Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Rate Accelerating Polymeric Cofactors in the Homogeneous Hydrogenation of Alkenes

D. E. Bergbreiter[a]; M. S. Bursten[a]
[a] Department of Chemistry, Texas ASM University College, Station, TX

To cite this Article Bergbreiter, D. E. and Bursten, M. S.(1981) 'Rate Accelerating Polymeric Cofactors in the Homogeneous Hydrogenation of Alkenes', Journal of Macromolecular Science, Part A, 16: 1, 369 — 381

To link to this Article: DOI: 10.1080/00222338108082057

URL: http://dx.doi.org/10.1080/00222338108082057

J. MACROMOL. SCI.-CHEM., A16(1), pp. 369-381 (1981)

Rate Accelerating Polymeric Cofactors in the Homogeneous Hydrogenation of Alkenes

D. E. Bergbreiter and M. S. Bursten
Department of Chemistry
Texas A&M University
College Station, TX 77843

ABSTRACT

The novel use of polymeric reagents as selective phosphine absorbers in a homogeneous catalysis is presented. Silver(I) p-toluene sulfonate (A) is shown to absorb tertiary phosphines from organic solution and to restore PPh_3-inhibited homogeneous hydrogenation of alkenes by $RhClL_3$ ($L=PPh_3$) to a non-inhibited rate. Treatment of $RhClL_3$ with ethylene in presence of A followed by addition of a second alkene and removal of ethylene under reduced pressure leads to an increased rate of hydrogenation for several alkenes.

INTRODUCTION

Dissociation of a nonvolatile ligand has become accepted as essential to alkene hydrogenations catalyzed by homogeneous transition metal compounds containing triphenylphosphine.[1] This

$$1 \qquad X_mML_n \rightleftharpoons X_mML_{n-1} + L \qquad L=PPh_3$$

dissociation was first postulated by Wilkinson and coworkers in 1966 to explain the low solution molecular weights obtained for

$RhClL_3$ ($L=PPh_3$), an active alkene hydrogenation catalyst.[2] Though subsequent studies indicated dissociation is less extensive than was originally claimed [3], the postulate that the active catalyst is a coordinatively unsaturated species formed by dissociation of a PPh_3 ligand is generally regarded as correct. [4,5]

Although dissociation of PPh_3 is not the rate-determining step for hydrogenations catalyzed by $RhClL_3$ [6], if equation 1 could be shifted to the right, faster rates of alkene hydrogenation might be achieved. This rightward shift could be accomplished by removal of PPh_3 from solution, thus generating more of the active form of the catalyst.

In the past several years attempts at selective removal of PPh_3 from a homogeneous solution have been made. Reverse osmosis has been effective but requires pressures up to 100 atmospheres. [7] Complexation of PPh_3 with soluble Lewis acids has also been attempted [8]; although side reactions were observed, no rate enhancement attributable to a shift of equation 1 was observed. Thus, although some attempts have been made, a rate enhancement in homogeneous hydrogenation by a rightward shift of equation 1 has not been demonstrated previously.

Herein we report the use of functionalized polymers to absorb free PPh_3 from homogeneous solutions. Although the use of supported homogeneous catalysts has become chemically fashionable in the last decade, polymer functionalization to selectively absorb a non-volatile ligand is a novel application of polymers to homogeneous catalysis. Such a polymer might be expected to effect a significant rate enhancement in a system which dissociates a ligand to form the catalytically active species. A supported Lewis acid should interact with free Lewis base, thus shifting equilibrium 1 in the desirable rightward direction. Side reactions, observed by Shriver [8] when he used soluble Lewis acids to shift this equilibrium, should be eliminated.

A polymeric cofactor for ligand absorption in homogeneous catalysis must meet several criteria. It must not be catalytically active itself nor absorb the homogeneous catalyst. It should be an efficient absorber of non-volatile ligand--in this case, PPh_3. Preferably, it should also be prepared from readily available precursors, and be air-stable.

EXPERIMENTAL

All solutions were handled under nitrogen, argon, hydrogen, or ethylene, using standard Schlenk techniques.[10] Gases were used without further purification. Toluene, diethyl ether, tetrahydrofuran, and pentane were freshly distilled under nitrogen from sodium benzophenone ketal. Ethanol and methanol were purged with a strong flow of nitrogen for one hour. 1-Hexene, 1-octene, cyclohexene, styrene, and norbornadiene were passed through neutral alumina to remove stabilizers and peroxides, carefully degassed, and then purged with nitrogen for 1/2 hour.

$RhClL_3$ ($L=PPh_3$), $[RhCl(C_8H_{14})]_2$, and $PEtPh_2$ were obtained from Strem Chemicals and used as received. PPh_3 was obtained from Fluka. $RhCl(PEtPh_2)_3$ [11] was prepared by literature methods and identified by nmr, ir and melting point. Macroreticular ion exchange resin, polystyrene sulfonic acid, (Amberlyst 15), was purchased from Chemalog and extracted for 48 hours in a Soxhlet extractor with dimethylformamide before use in order to remove kaolins and surfactants present. Conventional flow techniques were used for exchange of metal ions.[12] After exchange, the polymer was dried under vacuum for 24 h. Silver substitution was 1.0 mmol Ag^+/g polymer (analyzed as AgCl). Proton nmr spectra were taken on a Varian T-60 nmr; ^{31}P spectra on a Varian XL 200 MHz nmr spectrometer. Infrared spectra were run on a Perkin-Elmer 297 ir spectrometer. Melting points were determined in a Thomas/Hoover melting point apparatus and were uncorrected.

Adsorbtion of Phosphines by Polymeric Reagents

A solution of PPh_3, 0.04 M in THF or acetone, was prepared. 20 mL of this solution was injected into a flask containing 2 g (1.0 mmol metal ion/g polymer) of metal ion exchanged polystyrene sulfonate beads and covered with a serum cap. 0.05 mL aliquots of this solution were withdrawn after 1 and 12 hours and analyzed for PPh_3 concentration by ^1H and ^{31}P nmr; p-xylene and $OPPh_3$ were used as internal standards for ^1H and ^{31}P nmr respectively. Sodium polystyrene sulfonate and polystyrene sulfonic acid were both used in control experiments, and showed no detectable PPh_3 absorption at these concentrations. A similar experiment was run using a THF solution 0.04 M in styrene to determine whether the alkene were being absorbed by either silver(I) polystyrene sulfonate (A) or polystyrene sulfonic acid. In neither case was any change in styrene concentration observed.

Hydrogenations

Hydrogenations were run at 25.0 ± 0.1°C in a 100 mL three-necked flask equipped with a solid addition tube and a gas inlet tube covered with a serum cap. A 1 3/8" egg-shaped magnetic stirbar provided vigorous mixing. The flask was connected to a hydrogenation apparatus consisting of a two-way stopcock to vacuum and a three-way stopcock to the H_2 source and to a 50 mL buret. A leveling bulb was connected to the bottom of the buret with rubber tubing and filled with dibutyl pthalate. Constant atmospheric pressure was maintained throughout the reaction by adjusting this leveling bulb as the reaction proceeded.

In order to ascertain the effects of A, typical hydrogenations were run in the three following ways: 1) polymer beads were added at the start of (or during) a hydrogenation; 2) polymer beads were present as the catalyst dissolved under H_2, and were stirred with the solution of the transition metal catalyst under H_2 before the addition of alkene; or 3) procedure 2 was followed, but under C_2H_4 atmosphere, which was removed before hydrogenation commenced.

A typical hydrogenation using procedure 1 was as follows: The catalyst (10-60 mmol) was placed in the 100 mL 3-necked flask and the polymer beads (0.2-0.4 g) were put in the solid addition tube. The apparatus was carefully assembled, evacuated and flushed with H_2 three times, and then held under vacuum for 10 min. The apparatus was flushed with H_2 and evacuated three more times, then filled with H_2 and 10 mL of solvent (toluene, unless otherwise noted) was added. The solution was carefully degassed at reduced pressure and filled with H_2 three times and then stirred vigorously under H_2 until the catalyst was fully dissolved. At this point, stirring was stopped and alkene (2-20 mmol) was injected. When polymeric beads were to be added at the beginning of a hydrogenation, they were added at this point by turning the solid addition tube. Hydrogenation was initiated by resumption of stirring. Alternatively, polymeric beads were added after hydrogenation had been initiated.

Hydrogenations according to procedure 2 were run in essentially the same manner, except that the catalyst and polymeric beads were both placed in the hydrogenation vessel as the reaction was set up. The solid addition tube was not used; a glass stopper was inserted in its place. All other procedures were identical to those used in procedure 1.

The hydrogenations according to procedure 3 were run after utilizing an ethylene pretreatment. As in procedure 2, catalyst and polymer beads were placed in the hydrogenation vessel. The third neck was fitted with a gas inlet valve connected to the C_2H_4 source. The hydrogenation apparatus was evacuated and filled with C_2H_4 three times. Toluene (10 mL) was then added, and carefully degassed and flushed with C_2H_4 three times. The solution was allowed to stir under C_2H_4 for 900 s at which time the alkene to be hydrogenated (2-20 mmol) was injected. After an additional 100 s the apparatus was carefully evacuated and H_2 was introduced. The apparatus was carefully evacuated and vigorously stirred for 15 s; the apparatus was then carefully evacuated and flushed with H_2. After two more cycles consisting solely of flushing with H_2

and careful evacuation, the apparatus was filled with H_2 and hydrogenation begun by initiation of stirring.

When C_2H_4 was the alkene to be hydrogenated, the apparatus was carefully evacuated then filled with H_2 three times, after the catalyst had been stirred with polymer beads under C_2H_4 atmosphere for 1000 s, i.e., the solution was not stirred under reduced pressure.

Hydrogenation rates were calculated by plotting the consumption of H_2 vs. time and fitting a straight line to the region where the rate was nearly constant; this region encompassed at least the first 50-500 s after introduction of alkene. Rates are reported both as mmol H_2/s and mmol H_2/[catalyst],$\underline{M}$·min.

In order to determine whether any catalytic activity resided upon the polymer beads, some hydrogenation experiments were stopped before alkene had been consumed. The polymer beads were allowed to settle and the supernatant was transferred via syringe to another H_2-filled hydrogenation apparatus and hydrogenation resumed. The polymeric beads were stirred two times with toluene (15 mL) which was then syringed off. Fresh toluene (10 mL) and alkene (2-20 mmol) were injected and hydrogenation was initiated. No catalytic activity was observed to reside on these beads.

RESULTS AND DISCUSSION

Initial attempts to meet the criteria for an effective ligand absorbing polymer were focused on using polyethylene functionalized with transition metal organometallics.[13] Some PPh_3 was indeed absorbed by $FeCp(CO)_2$-polyethylene, but low functionalization (10^{-2} mmol Fe/g polymer) and low thermal and air stability caused abandonment of this functionalized polymer.[14] Alternatively, macroreticular ion exchange resin, polystyrene sulfonic acid (Amberlyst 15) was exchanged with various metal cations. These metal-ion containing polymers were checked for triphenylphosphine absorbtion by observing the change in PPh_3 concentration in THF or acetone solution by ^{1}H nmr. Results of these experiments are summarized in Table I. Silver(I) polystyrene sulfonate ($\underline{A}$) was clearly the most efficient phosphine absorber, and this polymer was used in subsequent studies.

To further elucidate the behavior of $\underline{A}$, absorption of PPh_3 was observed by ^{31}P nmr. Use of this technique permits low phosphine concentrations similar to those expected in a catalytic reaction to be observed. At 4×10^{-2} $\underline{M}$, the amount of PPh_3 remaining in solution was 44% of the original amount after 12 min and 17% after 46 min; at 106 min the amount of PPh_3 was still 11% of the original amount and a small signal due to $OPPh_3$ had appeared. This is not surprising as this reaction was run in air. As the amount of PPh_3 remaining in solution is decreasing much less than exponentially, this suggests an equilibrium may ultimately be attained (equation 2). The low concentration of PPh_3 remaining accounts for the nonobservance of a signal in the ^{1}H nmr. The interval observed

$$2 \qquad PPh_3 + \underline{A} \rightleftharpoons \underline{A}\text{-}PPh_3$$

for the disappearance of most of the PPh_3 is consistent with the length of the induction period in PPh_3-inhibited hydrogenations (vida infra).

Once the absorption of PPh_3 by $\underline{A}$ had been verified, attempts to use $\underline{A}$ as a rate accelerating cofactor in homogeneous catalysis were initiated. $RhClL_3$ was chosen as it is among the most-studied homogeneous hydrogenation catalysts.[1,5]

TABLE 1. Absorbtion of PPh_3 by Metal-ion Substituted Polystyrene sulfonate

metal ion	%PPh_3 absorbed from 0.04 $\underline{M}$ THF solution (12 h)
Co^{+3}	0
Co^{+2}	10
Ni^{+2}	10
Cu^{+2}	50
Ag^{+}	100 (1 h)

Initial results on hydrogenation of 1-octene, cyclohexene, and styrene proved somewhat disappointing in that the rate of hydrogenation, when A was added at the initiation of a hydrogenation (Procedure 1) was essentially unaffected. However, the efficiency of the polymeric reagent as a PPh_3 absorber in the presence of $RhClL_3$ was easily demonstrated by rapid formation of $[RhClL_2]_2$ when a solution of $RhClL_3$ was placed in contact with A under nitrogen. Dimer formation was observed both by ^{31}P nmr and by the formation of many small pale red crystals in the previously homogeneous solution. A control solution of $RhClL_3$ in absence of A showed no indication of dimer formation over a 3 h interval. The dimer is much less soluble than the monomer [2], and exhibits only 1/10 the catalytic activity of the monomer.[15] This greatly reduced activity was indeed observed when $RhClL_3$ was dissolved under N_2 in presence of A and subsequently used as a hydrogenation catalyst.

The lack of dimer formation in a catalytically active solution is largely attributable to the affinity of $RhClL_2$ for H_2.[16] Indeed, a solution prepared by dissolving $RhClL_3$ under H_2, in presence of A (procedure 2) displayed no loss in catalytic activity. H_2RhClL_3 is believed to dissociate to a much smaller degree than $RhClL_3$, and has a concomitantly smaller tendency to dimerize.[1,15]

Evidence of the effectiveness of A in absorbing PPh_3 from a catalytically active solution is illustrated in Figure 1. When A was added during a hydrogenation which was inhibited by excess PPh_3 the rate increased to that observed in the absence of any excess ligand. Thus A absorbs free PPh_3 from a catalytically active solution but does not activate H_2RhClL_3 during a catalysis.[16]

The difference between this ligand-absorbing polymer and its monomeric analog is apparent. Silver(I)p-toluene sulfonate (B) is light sensitive, decomposing over two days; samples of the polymeric analog (A) show no sign of decomposition or loss of activity after six months. When B was added to a catalytically active solution of $RhClL_3$, H_2, and styrene, the reaction quickly stopped and a black insoluble precipitate formed. This may be a silver-rhodium

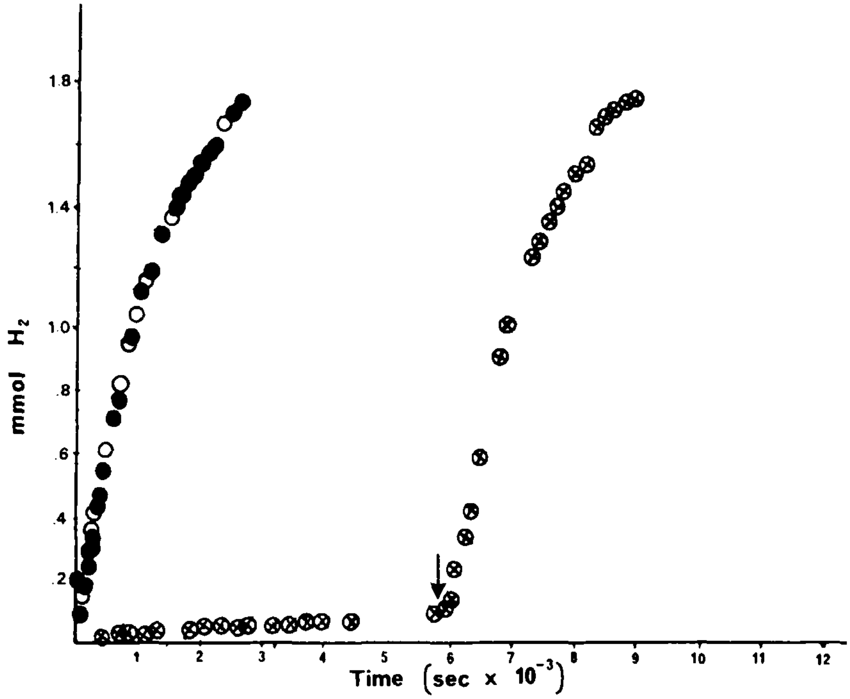

FIGURE 1. Hydrogenation of styrene (0.11 M) catalyzed by 2.3 x 10^{-3} M $RhClL_3$ in toluene at 25°C in the absence of both A and any excess PPh_3 (O), in the presence of A (●), and in the presence of excess PPh_3 (1.6 x 10^{-2} M (⊗)). The effect of rate acceleration in the latter experiments reflects addition of A at 5900 s (arrow in Figure).

complex of the type reported by Vrieze.[17] When excess PPh_3 was present, the addition of B gave the same result as addition of A. As [B] $\cong$ [PPh_3] in this case, apparently B reacts with PPh_3 rather than with $RhClL_3$.

Competition for the dissociated PPh_3 *ligand appeared to be* the reason for lack of any enhanced hydrogenation rate in presence of A. Therefore, displacement of a PPh_3 ligand prior to catalysis might lead to enhanced hydrogenation activity. Fortunately, $RhClL_3$ which is only a poor hydrogenation catalyst for ethylene [18], reversibly forms a π-complex with ethylene; this is stable in solution only under ethylene atmosphere.[19] (equation 3) $RhClL_3$ was

$$3 \quad RhClL_3 \;+\; C_2H_4 \rightleftharpoons (C_2H_4)RhClL_2 \;+\; L \qquad K_{eq} \cong 0.4 \; [19]$$

dissolved under ethylene atmosphere in presence of A; after 900 s alkene was added and after 1000 s ethylene was carefully removed. This solution hydrogenated various alkenes from 1.3 to 12 times faster than a solution which underwent ethylene pretreatment in absence of A, or a $RhClL_3$ solution which contained no polymeric reagent and did not undergo ethylene pretreatment, i.e., an unmodified hydrogenation. (These results are displayed in Table 2.) Apparently, ethylene displaces PPh_3 in $RhClL_3$, allowing PPh_3 to be absorbed by A while preventing dimerization of $RhClL_2$. Addition of alkene and removal of ethylene allow formation of a $RhClL_2$-(alkene) complex; once hydrogenation commenced, equilibrium 1 has effectively been shifted to the right and hydrogenation occurs at a faster rate. The rate enhancement observed is greatest for those alkenes which form strong complexes with $RhClL_3$ and are slowly hydrogenated, consistent with formation of a higher concentration of $RhClL_2$(alkene) in solution than would be found in absence of ethylene pretreatment in presence of A.

TABLE 2. Hydrogenation of Alkenes by $RhClL_3$ after Ethylene Pretreatment

alkene	[alkene],M	rate in presence of A[a]	rate in absence of A[a]	rate enhancement
1-hexene	0.35	23.9	12.2	1.96
cyclohexene	0.29	18.1	13.4	1.35
norbornene	1.03	36.6	21.3	1.72
norbornadiene	1.09	4.23	0.35	12.1
ethylene	--	4.4	0.74	5.8
styrene	0.21	60.	60.	1.0

[a] rate expressed as mmol hydrogen consumed/ $[RhClL_3]\cdot$min.

A comparison to work reported by Wilkinson in 1968 [11] is instructive. The catalyst $RhClL_n$ (n=2,3) was formed in situ by combination of varying ratios of PPh_3 and $[Rh(cod)Cl]_2$ with alkene under H_2. These reactions were run at rhodium and alkene concentrations comparable to those used in this work; a rate enhancement of 1.4 for hydrogenation of 1-hexene was observed for n=2 as opposed to n=3. This compares with the twofold rate enhancement seen in this work following ethylene activation in presence of A, as opposed to an unmodified hydrogenation using $RhClL_3$. The consistency of these results suggests that the concentration of $RhClL_2$ is indeed increased when ethylene pretreatment is employed in presence of A.

In order to test the effectiveness of ethylene pretreatment for complexes of the general formula $RhClL_3$, hydrogenations using $RhCl(PEtPh_2)_3$ were also investigated. All results with this compound were virtually identical to those found for $RhCl(PPh_3)_3$, except that ethylene pretreatment deactivated the catalyst. No ethylene complex with $RhCl(PEtPh_2)_3$ is known, so this is not entirely unexpected.

The effectiveness of a polymeric phosphine absorber as a rate-accelerating cofactor in homogeneous catalysis has been demonstrated. Application of this reagent to other phosphine-containing homogeneous transition metal catalysts is currently under investigation.

ACKNOWLEDGEMENTS

Generous support of this research was provided by the Department of Energy, the Office of Naval Research, and the Center for Energy and Mineral Resources at Texas A&M University.

REFERENCES

[1] James, B. R. "Homogeneous Hydrogenation"; John Wiley & Sons: New York, 1973.

[2] Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. J. Chem. Soc.(A) 1966, 1711-1732.

[3] Lehman, D. D.; Shriver, D. F.; Wharf, I. *J. Chem. Soc., Chem. Commun.* 1979, 1486. Arai, H.; Halpern, J. ibid 1971, 1571-2. Eaton, D. R.; Stuart, S. R. *J. Amer. Chem. Soc.* 1968, *90*, 4170-2.

[4] Hoffman, P. R.; Caulton, K. G. *J. Amer. Chem. Soc.* 1975, *97*, 4221-8.

[5] Dolcetti, G.; Hoffman, N. W. *Inorg. Chim. Act.* 1974, *9*, 269-303. Harmon, R. E.; Gupta, S. K.; Brown, D. J. *Chem. Rev.* 1973, *73*, 21-52.

[6] Halpern, J; Okamoto, T.; Zakhariev, A. *J. Molec. Catal.* 1976, *2*, 65-8 and references therein.

[7] Gosser, L. W.; Knoth, W. H.; Parshall, G. W. *J. Molec. Catal.* 1977, *2*, 253-263. Gosser, L. W.; Knoth, W. H.; Parshall, G. W. *J. Amer. Chem. Soc.* 1973, *95*, 3436-7.

[8] Strauss, S. H.; Shriver, D. F. *Inorg. Chem.* 1978, *17*, 3069-3074. Porter, R. A.; Shriver, D. F. *J. Organomet. Chem.* 1975, *90*, 41-7. Hidai, M.; Kuse, T.; Hidita, T.; Uchida, Y.; Misono, A. *Tetrahedron Lett.* 1970, 1715-6.

[9] Chaurm, Y.; Commereuc, C.; Dawans, F. *Prog. Polym. Sci.* 1977, *5*, 95-226.

[10] Shriver, D. H. "Manipulation of Air-Sensitive Compounds"; New York: McGraw-Hill, 1969.

[11] Moltelatici, S.; van der Ent, A.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. (A)* 1968, 1054-8.

[12] Dorfner, K. "Ion Exchangers: Properties and Applications"; Ann Arbor Science Publishers, Inc.: An Arbor, Mich., 1973; 99-115.

[13] Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G. M. *J. Amer. Chem. Soc.* 1977, *99*, 4736-4745. Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G. M. *J. Amer. Chem. Soc.* 1977, *99*, 4746-4756.

[14] A report on decarbonylation of metal carbonyls by $RhCl(PPh_3)_3$ led to abandonment of any metal carbonyl as a phosphine-acceptor: Varshavsky, Yu. S.; Shestakova, E. P.; Kiseleva, N. V.; Cherkasova, T. G.; Buzina, N. A.; Bresler, L. S.; Kormer, V. A. *J. Organomet. Chem.* 1979, *170*, 81-83.

[15] Halpern, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* 1973, 629-630. Meakin, P.; Jesson, J. P.; Tolman, C. A. *J. Amer. Chem. Soc.* 1972, *94*, 3240-3242.

[16] k for $RhClL_3 \rightleftharpoons RhClL_3H_2 \simeq 2 \times 10^4 \mathrm{mol}^{-}\mathrm{dm}^3$ [17] and Rousseau, C.; Evard, M.; Petit, F. *J. Molec. Catal.* 1977/8, *3*, 309-324.

[17] Kuyper, J.; Vrieze, K. J. Organomet. Chem. 1976, 107, 129-138.

[18] Ohtani, Y.; Yamagishi, A.; Fujumoto, M. Bull. Chem. Soc. Jpn. 1979, 52, 2149-50.

[19] Tolman, C. A.; Meakin, P. S.; Lindmer, D. L.; Jesson, J. P. J. Amer. Chem. Soc. 1974, 96, 2762-2774. Ohtani, Y.; Yamagishi, A.; Fujimoto, M. Bull. Chem. Soc. Jpn. 1979, 52, 69-72; 1979, 52, 1537-8; 1979, 52, 3437-8; 1977, 50, 1453-9.