

Catalytic oxidation of 1-hexene and cyclohexene with molecular oxygen by iridium nitro complexes

P.J. Baricelli^{a,*}, V.J. Sánchez^b, A.J. Pardey^c, S.A. Moya^d

^a Centro de Investigaciones Químicas, Facultad de Ingeniería, Universidad de Carabobo, Valencia, Venezuela

^b Escuela de Química, Facultad Experimental de Ciencias y Tecnología, Universidad de Carabobo, Valencia, Venezuela

^c Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela

^d Departamento de Química Aplicada, Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile

Received 9 September 1999; received in revised form 1 June 2000; accepted 16 June 2000

Abstract

The oxidation of 1-hexene and cyclohexene by molecular oxygen catalyzed by the iridium complexes $[\text{Ir}(\text{CH}_3\text{CN})_4\text{NO}_2](\text{A})_2$ ($\text{A}=\text{PF}_6$ (**1**) or BF_4 (**2**)) has been studied in acetonitrile under $P(\text{O}_2)=20$ atm, $T=120^\circ\text{C}$, substrate/catalyst=100, $t=20$ h. Both complexes are active for oxidizing 1-hexene to 1,2-epoxyhexane, 1-hexen-3-one, 2-hexenal, 1-hexen-3-ol and 2-hexen-1-ol and also oxidize cyclohexene to 2-cyclohexen-1-one, 7-oxabicyclo[4.1.0]hexane and 2-cyclohexen-1-ol. Preliminary kinetic parameters are reported for complex (**1**). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation; Iridium complexes; Cyclohexene; 1-Hexene; Nitro complexes

1. Introduction

The oxidation of olefins by transition metal nitro complexes [1,2] has become a very important field in homogeneous catalysis due to its relevance in the modern synthetic chemical industry. The interesting reaction is the intramolecular oxidation of the olefins (previously coordinated to the metal nitro complex) by the transfer of one oxygen atom from the nitro ligand of the metal complex to the olefins. The regeneration of the oxidant species occurs because two nitro groups are regenerated by O_2 [3]. These principles were used with the purpose of oxidizing a variety of organic and inorganic substrates by molecular oxygen [3–8].

A variety of nitro complexes of cobalt [9–11], rhodium [12], palladium [13], and ruthenium [14]

have been studied in the oxidation of olefins. We recently reported the oxidation of 1-hexene by O_2 catalyzed by iridium nitro complexes under mild conditions [15]. In this paper, we are reporting new advances in the oxidation of 1-hexene and cyclohexene under severe reaction conditions.

2. Experimental

2.1. General procedure

All manipulations were carried out under N_2 atmosphere by using standard Schlenk technique [16]. Solvents were purified by known procedures and saturated with nitrogen prior to use. The infrared spectra were recorded in a Perkin-Elmer Spectrum 1000 FTIR using samples as KBr disks. Analyses by NMR were obtained on a Bruker AM 300 spec-

* Corresponding author.

E-mail address: pbaricel@thor.uc.edu.ve (P.J. Baricelli).

trometer. GC analysis were performed on a Hewlett Packard 5890 Series II chromatograph with a flame ionization detector and ultra 2.5% phenyl methyl silicone, 25 m, 320 μm column. Quantification was achieved by using the internal standard (naphthalene) method and the peaks were identified by comparison with pure samples analyzed by a GC/MS HP 5890/5971 coupled system using Quadrex PONA 5% phenyl methyl silicone, 25 m, 320 μm column. The UV–VIS spectra were taken in a diode array Hewlett Packard 8452 spectrometer. $\text{IrCl}_3 \cdot \text{H}_2\text{O} \cdot \text{HCl}$, cyclooctadiene, 1-hexene, cyclohexene, diethylether, acetylacetone, acetone, petroleum ether, acetonitrile, dichloroethane, AgNO_2 , KPF_6 , NOBF_4 , were obtained from Aldrich Chemical. All other chemicals were commercial products and were used without further purification.

2.2. Synthesis of $[\text{Ir}(\text{CH}_3\text{CN})_4\text{NO}_2](\text{PF}_6)_2$ (**1**)

To a boiling solution of $\text{IrCl}_3 \cdot \text{H}_2\text{O} \cdot \text{HCl}$ (0.514 g, 2 mmol) in acetonitrile (40 ml) AgNO_2 was added (0.265 g, 2 mmol) dissolved in 5 ml of acetonitrile; the mixture was refluxed for 9 h and the color of the solution changed from purple to yellow together with a white precipitate of AgCl which was separated by filtration. The solution was heated until reflux, KPF_6 (0.634 g, 3 mmol) dissolved in 10 ml acetonitrile was added and immediately a white precipitate of KCl was formed and removed by filtration. The yellow solution was refluxed for 9 h and allowed to cool at room temperature. Diethylether (100 ml) was added with stirring; this caused precipitation of complex (**1**) as a light yellow powder, which was collected by filtration and washed with cold diethylether and finally dried under vacuum; yield 0.4981 g, 43%.

2.3. Synthesis of $[\text{Ir}(\text{CH}_3\text{CN})_4\text{NO}_2](\text{BF}_4)_2$ (**2**)

A 126 mg (0.225 mmol) sample of $[\text{Ir}(\text{CH}_3\text{CN})_4\text{NO}](\text{BF}_4)_2$, which was prepared as reported by Muccigrosso et al. [7] was placed in a Parr reactor in acetonitrile (30 ml) under O_2 pressure (3 atm) for 24 h; this caused the formation of the nitro complex (**2**); yield 60%. This is a modified method from the one in the literature [12,20,21].

2.4. Catalytic oxidation

The catalytic runs were performed according to the following conditions. The reactors used were two autoclaves from Parr Instruments (453HC5-T316, 50 ml and C51377/2AC-T3-03, 5 ml) with temperature-controlled unit and magnetic stirring. The reaction temperature was varied from 40 to 80°C (313–353 K); oxygen pressure varied from 4 to 27 atm and the substrate/catalyst ratio were (25:1, 50:1, 100:1). At the end of the reaction time liquid samples were removed from the reactor vessel and analyzed by GC and GC-MS techniques.

3. Results and discussion

3.1. Synthesis and characterization

The IR analysis of the complex (**1**) shows one band at 2929 cm^{-1} which is characteristic of C–H group from acetonitrile ligand coordinated to the iridium atom. Two bands at 2335 and 2320 cm^{-1} were assigned to the stretching $\text{C}\equiv\text{N}$ due to the acetonitrile bond to the complex. A group of asymmetric bands at 1422 and 1371 cm^{-1} were assigned to NO_2 -NO groups. A band at 1335 cm^{-1} characteristic of symmetric stretching of the NO_2 group. Two bands at 1664 and 1606 cm^{-1} were assigned to angular stretching of the NO group and finally one band at 845 cm^{-1} assigned to the flexion of the P–F bond [12,19].

The UV–VIS spectrum of the complex (**1**) showed two absorption bands at 208 and 214 nm assigned to transitions π – π^* and other two bands at 280 and 360 nm due to metal ligand charge transfer (MLCT) characteristic of the nitro group [18].

The ^1H NMR (CD_3CN) consists of two signals at 1.95 ppm (multiplet, free CH_3CN) and a singlet at 1.85 ppm assigned to the protons of the coordinated acetonitrile. The ^{13}P NMR spectrum displays a well-resolved sextuplet at –150 ppm assigned to the bond coupling P–F in the PF_6 species [12].

The yellow crystals of the complex (**1**) were analyzed using XRD technique, unfortunately the crystals grew twinned and we were unable to establish its crystal structure.

However, from the spectra of electronic densities of this complex we can postulate a theoretical confor-

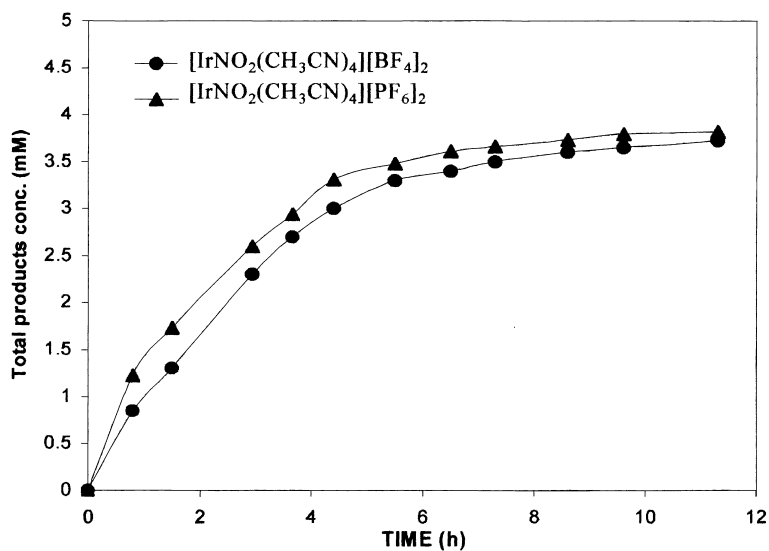


Fig. 1. Homogeneous oxidation of cyclohexene by $[\text{Ir}(\text{CH}_3\text{CN})_4\text{NO}_2](\text{A})_2$, ($\text{A}=\text{PF}_6$ or BF_4) ($P(\text{O}_2)=20$ atm, 120°C , $\text{S}/\text{C}=100$, 12 h). (Lines drawn for illustrative purposes only).

mation, which is in accordance with the spectroscopy data. We are proposing here a pentacoordinated iridium complex with a NO_2 group pending out of the plane surrounded by four acetonitrile ligands [17].

3.2. Oxidation catalysis

Initial catalytic tests were carried out in order to obtain a reaction profile for the oxidation of cyclohexene

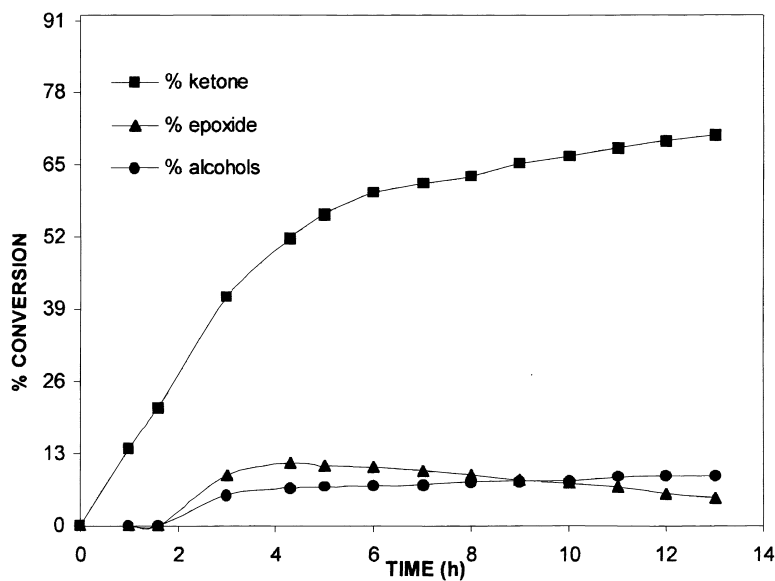


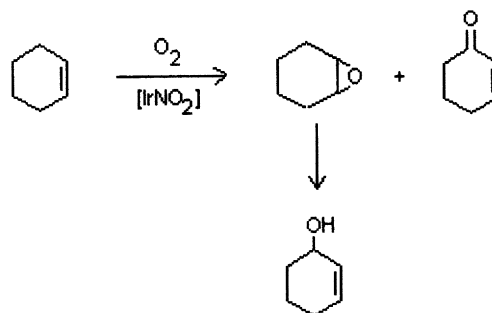
Fig. 2. Product distribution of the homogeneous oxidation of cyclohexene with $[\text{Ir}(\text{CH}_3\text{CN})_4\text{NO}_2](\text{PF}_6)_2$. ($P(\text{O}_2)=20$ atm, 120°C , $\text{S}/\text{C}=100$, 14 h). (Lines drawn for illustrative purposes only).

and 1-hexene under the following reaction conditions: $P(\text{O}_2)=20$ atm, $T=120^\circ\text{C}$, substrate/catalyst ratio=100, naphthalene as internal standard, reaction time=20 h and 30 ml of acetonitrile as a solvent.

Fig. 1 shows the profile for the homogeneous oxidation of cyclohexene catalyzed by complexes (1) and (2).

It can be observed from Fig. 1 that nature of the anion has no effect on the total conversion of cyclohexene. On the other hand, the two catalysts are stable for at least 12 h under the catalytic reactions conditions ($P(\text{O}_2)=20$ atm, $S/C=100$, $T=120^\circ\text{C}$) as seen in Fig. 1.

The distribution of products from the catalytic oxidation cyclohexene (in % conversion) can be observed in Fig. 2, from which it can be deduced that the main product of the reaction are 2-cyclohexen-1-one and 7-oxabicyclo[4.1.0]hexane. The later is subsequently transformed to 2-cyclohexen-1-ol, through the breaking of the C–O bond via hydrogen transfer, according to the Scheme 1 (the CH_3CN ligand on the iridium complex is omitted for clarity). The formation of 2-cyclohexen-1-one occurs via β -hydrogen elimination from a heterometallacyclo intermediary formed under the catalytic reaction conditions. The structure of this kind of intermediary has been reported in detail by Andrews and Cheng [22]. On the other hand, the formation of the 7-oxabicyclo[4.1.0]hexane



Scheme 1.

might involve a concerted fragmentation [23] of an heterometallacyclo intermediary or a ring contraction followed by reductive elimination [24].

Fig. 3 shows total conversion of the oxidation of 1-hexene versus time catalyzed by the nitro complexes (1) and (2) under O_2 atmosphere.

It can be observed from this figure a similar behavior to that of cyclohexene described above. The main products are depicted in Scheme 2 (the CH_3CN ligand on the iridium complex is omitted for clarity).

The formation of 2-hexen-1-ol is due to the protonation of 1,2-epoxyhexane but the appearance of the 1-hexen-3-one seems to be independent on the formation of the other products.

Table 1 shows the products and the total conversion of the oxidation of cyclohexene and 1-hexene

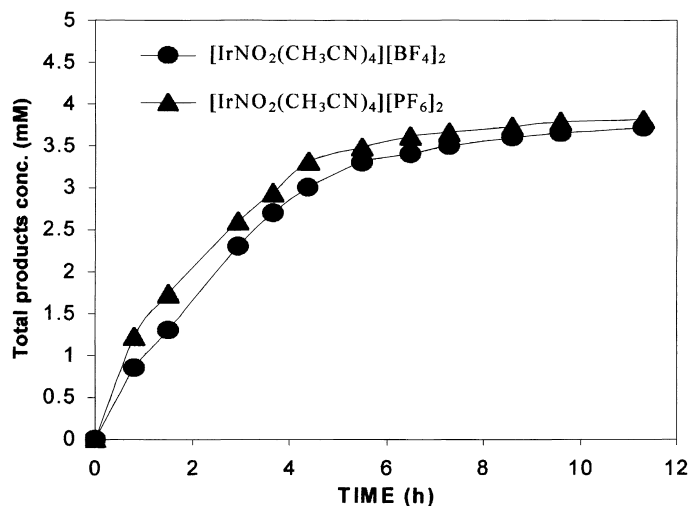


Fig. 3. Homogeneous 1-hexene oxidation by $[\text{Ir}(\text{CH}_3\text{CN})_4\text{NO}_2](\text{A})_2$, ($\text{A}=\text{PF}_6$ or BF_4) ($P(\text{O}_2)=20$ atm, 120°C , $S/C=100$, 12 h). (Lines drawn for illustrative purposes only).

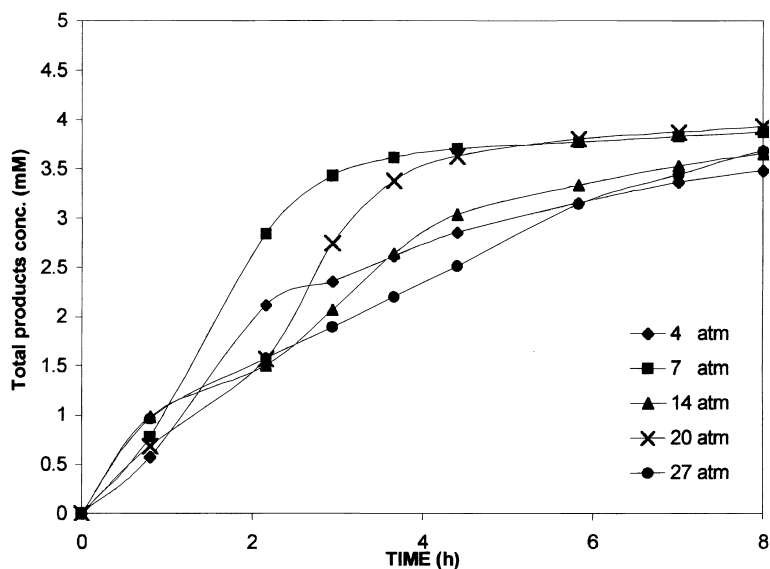


Fig. 4. Effect of the pressure of oxygen on the homogeneous oxidation of cyclohexene with $[\text{Ir}(\text{CH}_3\text{CN})_4\text{NO}_2](\text{PF}_6)_2$ (120°C , $S/C=100$, 8 h). (Lines drawn for illustrative purposes only).

3.3.1. Effect of oxygen pressure

The oxidation of cyclohexene was carried out at pressures from 7 to 27 atm (Fig. 4).

It can be deduced that the system is a function of the pressure, however, it is possible to infer that

20 atm could be the best working pressure, because at 20 atm only cyclohexen-1-one, 7-oxabicyclo[4.1.0]hexane and 2-cyclohexen-1-ol were obtained as products of the oxidation reaction, similar to those showed in Fig. 2.

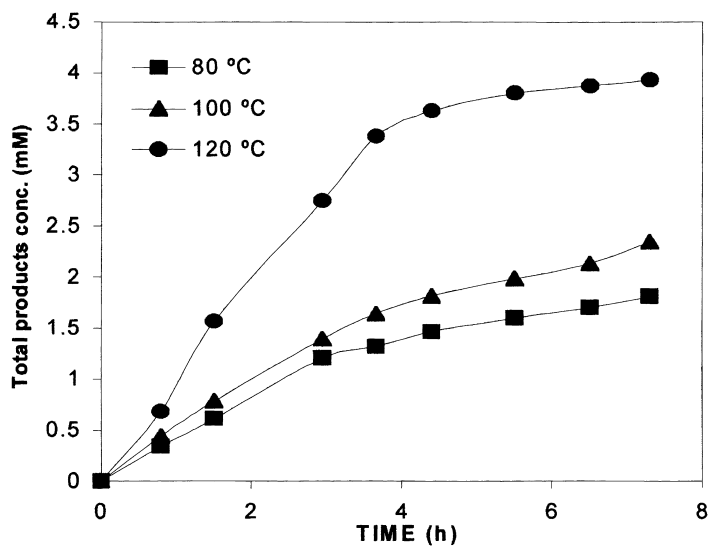


Fig. 5. Effect of the temperature on the homogeneous oxidation of cyclohexene with $[\text{Ir}(\text{CH}_3\text{CN})_4\text{NO}_2](\text{PF}_6)_2$ ($P(\text{O}_2)=20$ atm, 120°C , $S/C=100$, 8 h). (Lines drawn for illustrative purposes only).

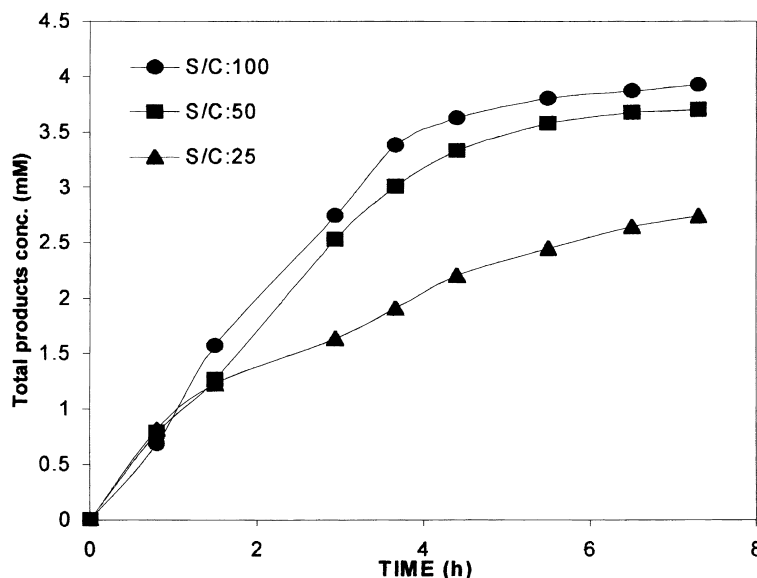


Fig. 6. Effect of the substrate/catalyst ratio on the oxidation of cyclohexene with $[\text{Ir}(\text{CH}_3\text{CN})_4\text{NO}_2](\text{PF}_6)_2$ ($P(\text{O}_2)=20$ atm, 120°C , 8 h). (Lines drawn for illustrative purposes only).

3.3.2. Effect of temperature

The catalytic oxidation was carried out at 20 atm, and the temperature was varied from 80 to 120°C (Fig. 5).

It is very clear that the best working temperature of this catalytic system is 120°C . At this temperature the best conversion to products were obtained. Over 120°C it can be observed the decomposition of the catalyst.

3.3.3. Effect of substrate/catalyst ratio

Runs were carried out for a series of different substrate/catalyst over the range 25–100 under $P(\text{O}_2)=20$ atm at 120°C for the catalytic oxidation of cyclohexene (Fig. 6). An increase in the substrate/catalyst ratio resulted a slightly increase in the total product conversion.

4. Conclusions

The complexes $[\text{Ir}(\text{CH}_3\text{CN})_4(\text{NO}_2)](\text{A})_2$ ($\text{A}=\text{PF}_6$ (**1**) or BF_4 (**2**)) are efficient catalytic precursors for the oxidation of cyclohexene and 1-hexene. There is not an anionic effect during the oxidation reactions and it

was demonstrated that the oxidation of the olefin substrates is carried out by oxygen transfer from the nitro complexes.

Acknowledgements

We thank Dr. Roberto Sánchez-Delgado (IVIC), Dr. Raul Isea (IVIC), Alberto Fuentes (IVIC) for the interesting discussions and use of laboratory facilities. P.B. thank CODECIHT-UC for financial support Project 94016. A.J.P. thank CDCH-UCV and S.M. thank FONDECYT-CHILE.

References

- [1] M.A. Andrews, K. Kelly, *J. Am. Chem. Soc.* 103 (1979) 2894.
- [2] B.S. Tovrog, S.E. Diamond, F. Mares, *J. Chem. Soc.* 101 (1979) 270.
- [3] B.S. Tovrog, F. Mares, S.E. Diamond, *J. Am. Chem. Soc.* 102 (1980) 6618.
- [4] I.E. Bekk, E.V. Gusevskaya, V.A. Likholobov, Yu.I. Yermakov, *React. Kinet. Catal. Lett.* 33 (1987) 209.
- [5] M.A. Andrews, T.C.T. Chang, C.W.F. Cheng, K.P. Kelly, *Organometallics* 3 (1984) 1779.
- [6] T.T. Wenzel, *J. Chem. Soc., Chem. Commun.* 932 (1989).

- [7] D.A. Muccigrosso, F. Mares, S.E. Diamond, L.P. Solar, *Inorg. Chem.* 22 (1983) 960.
- [8] B.L. Feringa, *J. Chem. Soc., Chem. Commun.* (1986) 909.
- [9] G. Booth, J. Chatt, *J. Chem. Soc.* (1962) 2099.
- [10] T. Ishiyama, T. Matsumura, *Annu. Rep. Radial. Cent. Osaka. Prefect* 11 (1979) 50.
- [11] S.G. Clarkson, F. Basolo, *Inorg. Chem.* 12 (1973) 1528.
- [12] A. Muccigrosso, F. Mares, S.E. Diamond, J.P. Solar, *Inorg. Chem.* 22 (1983) 960.
- [13] R. Ugo, S. Bhaduri, B.F.G. Jhonson, A. Kahir, H. Pickard, Y. Benn-Taarit, *J. Chem. Soc., Chem. Commun.* (1976) 694.
- [14] R.A. Leising, K.T. Kenneth, *J. Am. Chem. Soc.* 110 (1988) 4079.
- [15] L.A. Quijije, M. Mediavilla, A.J. Pardey, C. Longo de Pardey, P. Baricelli, S.A. Moya, *React. Kinet. Catal. Lett.* 62 (1997) 251.
- [16] D.F. Shriver, *The manipulation of Air-Sensitive Compounds*, McGraw-Hill, New York, 1969.
- [17] S.D. Robinson, B.L. Shaw, *J. Chem. Soc.* 4 (1965) 4997.
- [18] A. Castillo, P. Baricelli, F. López, A. Pardey, *Actas XV Simposio Iberoamericano de Catálisis* 3 (1996) 2045.
- [19] M. Green, T.A. Kuc, Susan, H. Taylor, *J. Chem. Soc. (A)*. 2334 (1971).
- [20] N. Connelly, P.T. Draggnett, M. Green, T.A. Kuc, *J. Chem. Soc., Dalton Trans.* 70 (1977).
- [21] N. Connelly, M. Green, T.A. Kuc, *J. Chem. Soc., Chem. Commun.* 542 (1975).
- [22] M.A. Andrews, C.-W.F. Cheng, *J. Am. Chem. Soc.* 104 (1982) 4268.
- [23] H. Mimoun, R. Charptier, A. Mitschler, J. Fischer, R. Weiss, *J. Am. Chem. Soc.* 102 (1980) 1047.
- [24] K.B. Sharpless, A.Y. Terenishi, J.-E. J Backvall, *J. Am. Chem. Soc.* 99 (1977) 3120.
- [25] D.R. Anton, R.H. Crabtree, *Organometallics* 2 (1983) 855.