An active and stable $RhH(CO)(PPh_3)_3$-derived SiO_2-tethered catalyst via a thiol ligand for cyclohexene hydroformylation

L. Huang* and S. Kawi

Chemical and Process Engineering Centre, and Department of Chemical and Environmental Engineering,
National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

Received 13 May 2003; accepted 22 July 2003

A $RhH(CO)(PPh_3)_3$-derived SiO_2-tethered catalyst via a thiol ligand is not only quite effective and stable for cyclohexene hydroformylation under the milder conditions of 100 °C and 28 bar of equimolar CO and H_2 but also more active than the corresponding homogeneous catalyst. This catalyst has the advantage in resistance to rhodium leaching over homologous tethered catalysts via phosphine and amine ligands.

KEY WORDS: $RhH(CO)(PPh_3)_3$; SiO_2-tethered catalyst; thiol ligand; cyclohexene hydroformylation.

1. Introduction

The hydridic complex $RhH(CO)(PPh_3)_3$ is known as a most effective catalyst precursor used in hydroformylation [1,2]. It has never been extensively studied in the area of homogeneous olefin hydroformylation [1–8] since the dissociation of a PPh_3 ligand gives directly a catalytic active species $RhH(CO)(PPh_3)_2$. Great research interest has been shown in the use of the title complex in that not only do the reaction proceeds at ambient temperature and pressure and from alk-1-enes produce ~95.5% of the straight-chain aldehyde but the complex is also indefinitely stable in air and is readily prepared [2]. Also, wide attempts have been made to immobilize this complex to organic polymers and inorganic materials for the heterogenization purpose [9–13]. Some satisfactory achievements have been made regarding the recycling of supported catalysts and the exploitation of fixed-bed catalysts with high activity, selectivity and *n*/*i*-aldehyde ratio in hydroformylation, which are comparable to those of homogeneous catalysts. Loss of the rhodium by leaching was claimed to be dependent on the property of support and the reaction conditions. Of all the techniques of heterogenizing this complex, complexation of donor ligands to rhodium is the most effective and attractive, which is referred to as a key factor linking the complex to the support by chemical bond. This approach may prevent rhodium leaching efficiently on principle. To date, only a phosphorus-containing organosilane has been reported to be used to prepare an SiO_2-supported $RhH(CO)(Ph_2P(CH_2)_2Si(O_s)_3)_3$ (O_s: surface oxygen) via $RhH(CO)(Ph_2P(CH_2)_2Si(OEt)_3)_3$ [14]. The $RhH(CO)(Ph_2P(CH_2)_2Si(O_s)_3)_3/SiO_2$-derived catalyst was shown to not only have high activity and *n*/*i*-aldehyde ratio for hexene-1 hydroformylation but also have good resistance to rhodium leaching [15,16]. No other donor ligands have been reported to affect the catalytic properties and stability of this kind of catalysts. Meanwhile, it is well known that various rhodium thiolate complexes such as $[Rh(\mu\text{-}SR)(L)(L')]_2$ (L, L = COD or L = CO, L′ = PR3; COD = cyclooctadiene), $Rh_2(CO)_2(PBu^t_3)_2(\mu\text{-}Cl)(\mu\text{-}SR)(R = (CH_2)_3\ Si(OEt)_3)$ and $[Rh(\mu\text{-}S(CH_2)_3Si(OMe)_3)_2(CO)_2]_2$ are active catalyst precursors for homogeneous and heterogeneous olefin hydroformylation [8,17–32].

In this context, we were interested in choosing phosphorus-, nitrogen- and sulphur-containing organosilanes as donor ligands to prepare and study $RhH(CO)(PPh_3)_3$-derived SiO_2-tethered catalysts for hydroformylation. We intended to understand the effects of different donor ligands on the catalytic properties and stability of supported phosphine-containing rhodium complexes by comparison of the results obtained with phosphine, amine and thiol ligands.

2. Experimental

SiO_2, which is a silica "Aerosil" with a surface area of $380\,m^2/g$, was purchased from Degussa. Cyclohexene (99%) was purchased from Merck. $Cl(CH_2)_3Si(OMe)_3$ (97%), $H_2N(CH_2)_3Si(OEt)_3$ (99%), $HS(CH_2)_3Si(OMe)_3$ (96%) and $KPPh_2$ (0.5 M solution in tetrahydrofuran (THF)) were supplied by Aldrich. $RhH(CO)(PPh_3)_3$ (98%) was supplied by Strem. All other reagents were purchased commercially. Organic solvents were distilled and dried prior to use. The gases $CO + H_2$ and N_2 had a purity of 99.999%.

---

*To whom correspondence should be addressed.
E-mail: huanglin1@yahoo.com

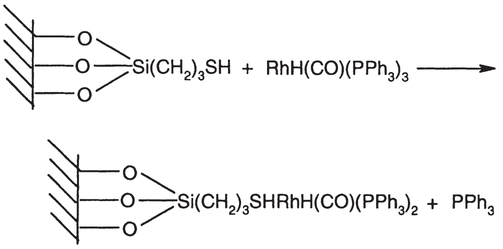
SiO_2 was subjected to dehydration at 200 °C prior to the following experiments. Donor ligand-functionalized SiO_2 was prepared by reacting SiO_2 (2.0 g) with a toluene (150 mL) solution of organosilane (10 mL) under refluxing under N_2 for 16 h. The resulting solid was filtered off, washed with chloroform (200 mL) and dried in vacuum. The chlorinated, aminated and thiolated SiO_2 samples thus prepared contained 1.6% Cl, 1.1% N, and 1.3% S, respectively. The chlorinated SiO_2 was further refluxed with $KPPh_2$ (1 mL) in THF (25 mL) under N_2 for 1 h. After filtration, washing with 100 mL of methanol and drying in vacuum, the resulting phosphinated SiO_2 contained 0.1% Cl and 0.8% P. Phosphinated, aminated and thiolated SiO_2 samples are denoted as $SiO_2(PPh_2)$, $SiO_2(NH_2)$, and $SiO_2(SH)$, respectively. Tethered catalyst precursors were prepared by stirring functionalized SiO_2 (1.0 g) with a toluene (50 mL) solution of $RhH(CO)(PPh_3)_3$ (0.180 g) at 70 °C under N_2 for 16 h. In all cases, the solid color turned green and the green solution became almost colorless at the end of the reaction, indicative of the tethering of $RhH(CO)(PPh_3)_3$ to the support via complexation of supported thiol. Afterward the liquid was drawn off with a syringe under N_2, and the solid was washed three times with toluene under N_2 followed by drying in vacuum. The rhodium contents of $SiO_2(PPh_2)$-, $SiO_2(NH_2)$-, and $SiO_2(SH)$-tethered catalyst precursors were 1.75, 1.75, and 1.73%, respectively.

Hydroformylation of cyclohexene was conducted under 28 bar of an equimolar CO and H_2 mixture at 100 °C in an autoclave. 300 mg of catalyst precursor, 12 mL of cyclohexene and 55 mL of THF were first transferred to the autoclave inside a glove box. Subsequently, the $CO + H_2$ mixture was charged after the reaction system had been purged with this reaction gas mixture. Sampling of the reaction mixture was done during the course of the reaction. The samples were analyzed by gas chromatography.

^{31}P NMR spectra were recorded on a 300-MHz Bruker ACF 300 FT-NMR spectrophotometer. Chemical shifts were referenced to Na_2HPO_4 at 0 ppm. The rhodium contents of the samples were determined by atomic absorption spectroscopy. The chlorine, sulfur and phosphorus contents of the samples were analyzed by X-ray fluorescence. Thermogravimetric analysis was used to estimate the contents of chlorine, nitrogen and sulfur in $SiO_2(Cl)$, $SiO_2(NH_2)$, and $SiO_2(SH)$.

3. Results and discussion

Figure 1 shows the solid state ^{31}P NMR spectra before and after the reaction of $RhH(CO)(PPh_3)_3$ with $SiO_2(SH)$. The spectrum of solid $RhH(CO)(PPh_3)_3$ exhibited a set of signals at δ 44.4, 34.1, 33.6, and 32.8sh, while the spectrum of $RhH(CO)(PPh_3)_3/SiO_2(SH)$ presented a broad signal at δ 32.8 and a sharp signal at δ 0. The organometallic chemistry of phosphine-containing rhodium complexes with sulfur donor ligands is poorly established and there are no solid-state ^{31}P NMP data available of phosphino–rhodium–thiolate complexes. However, the observed ^{31}P NMR signal positions of supported complex are significantly different from those of solid $RhH(CO)(PPh_3)_3$. This spectral evolution may be closely related to the coordination of a supported thiol to the rhodium center of $RhH(CO)(PPh_3)_3$. Referring to the case with immobilization of $Rh(PPh_3)_3Cl$ on MCM-41(PPh_2) reported recently [31], a similar ^{31}P NMR spectral evolution before and after immobilization has been explained by substitution of a PPh_3 with a supported phosphine with the formation of MCM-41($PPh_2RhCl(PPh_3)_2$). Earlier studies have also demonstrated that the reaction of a complex on the surface is favored with only one supported ligand to form a simple product [32]. Thus, we infer without direct evidence that the reaction between $RhH(CO)(PPh_3)_3$ and $SiO_2(SH)$ would follow the same mechanism and form $SiO_2(SHRhH(CO)(PPh_3)_2)$ with the concomitant dissociation of a PPh_3:



Similar results may be speculated with the formation of $SiO_2(PPh_2RhH(CO)(PPh_3)_2)$ and $SiO_2(NH_2RhH(CO)(PPh_3)_2)$ on $SiO_2(PPh_2)$, and $SiO_2(NH_2)$.

The functionalized SiO_2-tethered $RhH(CO)(PPh_3)_3$ was tested in cyclohexene hydroformylation. Table 1 lists the comparative catalytic results after 20 h of reaction over the catalyst systems studied. All the catalysts displayed selectivity as high as above 98% to cyclohexane carboxaldehyde with no activity to alcohols. $RhH(CO)(PPh_3)_3/SiO_2(SH)$ resulted in continuously increased turnover for conversion of cyclohexene during three reaction cycles running. From the second cycle, it was noted that the activity of RhH(CO), $(PPh_3)_3/SiO_2(SH)$-derived catalyst was higher than that of a homogeneous catalyst derived from $RhH(CO)(PPh_3)_3$. In the third cycle, the turnover attained to 2400 (mol cyclohexene/mol Rh). When a reaction cycle of 20 h ceased, the solid catalyst was filtered off from the reaction mixture in air for the next cycle and elemental analysis. The green color of the catalyst remained unchanged during the three cycles. 1.65% of Rh was retained on the support and the liquid-phase color was light green after the first cycle. The rhodium content of the catalyst no longer declined and the liquid phase was colorless from the second cycle.

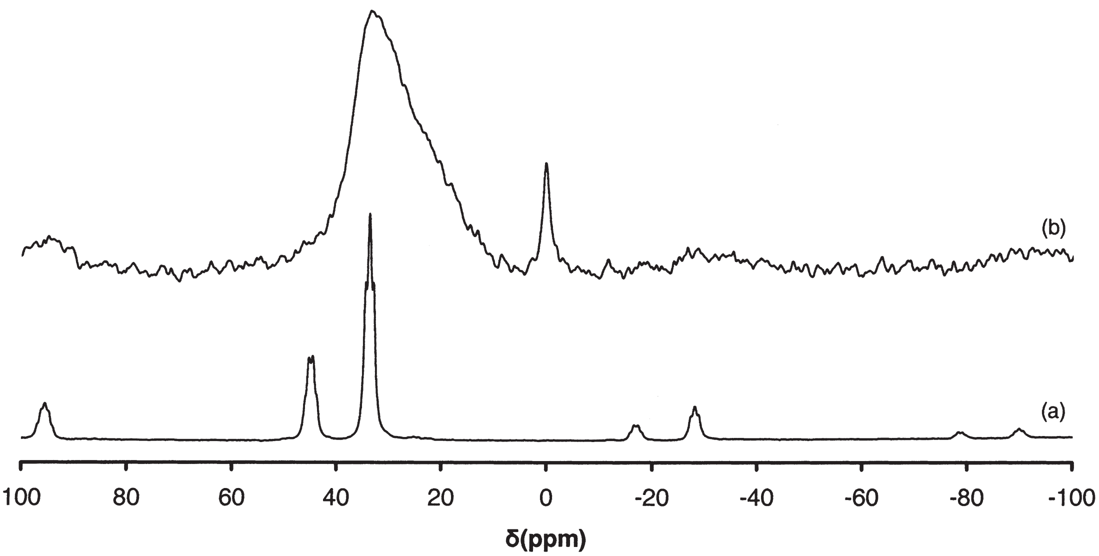


Figure 1. Solid state ^{31}P NMR spectra of (a) $RhH(CO)(PPh_3)_3$ and (b) $RhH(CO)(PPh_3)_3/SiO_2(SH)$.

This demonstrates that only a weak leaching of rhodium from the support occurs relative to the initial rhodium loading (1.73%) under catalytic conditions. Comparatively, a considerable rhodium leaching was found from $RhH(CO)(PPh_3)_3/SiO_2(NH_2)$ during the first cycle, although it gave rise to a satisfactory turnover for the conversion of cyclohexene at 1590 (mol cyclohexene/mol Rh). The liquid-phase color became green and the detected rhodium content on the catalyst was 0.85% after the first cycle, referring to the initial rhodium loading (1.75%). An even heavier rhodium leaching was observed with $RhH(CO)(PPh_3)_3/SiO_2(PPh_2)$. The solid phase became nearly colorless and the remaining rhodium content on the catalyst was as low as 0.12% after the first cycle, starting from 1.75% of rhodium loading. Moreover, this catalyst system led to a worse turnover for conversion of cyclohexene at 316 (mol cyclohexene/mol Rh).

From the variation of turnovers of cyclohexane carboxaldehyde formed on these catalyst systems with reaction time shown in figure 2, it is seen that all the catalyst systems maintained hydroformylation activity throughout the 20-h reaction since their turnovers of aldehyde formed increased continuously with reaction time. In the first hour, the homogeneous RhH, $(CO)(PPh_3)_3$ system was the most active and all the supported catalyst systems were less active. Then, the activity of the former greatly decreased so that the turnover of aldehyde on it became inferior to those on $RhH(CO)(PPh_3)_3/SiO_2(SH)$ (second and third cycles). Thus, the $SiO_2(SH)$-tethered catalyst is regarded as being stable for recycling and more active after undergoing a reaction period.

The results reveal that the $SiO_2(SH)$-tethered catalyst is not only more active than the homogeneous catalyst from the second cycle but is also quite stable for recycling, that the $SiO_2(NH_2)$-tethered catalyst is fairly active in the first cycle but has high rhodium leaching and that the $SiO_2(PPh_2)$-tethered catalyst not only is much less active than the homogeneous catalyst but also

Table 1
Catalytic properties of $RhH(CO)(PPh_3)_3$-derived catalysts[a] in cyclohexene hydroformylation[b]

Catalyst precursor	Cyclohexene conversion (%)	Turnover[c] (mol/mol Rh)	Product distribution (mol%)	
			Cyclohexane	Cyclohexane carboxyaldehyde
$RhH(CO(PPh_3)_3$[d]	44.2	1632	0.5	99.5
$RhH(CO(PPh_3)_3/SiO_2(SH)$				
1st cycle	56.6	1332	0.7	99.3
2nd cycle	81.9	2020	0.4	99.6
3rd cycle	97.3	2400	0.7	99.3
$RhH(CO(PPh_3)_3/SiO_2(NH_2)$	68.4	1590	2.1	97.9
$RhH(CO(PPh_3)_3/SiO_2(PPh_2)$	13.6	316	0.7	99.3
$Rh_4(CO)12/SiO_2(SH)$	0	—	—	—

[a] 0.30 g of catalyst precursor with nearly 2.0% Rh loading.

[b] Reaction conditions: 12 mL of cyclohexene, $H_2/CO = 1$, 28 bar, 100 °C, 20 h/cycle.

[c] For conversion of cyclohexene.

[d] 0.030 g.

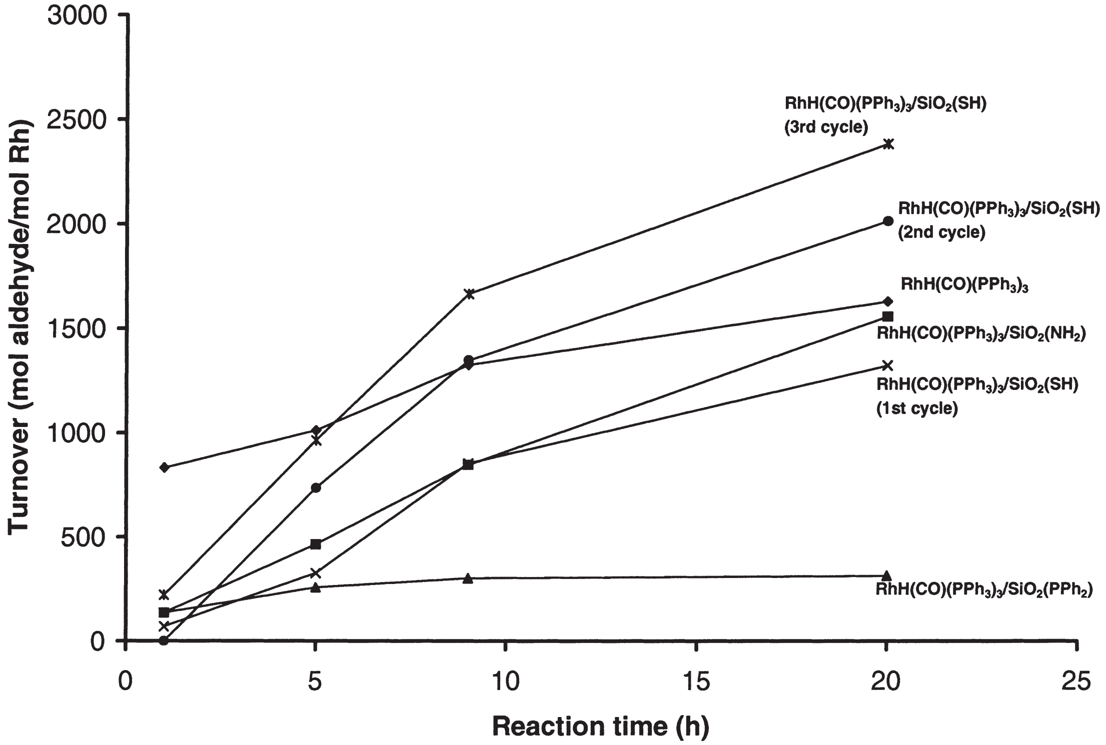


Figure 2. Turnovers of cyclohexane carboxaldehyde formed as a function of reaction time over $RhH(CO)(PPh_3)_3$-derived catalysts.

has heavy rhodium leaching. Of equal catalytic results can be $RhH(CO)(PPh_3)_3/SiO_2$ without tethering and $RhH(CO)(PPh_3)_3$. Without tethering, a silica-supported rhodium complex can be referred to as a *rhodium complex* simply physisorbed on the silica surface. Such a catalyst system has proven to result in almost complete rhodium complex leaching during the liquid-phase cyclohexene hydroformylation and to exhibit catalytic properties quite similar to those of a corresponding homogeneous catalyst [33]. Therefore, $RhH(CO)(PPh_3)_3/SiO_2$ without tethering is insignificant for use in heterogeneously catalytic cyclohexene hydroformylation. The good performances of the $SiO_2(SH)$-tethered catalyst are suggested to result from the promotion and stabilization of supported thiol on the catalysis of a phosphine-containing rhodium complex because a $SiO_2(SH)$-tethered phosphine-free rhodium complex is inactive for cyclohexene hydroformylation, as seen in table 1. The distinct properties of $RhH(CO)(PPh_3)_3$-derived SiO_2-tethered catalysts via the three kinds of donor ligands in hydroformylation may be correlated to the strength of coordination of the donor ligands to the rhodium center of $RhH(CO)(PPh_3)_3$. As compared to phosphine and amine, coordination of a thiol produces a strong S–Rh bond, which is attributed to the strong $d\pi$–$p\pi$ bonding, and thus may not only improve the electronic factor of the complex toward catalytic hydroformylation but also favor the immobilization of the resulting rhodium complex. Such an electronic effect of thiol is essentially accompanied by the concerted action of thiol and phosphine on the catalysis for hydroformylation that leads to the enhancement of catalytic activity compared to that of the homogeneous catalyst derived from $RhH(CO)(PPh_3)_3$.

4. Conclusions

$RhH(CO)(PPh_3)_3$ is tethered on $SiO_2(PPh_2)$, $SiO_2(NH_2)$, and $SiO_2(SH)$ possibly in the forms of $SiO_2(PPh_2RhH(CO)(PPh_3)_2)$, $SiO_2(NH_2RhH(CO)(PPh_3)_2)$ and $SiO_2(SHRhH(CO)(PPh_3)_2)$ respectively. The $SiO_2(SHRhH(CO)(PPh_3)_2)$-derived catalyst exhibits high activity for cyclohexene hydroformylation at 28 bar of equimolar CO and H_2 and at 100 °C and fair stability for recycling. Its activity is superior to that of the $RhH(CO)(PPh_3)_3$-derived homogeneous catalyst. The catalysts derived from $SiO_2(PPh_2RhH(CO)(PPh_3)_2)$ and $SiO_2(NH_2RhH(CO)(PPh_3)_2)$ display serious rhodium leaching during the reaction.

References

[1] J.A. Osborn, G. Wilkinson and J.F. Young, Chem. Commun. (1965) 17.
[2] C.K. Brown and G. Wilkinson, J. Chem. Soc. A (1970) 2753.
[3] D. Evans, G. Yagupsky and G. Wilkinson, J. Chem. Soc. A (1968) 2660.
[4] K.L. Olivier and F.B. Booth, Hydrocarbon Process. 49 (1970) 112.
[5] B. Cornils, R. Payer and K.C. Traenckner, Hydrocarbon Process 54 (1975) 83.
[6] T. Shimizu, German Patent 2,538,364 (1976).

[7] B.E. Hanson and M.E. Davis, J. Chem. Educ. 64 (1987) 928.

[8] Ph. Kalck and F.S. Spirau, New J. Chem. 13 (1989) 515.

[9] C.U. Pittman, Jr. and R.M. Hanes, J. Am. Chem. Soc. 98 (1976) 5402 and references therein.

[10] L.A.Gerritsen, A. van Meerberk, M.H. Vreugdenhil and J.J.F. Scholton, J. Mol. Catal. 9 (1980) 139.

[11] R.S. Drago, M.J. Barnes and M.J. Naughton, U.S. Patent 5,012,008 (1991).

[12] K. Mukhopadhyay and R.V. Chaudhari, J. Catal. 213 (2003) 73.

[13] K. Mukhopadhyay, A.B. Mandale and R.V. Chaudhari, Chem. Mater. 15 (2003) 1766.

[14] K.G. Allum, R.D. Hancock, S. Mckenzie and R.C. Pitkethly, in *Catalysis*, J.W. Hightower (ed), Vol. 1 (Amsterdam, 1963) p. 477.

[15] R.D. Hancock, I.V. Howell, R.C. Pitkethly and P.J. Robinson, in *Catalysis: Heterogeneous and Homogeneous*, B. Delmon and G. James (eds) (Amsterdam, 1975), p. 361.

[16] K.G. Allum, R.D. Hancock, I.V. Howell, S. Mckenzie, R.C. Pitkethly and P.J. Robinson, J. Catal. 43 (1976) 322.

[17] Ph. Kalck, J.M. Frances, P.M. Pfister, T.G. Southern and A. Thorez, J. Chem. Soc., Chem. Commun. (1983) 510.

[18] A. Dedieu, P. Escaffre, J.M. Frances, Ph. Kalck and A. Thorez, New J. Chem. 10 (1986) 631.

[19] C. Claver, Ph. Kalch, M. Ridmy, A. Thorez, L.A. Oro, M.T. Pinillos, M.C. Apreda, F.H. Cano and C. Foces-Foces, J. Chem. Soc., Dalton Trans. (1988) 1523.

[20] R.M. Catala, D. Cruz-Garritz, A. Hills, D.L. Hughes, R.L. Richards, P. Sosa, P. Terreros and H. Terrens, J. Organomet. Chem. 359 (1989) 219.

[21] C. Claver, A.M. Masdeu, N. Ruiz, C. Foces-Foces, F.H. Cano, M.C. Apreda, L.A. Oro, J. Garcia-Alejandre and H. Torrens, J. Organomet. Chem. 398 (1990) 177.

[22] J.C. Bayon, P. Esteban, J. Read, C. Claver and A. Ruiz, J. Chem. Soc., Chem. Commun. (1989)1056.

[23] A. Polo, C. Claver, S. Castillon, A. Ruiz, J.C. Bayon, J. Read, C. Mealli and D. Masi, Organometallics 11 (1992) 3525.

[24] A. Polo, E. Fernandez, C. Claver and S. Castillon, J. Chem. Soc., Chem. Commun. (1992) 639.

[25] A.M. Masdeu, A. Orejion, A. Ruiz, S. Castillon and C. Claver, J. Mol. Catal. 94 (1994) 149.

[26] A. Aaliti, A.M. Masdeu, A. Ruiz and C. Claver, J. Organomet. Chem. 489 (1995) 101.

[27] M. Eisen, J. Blum, H. Schumann and S. Jurgis, J. Mol. Catal. 31 (1985) 317.

[28] M. Eisen, T. Bernstein, J. Blum and H. Schumann, J. Mol. Catal. 43 (1987) 199.

[29] H. Gao and R.J. Angelici, Organometallics 17 (1998) 3063.

[30] H. Gao and R.J. Angelici, J. Mol. Catal. A 145 (1999) 83.

[31] S-G. Shyu, S-W. Cheng and D-L. Tzou, Chem. Commun. (1999) 2337.

[32] K.G. Allum, R.D. Hancock, I.V. Howell, S. Mckenzie, R.C. Pitkethly and P.J. Robinson, J. Organomet. Chem. 87 (1975) 203.

[33] L. Huang, J.C. Wu and S. Kawi, J. Mol. Catal. in press.