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Activity of homogeneous transition metal catalysts for oxidative carbonylation of aniline to *N,N'*diphenyl urea

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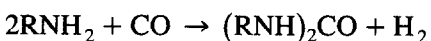
Abstract

Oxidative carbonylation of aniline to *N,N'*diphenyl urea was achieved at 100°C and atmospheric pressure conditions. The screening of several homogeneous transition metal complexes was carried out. The best catalytic activity was shown by [Ru(CO)₃I₃]NBu₄ catalyst. The effect of solvents, temperature, aniline and promoter concentration etc. on the activity and selectivity of this catalyst was studied. The activation energy of the reaction is evaluated as 26.6 kcal/mol. A plausible mechanistic pathway for oxidative carbonylation of aniline to diphenyl urea has also been proposed. © 1997 Published by Elsevier Science B.V.

Keywords: Carbonylation; Oxidative carbonylation; Homogeneous catalysts; Transition metal catalyst; Diphenyl urea; Aniline

1. Introduction

Catalytic carbonylation of aromatic amines to diarylurea derivatives in presence of metal carbonyls is well known [1–3]. Generally severe conditions are required to catalyze this reaction. This is due to the fact that abstraction of hydrogen atom from amine is a highly energetic step [4].



$$\Delta G_f^0_{298} = -7.5 \text{ kcal/mol}$$

The presence of hydrogen acceptor compounds such as sulphur in the system facilitates this reaction and reaction proceeds under comparatively mild conditions [5,6]. Aromatic nitro

compounds are often used as a hydrogen acceptor in carbonylation of aromatic amines to ureas [7]. The use of dioxygen in the system as a hydrogen acceptor greatly enhances the carbonylation rate and reaction proceeds under mild conditions [8].

The use of Se, Te and Co as carbonylation catalyst has also been demonstrated [9–11]. These catalysts convert aliphatic amines to, corresponding urea derivatives in high yields but show poor activity for oxidative carbonylation of aromatic amines [12].

Isocyanates are conventionally manufactured by phosgenation route, but this route faces severe corrosion problems. In recent years, an alternate route has been developed via carbonylation of nitrocompounds. More than three decades have passed since the feasibility of this route was shown by Hardy and Bennet in 1966, [13]. However, commercial production of iso-

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cyanates by this route has been delayed mainly because of following reasons:

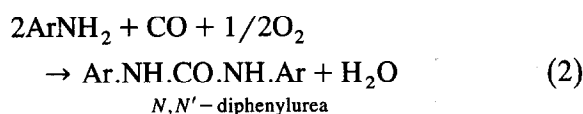
- The process utilizes three CO molecules and unless CO is available at a negligible cost (as a byproduct) the process is not going to be economical.

- Utilizes precious metal catalyst (Pd, Rh, Pt) the recycle and recovery of which is difficult.

- Isocyanates are highly reactive intermediates and hence their selectivity is sensitive to process parameters.

Fukuoka et al. [14,15] have shown that oxidative carbonylation of aniline in presence of Pd⁰/NaI, produces phenylcarbamate in high yield. Arylcarbamates are commercially important intermediates in pesticide and polymer industry. Decomposition of carbamates readily gives isocyanates used in making monomeric MDI (methylene diphenyl diisocyanate).

Oxidative carbonylation of various amines has been studied in detail, however, in most of the earlier reports, supported Pd catalysts have been used [16] and there are very few reports on the homogeneously catalyzed oxidative carbonylation of amines [17,18]. In this paper we report the oxidative carbonylation of aniline using homogeneous transition metal complexes at atmospheric pressure. The stoichiometric reaction can be described as:



The aim of the present work was to study various homogeneous Pd, Rh, Ru metal catalysts, effect of iodide containing promoters and solvents on the conversion of aniline and selectivity of *N,N'*diphenylurea.

2. Experimental

2.1. Materials

The transition metal salts such as PdCl₂, RuCl₃ · 3H₂O and RhCl₃ · 3H₂O, were pro-

cured from Arora-Matthey; India and were used as such. Aniline A.R. grade was freshly distilled before use. Carbon monoxide having a purity greater than 99.5% was used from the cylinder. Oxygen was supplied by Indian Oxygen, Mumbai.

2.2. Experimental procedure

2.2.1. Catalytic reactions

The transition metal salts such as PdCl₂, RhCl₃ · 3H₂O and RuCl₃ · 3H₂O were procured from Arora-Matthey and were used as such. Aniline A.R. grade was freshly distilled before use. Carbon monoxide gas was used from cylinders, purity of which was found to be greater than 99.5% by GC analysis. Infrared spectra were recorded on a Perkin Elmer 283 B spectrophotometer.

In a typical experiment, known quantities of aniline, catalyst, promoter and solvent were charged into the 75 cc glass reactor, and the contents were flushed with nitrogen. The glass reactor was heated to a desired temperature, and then flushed with CO:O₂, (2:1) and equalized to atmospheric pressure. All the experiments were carried out at atmospheric pressure using glass reactor and absorption of CO + O₂ was measured using glass burette apparatus. The details of experimental set-up are given elsewhere [19]. The reaction was carried out for five hours. After five hours, the contents were cooled, the liquid and gas samples were analyzed by GC Urea analysis was carried out on HPLC using Bondapak μ-phenyl S.S. column.

3. Results and discussion

The aim of this work was to study the activity and selectivity of homogeneous transition metal complex catalysts for the oxidative carbonylation of aniline. Several experiments were carried out in which product concentration versus time profiles were observed. The activity and selectivity for the fixed time duration were

calculated. The material balance was calculated by measuring the gas absorption as well as by the GC and HPLC analysis of the liquid samples for concentration of reactants and products. The material balance agreed to the extent of 95%, and there was no formation of CO₂ under the conditions of present study. In order to ensure that the catalyst activity remains constant throughout the run, some experiments on the reusability of the catalyst were also carried out. For this purpose, the reaction solution containing [Ru(CO)₃I₃]N(Bu)₄ catalyst was reused with fresh charge of aniline several times. Such experiments were carried out at 100°C, it was observed that even after five reuses, more than 95% of the catalyst activity was retained. The results on screening of catalysts effect of promoter and solvents are discussed in Section 3.1.

3.1. Screening of catalysts

Several Pd, Ru and Rh complex catalysts were tested for their activity and selectivity for oxidative carbonylation of aniline at 100°C and atmospheric pressure (CO + O₂). These experiments were carried out using dimethyl formamide (DMF) as a solvent. In all the cases only *N,N'*-diphenyl urea (DPU) was formed as a product. Table 1 shows the activity and selectiv-

ity of several transition metal complexes used in this work. It can be seen from the results (Table 1) that, the presence of iodine either as a promoter or as a ligand is essential for catalytic activity. The activity of catalysts containing Ru, was higher than those catalysts containing other noble metals like Pd and Rh. It was also observed that the activity of catalysts without iodine was very low (5, 9, 10, 13 in Table 1) as compared to the activity of catalyst systems containing iodine. Also the catalytic activity varies with variation in the ligand environment around the central metal atom. The highest activity was observed with [Ru(CO)₃I₃]NBu₄ complex as a catalyst and therefore, further studies were carried out using this catalyst. A typical plot of aniline concentration–time profile of aniline and urea along with the (CO + O₂) absorption is shown in Fig. 1. This figure indicates 97.5% material balance of liquid phase components and greater than 95% material balance of CO and O₂ consumed. This also confirms that no other side reaction occurs under the conditions of this study.

3.2. Screening of promoters

Iodide containing promoters are believed to play a key role in the mechanism of oxidative

Table 1
Screening of catalyst for oxidative carbonylation of aniline to *N,N'*-diphenylurea

No.	Catalyst ^a	Promoter	CO + O ₂ absorbed (cm ³)	Conversion of aniline (%)	Selectivity (%)
1	Ru(CO) ₃ I ₃ 18 crown 6 ether	Nil	235	52	100
2	Ru(CO) ₂ Cl ₂ (py) ₂	NaI	212	47	99
3	NBu ₄ Ru(CO) ₃ I ₃	Nil	267	59	99
4	Rh(CO) ₂ (acac)	NaI	163	36	98
5	RhCOCl(PPh ₃) ₂	Nil	45	10	98
6	RhCOCl(PPh ₃) ₂	NaI	131	29	99
7	RhCl ₃ (py) ₃	NaI	149	33	100
8	PdI ₂	Nil	118	26	99
9	Pd(C ₆ H ₅ NH ₂) ₂ Cl ₂	Nil	72	16	99
10	PdCl ₂ (PPh ₃) ₂	Nil	—	Nil	—
11	PdCl ₂ (PPh ₃) ₂	NaI	154	34	100
12	Pd(ppcn ₂)Cl ₂	NaI	149	33	98
13	Pd(SbPh ₃) ₃ Cl ₂	Nil	—	Nil	—

Conditions: Temperature = 100°C, concentration of aniline = 21.5 mmol, contact time = 5 h, CO + O₂ (atmospheric) = 2:1, concentration of catalyst = 1.3 mmol, solvent = DMF and reaction volume = 37 cm³.

^a Catalysts were prepared by procedures described elsewhere [27].

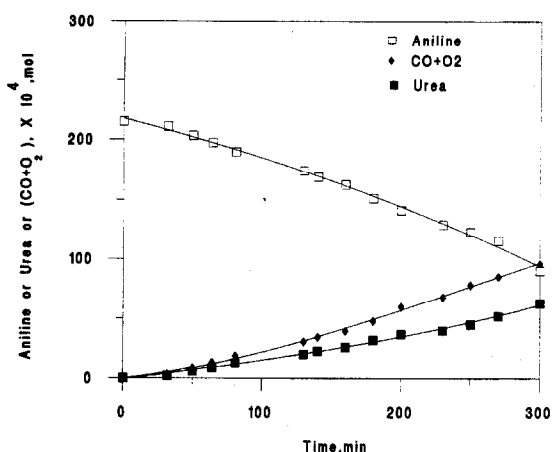


Fig. 1. A typical concentration–time profile for oxidative carbonylation of aniline. Reaction conditions: $[\text{Ru}(\text{CO})_3\text{I}_3]\text{NBu}_4$, (1.3 mmol); $\text{CO} + \text{O}_2$, (2:1); Pressure, (atmospheric); Temperature, (100°C); Stirrer speed, (2000 rpm); Reaction volume, (37 ml); Solvent, (DMF).

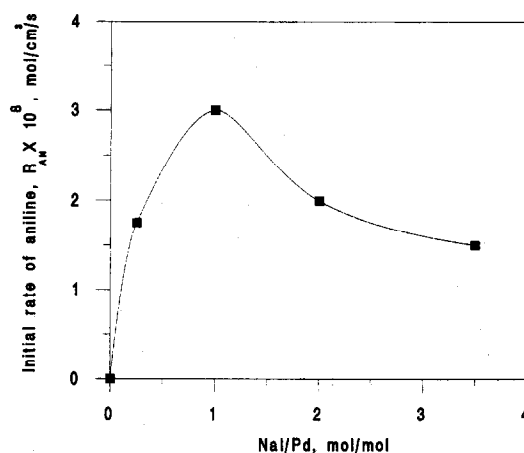


Fig. 2. Effect of NaI/Pd mol ratio on initial rate of reaction. Reaction conditions: NaI, (1.3 mmol); $\text{CO} + \text{O}_2$, (2:1); Pressure, (atmospheric); Temperature, (100 C); Reaction volume, (37 ml); Solvent, (DMF).

carbonylation reactions. Various iodine containing promoters were investigated with Rh complex catalyst and the results are presented in Table 2. It was found that the activity of the catalyst system is directly proportional to the ease with which an iodide containing promoter can release its iodine to the system. I_2 probably facilitates the formation of free anionic species of the type $[\text{Pd}(\text{CO})_x\text{I}_y]^-$ which is an active catalytic intermediate in oxidative carbonylation reaction. While in presence of cations such as C_2H_5^+ , CH_3^+ or Na^+ the concentration of free anion available for the reaction is decreased, due to the varied degree of ion pairing in the solution. Therefore lower reaction rates are ob-

served when cations with higher affinity for anions are used indicating a strong ion pairing effect. Thus promoters in decreasing order of their activity can be given as follows $\text{I}_2 > \text{NaI}-\text{C}_2\text{H}_5\text{I} > \text{CH}_3\text{I} > \text{KIO}_3-\text{KI}$.

Activity of the catalyst depends on the concentration of the iodide promoters. Effect of NaI concentration on catalyst activity for Pd–NaI catalyst system is studied (Fig. 2). The figure shows that the optimum concentration of iodide containing promoter is achieved at NaI/Pd mole ratio of one and that this value is highly sensitive to the iodide concentration. As can be seen from this figure, conversion of aniline increases sharply as the ratio approaches close to one and then decreases with further increase in NaI/Pd ratio. Thus higher concentration of the promoter has a poisoning effect on catalyst. It is known that ionic complexes exhibit different catalytic activity and selectivity depending on the oxidation state of the metal [20]. In the present system increase in the concentration of iodide increases the concentration of active complex, probably by forming $[\text{Pd}(\text{CO})_3\text{I}]^-$ from Pd metal and CO. Further increase in the concentration of I beyond the optimum value, converts $[\text{Pd}(\text{CO})_3\text{I}]^-$ into complexes having higher oxidation states which are probably inactive. Thus

Table 2
Oxidative carbonylation of aniline: Effect of iodide

Promoter	Conversion of aniline (%)	Yield of urea (mmol)	Selectivity (%)
I_2	66	7.06	99
NaI	58	6.10	98
$\text{C}_2\text{H}_5\text{I}$	49	5.30	99
CH_3I	45	4.86	98
KIO_3	7	0.76	99
KI	5	0.54	98

Conditions: Aniline (21.5 mmol); $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ (1.3 mmol); promoter (1.3 mmol); $\text{CO}:\text{O}_2$ (2:1, atmospheric); temperature (100°C); solvent (DMF, 35 cc); contact time (5 h).

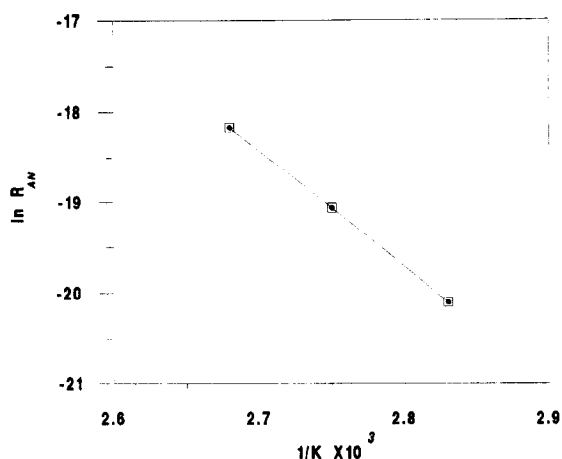


Fig. 3. Arrhenius plot.

we get a maximum in conversion of aniline for NaI/Pd ratio of one indicating that the active catalytic complex probably contains only one iodine per ligand in the complex.

3.3. Effect of solvents

Table 3 shows the conversion of aniline using different solvents. In non-polar solvents like toluene, xylene etc. poor conversion of aniline is obtained, while in polar solvents, e.g. DMF, DMSO, high conversion of aniline is obtained. Generally non polar solvents favor the formation of covalent species, while ionic species are stabilized in polar solvents [21]. The results obtained indicate that the formation of ionic species is favored [22], thus activation of O_2 is easily accomplished in polar solvents and therefore higher rates of oxidative carbonylation are achieved in polar solvents. The solvent effect can also be understood in terms of activity enhancement via the formation of reactive

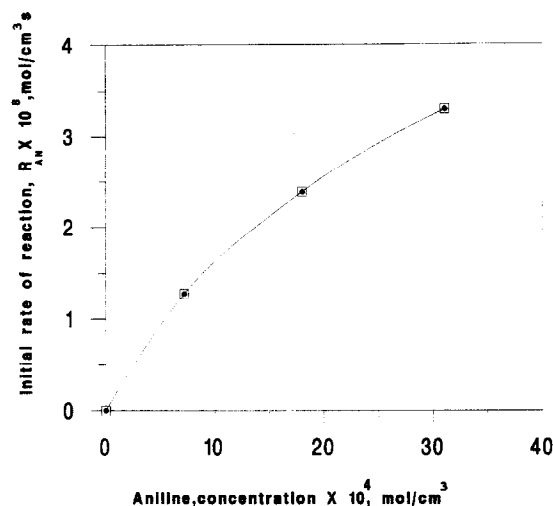


Fig. 4. Effect of aniline concentration on initial rate of reaction. Reaction conditions: Same as Fig. 1.

'naked' carbonyl anion in solvent that decreases the tendency for ion pairing [23]. The solvent effect on the activity of catalyst strongly support the possibility of ion-pair effect, e.g. catalyst activity is substantially increased when DMSO is used as a solvent. The dielectric constant for the solvents studied are also listed in Table 3. The activity of the $[Ru(CO)_3I_3]N(Bu)_4$ catalyst increases with an increase in the dielectric constant of solvent.

3.4. Effect of temperature

Effect of temperature on the initial rate of reaction of aniline was studied using $[Ru(CO)_3I_3]N(Bu)_4$ catalyst and DMF as a solvent. For this purpose, experiments were carried out at 80, 90 and 100°C. The results are presented in Fig. 3 as a plot of $\ln R_{AN}$ versus $1/T$, from which the activation energy was calculated as 26.6 kcal/mol.

Table 3
Effect of solvent on oxidative carbonylation of aniline

Solvent	Conversion of aniline (%)	Selectivity of urea (%)	Dielectric constant ^a (ϵ , 20°)	Protic	Aprotic
<i>p</i> -xylene	nil	—	2.3	—	✓
Toluene	nil	—	2.4	—	✓
DMF	59	98	36.7	—	✓
DMSO	65	96	46.7	—	✓

Conditions: Aniline (21.5 mmol); $[Ru(CO)_3I_3]N(Bu)_4$ (1.3 mmol); $CO:O_2$ (2:1, atmospheric); temperature (100°C); contact time (5 h).
^a [28].

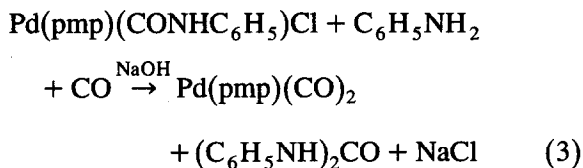
3.5. Effect of aniline concentration

The effect of initial aniline concentration on the activity of $[\text{Ru}(\text{CO})_3\text{I}_3]\text{N}(\text{Bu})_4$ catalyst was studied at 100°C at atmospheric pressure using DMF as a solvent. The results are shown in Fig. 4 which indicates that the rate of oxidative carbonylation of aniline increases with increase in aniline concentration.

4. Proposed mechanism

The mechanism of oxidative carbonylation of aromatic amines to phenyl ureas is not clearly understood. Fukuoka et al. 1984; [14,15] have proposed a possible mechanism of oxidative carbonylation reaction but in their work the role of iodide containing promoter was not explained. In order to understand the complete reaction mechanism, it is important to know the interaction of promoters with the catalyst. The results obtained in the present study shed some light on these aspects.

Certain Pd complexes are known to activate aromatic amines in the presence of carbon monoxide to give carbamoyl type of complexes [24], which on further treatment with amine and CO gives rise to diphenyl urea formation. The mechanism of formation of urea by carbonylation of aromatic amine is fairly well understood. The chloride ligands in the Pd complex acts as a H atom acceptor [24].



These reactions are stoichiometric in nature and not really catalytic. The problem was however overcome by the use of dioxygen as a source of H atom acceptor. Thus in presence of oxygen this reaction becomes catalytic in nature. A speculative mechanism of oxidative carbonylation of aniline to *N,N'*-diphenyl urea catalyzed

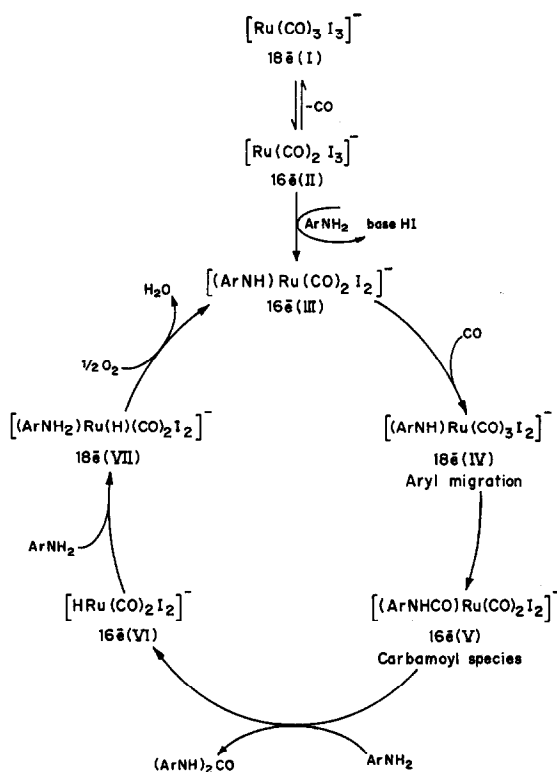


Fig. 5. A plausible reaction mechanism of oxidative carbonylation of aniline.

by $[\text{Ru}(\text{CO})_3\text{I}_3]\text{N}(\text{Bu})_4$ catalyst has been proposed (see Fig. 5). The formation of carbamoyl species (V) is the key step in the proposed mechanism. The catalyst precursor a d^6 , 18 electron complex $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ reacts dissociatively with carbon monoxide to form a catalytic intermediate (II). Species (II) reacts with aniline to form species (III) and liberates HI, which is stabilized by basic reaction media. Stoichiometric reactions of Ru complexes of this type were earlier reported, and are assumed to be the active catalytic intermediate in carbonylation reaction [25,26]. Species (III) adds on to one CO and is converted into species (IV). Aryl migration at this stage gives a carbamoyl species (V).

Addition of one molecule of aniline to species (V), and subsequent product elimination gives rise to hydrido carbonyl species (VI). Species (VI) add on to another aniline forming (VII),

which upon interaction with O₂ eliminates a molecule of water and active amino species (III) is regenerated. This is a plausible reaction mechanism and more work will have to be done to arrive at a definitive reaction mechanism.

5. Conclusion

Several homogeneous transition metal complex catalysts and iodine containing promoters were investigated for oxidative carbonylation of aniline to *N,N'*-diphenyl urea, at atmospheric pressure. For a catalyst system containing Pd, the optimum NaI/Pd ratio was found to be one. It was observed that the best results (59% conversion and 99% selectivity) were obtained with [Ru(CO)₃I₃]N(Bu)₄ catalyst. Initial rate of reaction was found to increase with increase in aniline concentration and temperature. Activation energy evaluated from Arrhenius plot was found to be 26.6 kcal/mol. It was also found that the polar solvents are suitable for this reaction. A plausible reaction mechanism has been discussed.

References

- [1] T.N. Iwamoto, Chem. Commun. (1966) 380.
- [2] Wender and P. Pino (Eds.), Organic synthesis via metal carbonyls, Vol. 1, Interscience, New York, 1968, p. 405.
- [3] R.A. Sheldon, Chemicals from Syngas, Reidel, Dordrecht, 1983.
- [4] D.R. Stull, E.F. Westrum, G.C. Sinke, The Chemical Thermodynamic of Organic Compounds, John Wiley, New York, 1969.
- [5] R.A. Franz, F. Applegath, F.V. Morriss, F. Baiocchi, C. Bolze, J. Org. Chem. 26 (1961) 3309.
- [6] J.J. Harper, J. Chem. Eng. Data 21 (1976) 345.
- [7] H.A. Dieck, R.M. Laine, R.F. Heck, J. Org. Chem. 19 (1975) 2819.
- [8] Y.L. Sheludyakov, V.A. Golodov, D.V. Sokolskii, Dokl. Akad. Nauk USSR 249 (1979) 658.
- [9] N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda, S. Tsutsumi, J. Am. Chem. Soc. 93 (1971) 6344.
- [10] N. Kambe, K. Kondo, H. Ishh, N. Sonoda, Bull. Chem. Soc. Jpn. 54 (1981) 1460.
- [11] F. Benedini, Micaelanali, B. Rindone, S. Tollari, S. Cenini, G. La Monica, F. Porta, J. Mol. Catal. 34 (1986) 155.
- [12] K. Kondo, S. Yokoyama, N. Myoshi, S. Murai, N. Sonoda, Angew. Chem. Int. Ed. Engl. 18 (1979) 692.
- [13] W.B. Hardy, R.P. Bennett, Tetrahedron Lett. 961 (1967).
- [14] S. Fukuoka, M. Chono, M. Kohno, ChemTech. (Nov. 1984) 670–676.
- [15] S. Fukuoka, M. Chono, J. Chem. Soc. Chem. Commun. (1984) 399.
- [16] S.P. Gupte, R.V. Chaudhari, J. Catal. 114 (1988) 246.
- [17] A. Alper, F.W. Hartstock, J. Chem. Soc. Chem. Commun. (1985) 1141.
- [18] K.T. Li, Y.J. Peng, J. Catal. 143 (1993) 631.
- [19] S.S. Tamhankar, S.P. Gupte, R.V. Chaudhari, Chem. Eng. J. 223 (1981) 15.
- [20] B.D. Dombek, Organometallics 4 (1985) 1070.
- [21] E. Cesarotti, R. Ugo, L. Kaplan, Chem. Rev. 43 (1982) 275.
- [22] R. Ugo, A. Pasani, A. Fusi, S. Cenini, J. Am. Chem. Soc. 92 (1972) 7364.
- [23] G. Braca, A.M.R. Galletti, G. Shrana, in: D.R. Fahey (Ed.), Industrial Chemicals via C₁ Processes, 1987, p. 220.
- [24] G. Vasapollo, C.F. Nobile, A. Sacco, J. Organomet. Chem. 296 (1985) 435.
- [25] S. Cenini, M. Pizzotti, F. Porta, G. La. Monica, J. Orgmet. Chem. 125 (1977) 95.
- [26] P.S. Hallman, B.R. McGarvey, G. Wilkinson, J. Chem. Soc. (A) (1968) 3143.
- [27] S.A.R. Mulla, S.P. Gupte, R.V. Chaudhari, J. Mol. Catal. 67 (1991) L7.
- [28] J.A. Dean (Ed.), Lange's Handbook of Chemistry, McGraw-Hill, New York, 1979.