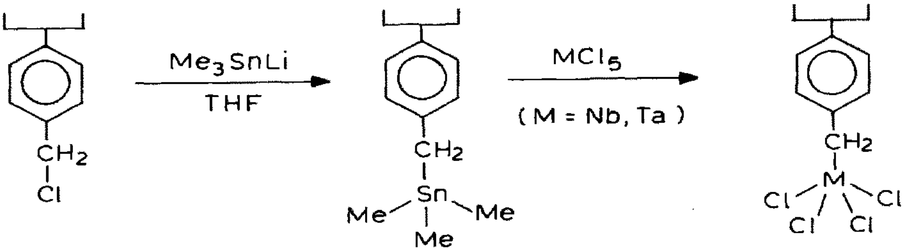
Treatment of the cyclopentadiene-substituted copolymer beads with n-butyllithium followed by the addition of R_3SnCl ($R = Me$ or n-Bu) gave pale yellow polymer-attached $CpSnR_3$ beads. Then the direct reaction of supported $CpSnR_3$ with MCl_5 gave supported $CpMCl_4$ beads. These species were confirmed by the comparison of their colors with unattached species and by elemental analyses.



SCHEME 1. Preparation of polymer-attached $CpMCl_4$ ($M = Nb$, Ta).

Preparation of polymer-attached (η^1-PhCH$_2$)MCl$_4$ (M = Nb and Ta)

Transition metal complexes attached to polymers by means of phosphine, nitrogen of π-bonded ligands have been studied extensively. However, polymers where the transition metal complex is attached to the matrix by a carbon-to-metal σ-bond have rarely been studied [15–19]. Pittman and co-workers [16–18] found the use of metal carbonyl anions provided convenient routes to incorporate transition metal carbonyl moieties into polymers. In this research, polymer-bound η^1-benzyl-niobium and -tantalum chlorides have been prepared by treating polymer-bound η^1-benzylalkyltins with anhydrous niobium and tantalum pentachlorides respectively. Polymer-bound η^1-benzyltrimethyltin can be prepared in good yield by treating chloromethylated polystyrene beads with trimethylstannyllithium which was prepared by treatment of a tetrahydrofuran solution of hexamethyldistannane with methyllithium [20]. The proposed reaction may be illustrated in Scheme 2. This method provides convenient routes for attaching transition metal halides to polymers through a η^1-benzyl ligand.



SCHEME 2. Preparation of Polymer-Attached (η^1-PhCH$_2$)MCl$_4$ (M = Nb and Ta)

Catalytic activities of polymer-attached niobium and tantalum complexes

The unsaturated metallocene and transition metal hydrides are recognized as important intermediates and catalysts in a variety of reactions including olefin hydrogenation, isomerization, etc. Niobium hydrides have been reported to react with olefins [21,22].

We have also previously demonstrated [1,2] that polymer-attached titanocene, zirconocene and hafnocene are excellent catalysts for olefin hydrogenation and isomerization.

Therefore, it is not unexpected that the reduced species of polymer-attached niobium and tantalum chlorides can serve as catalysts for hydrogenation and isomerization of unsaturated organic compounds.

Hydrogenation of olefins and diphenylacetylene

Studies on hydrogenation of olefins with the reduced species of the polymer-attached niobium and tantalum chlorides show that they are much poorer hydrogenation catalysts than titanium analogs [4]. The rates of hydrogen uptake at room temperature for 1-hexene and cyclohexene catalyzed by the reduced polymer-attached CpNbCl$_3$ are only 1.49 ml and 1.11 ml/min-mmol of Nb metal, respectively. Other reduced polymer-attached niobium and tantalum chlorides do not show any appreciable amounts of hydrogen uptake in the hydrogenation of 1-hexene at 1 atm of H$_2$ and 25°C.

However, the reduction products of these beads are active catalysts for the hydrogenation of diphenylacetylene at 100°C and at 1 atm of H_2. For example, diphenylacetylene (1.5 mmol) was completely hydrogenated to give 1,2-diphenylethane via *trans*-stilbene as an intermediate within 23 h, when 0.63 g of reduced supported $CpTaCl_4$ beads (0.79 mmol Ta/g of beads) was used. The reduced polymer-attached $CpNbCl_4$ beads were much less reactive and brought the hydrogenation to an extent of 20% under the same conditions. The hydrogenations catalyzed by reduction products of polymer-bound η^1-benzyl-niobium and -tantalum chlorides were not examined in detail in this case.

Isomerization of allylbenzene

It has been known that homogeneous $NbCp_2Cl_2$ reacts with BuLi to form $NbCp_2HCl$ [22]; this monohydride complex might be a potential catalyst for hydrogenation, isomerization, etc. Polymer-supported $NbCp_2Cl_2$ has been treated with BuLi to give black beads; Nb and Cl analyses of which yielded a Cl/Nb ratio of 1.05. This result clearly indicated that one of the chloride ligands remained bonded to the metal center. Nb–H stretching could scarcely be observed in the IR spectrum because the very broad peak due to the copolymer at 1600 cm^{-1} might have covered the ν(Nb–H). Nevertheless, it is not unreasonable to expect that the reaction between polymer-supported $NbCp_2Cl_2$ and BuLi has formed the same product as in the homogeneous case, i.e., the polymer-supported $NbCp_2HCl$.

Polymer-supported $NbCp_2HCl$ has been employed for isomerization of allylbenzene, it is found that 0.18 g (0.14 mmol Nb/g beads) can effect 90% isomerization of 4 ml allylbenzene (80% *trans*-propenylbenzene and 10% *cis*-propenylbenzene) in 15 h at 145°C.

Isomerization of allylbenzene with reduced polymer-attached $CpNbCl_3$, $CpTaCl_4$, $(PhCH_2)$ $NbCl_4$ and $(PhCH_2)TaCl_4$ has also been attempted. A 0.2 g sample of reduced polymer-attached $CpNbCl_3$ (0.94 mmol Nb/g of beads) was found to effect a total of 7.4% isomerization of 4 ml allylbenzene, 5.4% to *trans*-propenylbenzene and 2% to *cis*-propenylbenzene on 15 h at 145°C. Comparison of reactions with supported $CpNbCl_4$ and $CpTaCl_4$ shows that 0.25 g of polymer-attached $CpTaCl_4$ (0.21 mmol Ta/g of beads), when reduced, can effect about 97% isomerization of 4 ml of allylbenzene in 4 h, while approximately the same amount of supported $CpNbCl_4$ can only effect about 15% isomerization. The reduction products of polymer-attached η^1-benzyl-niobium and -tantalum chlorides are also active catalysts for isomerization of allylbenzene and their activities are as good as those of supported $CpNbCl_4$ and $CpTaCl_4$.

Polymer-attached $Cp_2Nb(BH_4)$ was prepared by treating resin bound Cp_2NbCl_2 with $LiBH_4$ in THF. Addition of triethylamine to the borohydride derivative yielded yellow beads, whose IR spectrum showed a sharp peak at 1665 cm^{-1} not present in that of the supported niobocene borohydride. This sharp peak might be attributed to the Nb–H stretching. The yellow beads were suspected to be the polymer-attached niobocene monohydride, i.e., Cp_2NbH. When the supported niobocene monohydride was used for the catalytic isomerization of allylbenzene, 0.2 g of catalyst (0.14 mmol Nb/g of beads) could effect about 10% isomerization of 4 ml of allylbenzene in 15 h at 145°C. In another experiment, polymer-attached $Cp_2Nb(BH_4)$ was treated with triethylamine under an atmosphere of carbon monoxide, no formation of supported $Cp_2NbH(CO)$ or $Cp_2Nb(CO)_2$ was observed.

Ethylene dimerization catalyzed by polymer-attached tantalum complexes

Schrock and co-workers [23,24] reported that a neopentylidene complex, $CpTa(CHCMe_3)Cl_2$, reacts with ethylene to give a tantalo-cyclopentane complex which could be an intermediate in selective dimerization of ethylene to give 1-butene. The dimerization of ethylene catalyzed by polymer-attached $CpTaCl_4$ has been attempted. Treatment of polymer-attached $CpTaCl_4$ with two equivalents of neopentyllithium in pentane gave brown beads which might be a supported neopentylidene complex of tantalum. The brown beads can effect dimerization of ethylene at 80 psig pressure and 100°C to give 1-butene with a turnover number of 18 mmol/h-mmol of Ta metal. A carbonyl complex, possibly a supported $CpTaCl_2(CO)_2$ (ν(CO) 2040 and 1960 cm^{-1}) [23], was formed when the brown beads were treated with 60 psig of ethylene and then treated with 90 psig of carbon monoxide.

Acknowledgment

The authors gratefully acknowledge the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References

1 W.D. Bonds, Jr., C.H. Brubaker, Jr., E.S. Chandrasekaran, C. Gibbons, R.H. Grubbs and L.C. Kroll, J. Am. Chem. Soc., 97 (1975) 2128.
2 B.H. Chang, R.H. Grubbs and C.H. Brubaker, Jr., to be published.
3 E.S. Chandrasekaran, R.H. Grubbs and C.H. Brubaker, Jr., J. Organomet. Chem., 120 (1976) 49.
4 R.H. Grubbs, C.P. Lau, R. Cukier and C.H. Brubaker, Jr., J. Am. Chem. Soc., 99 (1977) 4517.
5 C.U. Pittman, Jr. and R.M. Hanes, private communication.
6 The Federal Register Vol. 39, No. 20, Part III, Occupational Safety and Health Administration, Carcinogens.
7 C.W. Bird, Transition Metal Intermediates in Organic Systems, Logos Press, London, 1967, p. 30.
8 N.H. Kilmer and C.H. Brubaker, Jr., Inorg. Chem., 18 (1979) 3283.
9 F.W. Siegert and H.J. de Liefde Meijer, J. Organomet. Chem., 23 (1970) 177.
10 F.W. Siegert and H.J. de Liefde Meijer, Rec. Trav. Chim. Pays-Bas, 88 (1969) 1445.
11 C.P. Steward and A.L. Porte, J. Chem. Soc. Dalton, (1973) 772.
12 J.G.S. Lee and C.H. Brubaker, Jr., J. Organomet. Chem., 135 (1977) 115.
13 R.J. Burt, J. Chatt, G.J. Leigh, J.H. Teuben and A. Westerhof, J. Organomet. Chem., 129 (1977) C33.
14 M.J. Bunder, A. DeCian and M.L.H. Green, J. Chem. Soc., Chem. Comm., (1977) 59.
15 W. Beck, R. Hoefer, J. Erbe, H. Menzel, U. Nagel and G. Platzen, Z. Naturfoschg., B, 29 (1974) 567.
16 C.U. Pittman, O.E. Ayers and S.P. McManus, J. Macromol. Sci. Chem., A, 7 (1973) 1563.
17 C.U. Pittman and G.O. Evans, Chem. Technol., 3 (1973) 560.
18 C.U. Pittman and R.F. Felis, J. Organomet. Chem., 72 (1974) 389.
19 S. Warwell and P. Buschmeyer, Angew. Chem. Int. Ed. Engl., 17 (1978) 131.
20 W.C. Still, J. Amer. Chem. Soc., 99 (1977) 4836.
21 I.H. Elson, J.K. Kochi, U. Klabunde, L.E. Manzer, G.W. Parshall and F.N. Tebbe, J. Am. Chem. Soc., 96 (1974) 7374.
22 I.H. Elson and J.K. Kochi, J. Am. Chem. Soc., 97 (1975) 1262.
23 S.J. McLain, C.D. Wood and R.R. Schrock, J. Am. Chem. Soc., 99 (1977) 3519.
24 S.J. McLain and R.R. Schrock, J. Am. Chem. Soc., 100 (1978) 1315.