10 G. Primet, J. C. Vedrine and C. Naccache, *J. Mol. Catal.*, 4 (1978) 411 and references therein.
11 W. McFarlane and G. Wilkinson, in H. F. Holtzclaw (ed.), *Inorganic Syntheses*, Vol. 8, McGraw-Hill, New York, 1966, p. 181. R. B. King and F. G. A. Stone, in J. Kleinberg (ed.), *Inorganic Syntheses*, Vol. 7, McGraw-Hill, New York, 1963, p. 193.
12 A. Mantovani and S. Cenini, in F. Basolo (ed.), *Inorganic Syntheses*, Vol. 16, McGraw-Hill, New York, 1976, p. 47.
13 B. F. G. Johnson and J. Lewis, in F. A. Cotton (ed.), *Inorganic Syntheses*, Vol. 13, McGraw-Hill, New York, 1972, p. 92.
14 P. Chini, V. Albano and S. Martinengo, *J. Organomet. Chem.*, 16 (1969) 471.
15 L. Malatesta, G. Caglio and M. Angoletta, in F. A. Cotton (ed.), *Inorganic Syntheses*, Vol. 13, McGraw-Hill, New York, 1972, p. 95.
16 B. R. James, G. L. Rempel and W. K. Teo, in F. Basolo (ed.), *Inorganic Syntheses*, Vol. 16, McGraw-Hill, New York, 1976, p. 49.
17 R. Eady, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1975) 2606.
18 J. A. Connor, *Topics Current Chem.*, 71 (1977) 71.
19 F. Hugues and J. M. Basset, *J. Chem. Soc. Comm.*, in press.
20 N. Sheppard and T. Nguyen, in R. J. H. Clark and R. E. Hester (eds.), *Advances in Infrared and Raman Spectroscopy*, Vol. 5, Heiden, London and New York, 1978, p. 67.
21 R. Ugo, R. Psaro, G. M. Zanderighi, J. M. Basset, A. Theolier and A. K. Smith, in M. Tsutsui (ed.), *Fundamental Research in Homogeneous Catalysis*, Vol. 3, Plenum Press, New York, 1979, p. 279.

Journal of Molecular Catalysis, 7 (1980) 523 - 530

BUTADIENE 1,4-POLYMERIZATION CATALYSIS PART III*: SOLVENTS EFFECTS ON THE MOLECULAR DYNAMICS OF BIS [η^3-ALLYLNICKEL(II) TRIFLUOROACETATE] — A SPECTROSCOPIC STUDY

M. JULÉMONT, R. WARIN and PH. TEYSSIÉ

Macromolecular Chemistry and Organic Catalysis Department, Institute of Chemistry, University of Liège, Sart-Tilman, 4000 Liège (Belgium)

(Received July 17, 1979)

Summary

Spectroscopic studies of the structure and dynamical behaviour of bis [η^3-allylnickel(II) trifluoroacetate] in different solvents have been carried out in order to interpret the striking solvent effect observed in the polymerization process. A random solvation sphere resulting from dipolar interactions between the complex and the solvent molecules accounts for these spectroscopic observations.

Introduction

Recent studies on butadiene 1,4-polymerization initiated by bis [η^3-allylnickel(II) trifluoroacetate], or $(\mathrm{ANiTFA})_2$, have pointed out the important role of the solvent in the resulting polybutadiene microstructure [2 - 6]. While 1,4-*cis* polybutadiene is obtained in saturated hydrocarbon solvents [2, 3], a 1,4-polybutadiene containing practically equal amount of *cis* and *trans* units (for which we have coined the name 1,4-equibinary polybutadiene) can be obtained in aromatic (benzene) or chlorinated solvents (methylene chloride) displaying, respectively, a random or a rather alternating distribution of stereoisomers [4 - 6]. These striking changes in both the composition and the isomer distribution are probably related to the dependence of key kinetic and/or thermodynamic parameters controlling the overall propagation process towards the nature of the solvent [7, 8].

We want to report here the first results of a spectroscopic analysis of the catalytic system, performed in order to clarify this solvent influence by defining at best the nature of the interaction between the solvent and the solute molecules.

---

*Part II, see ref. 1.

In fact, the binuclear complex $(ANiTFA)_2$ can exist in solution as two different isomers [1], (see Fig. 1):

—an asymmetrical species having a plane of symmetry containing the Ni–Ni axis;

—a symmetrical species having moreover a plane of symmetry perpendicular to the same axis.

A previous ^1H NMR analysis of the temperature-dependent behaviour of this catalyst in chlorobenzene solution [1] demonstrated an equilibrium exchange between these two isomers (equilibrium 1), in addition to allyl ligand interchange in the asymmetrical species (equilibrium 2).

Owing to the mechanistic and practical interest of the corresponding results obtained in the polymerization, we then focused our efforts on the dynamic behaviour in d^2-methylene chloride*, as well as in d^8-toluene* (instead of d^6-benzene which crystallizes at 6 °C and of which the interaction properties with the solute molecules seems to be identical (see Table 1)).

Experimental

Bis [η^3-allylnickel(II) trifluoroacetate] was synthesized as described previously [1]. The spectroscopic studies were performed under an atmosphere of argon in carefully cleaned cells as follows:

—on an RPQ 20 Zeiss spectrophotometer for electronic spectra, using 5×10^3 molar solutions, in quartz cells (10 mm);

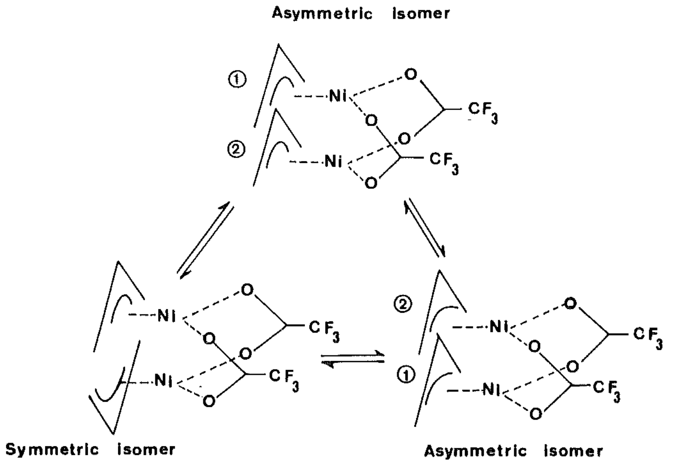

Fig. 1. Dynamic behaviour of $(ANiTFA)_2$ binuclear complexes. Equilibrium 1, exchange between symmetric and asymmetric isomers; equilibrium 2, η^3-allyl-ligand interchange in the asymmetric isomer.

---

*In these solvents, equilibrium 2 has not been detected; it probably occurs at too low a temperature, close to the crystallisation temperature of the solutions.

TABLE 1

Influence of the solvent on ^1H and ^{13}C NMR chemical shifts of η^3-allylic nuclei in $(ANiTFA)_2$ complexes (at room temperature, in ppm *versus* TMS)

Solvent	CD_2Cl_2	C_6D_{12}	C_6D_6	C_7D_8
H-syn	3.25	3.05	2.58	2.56
H-anti	2.58	2.40	1.85	1.84
C_1 and C_3	52.4	–	52.1	–
C_2	110.9	–	112.1	–

—on a Perkin–Elmer 21 spectrophotometer for infrared spectra, with 5×10^{-2} molar solutions in NaCl cells (0.1 mm);

—on an HA 100 Varian spectrometer for ^1H NMR spectra and on an HFX 90 Bruker spectrometer for ^{13}C NMR spectra using in both cases 3×10^{-1} molar solutions containing tetramethylsilane (TMS) as internal standard.

Results and discussion

Nature of the interaction between the solvent and $(ANiTFA)_2$ molecules — an exploratory prospection

Evidence for a possible coordinative interaction between the solvent and the solute complex molecules does not appear from studies of either the η^3-allyl group symmetry, or of the overall geometry of the complex. Indeed, in any solvent at room temperature:

—^1H NMR spectra appear as an A_2M_2X pattern, both syn protons, (as with the anti protons) remaining equivalent (see Table 1 and Fig. 2);

—the magnetic equivalence of terminal carbon atoms is shown by the presence of only one ^{13}C NMR resonance characteristic of C_1 and C_3 allylic carbon atoms;

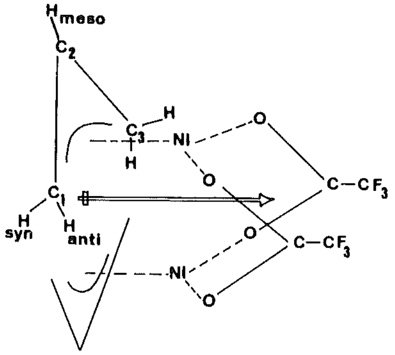

Fig. 2. Symmetric isomer of $(ANiTFA)_2$; the mean dipolar moment is in the dotted line.

—both carboxylate groups of the binuclear species seem to be equivalent, related IR absorptions being indistinguishable (ν(COO asymmetric stretching) at 1685 cm^{-1}; ν(COO symmetric stretching) at 1460 cm^{-1}, in cyclohexane, benzene, methylene chloride and o-dichlorobenzene) [6a, 9],

—the square planar geometry of the complex is supported by the recording of identical electronic spectra (a single broad absorption band at 415 nm; ϵ = 60 l mol^{-1} cm^{-1} in aliphatic, aromatic and chlorinated solvents [6a, 10].

As a result of these observations, coordination of solvent molecules to $(ANiTFA)_2$ cannot be invoked neither in an apical nor in an equatorial position.

In opposition to the results of our analysis, this type of interaction would involve some geometry changes (square planar to square-pyramidal complexes) in the first case, or a loss of symmetry in the nickel square plane in the second case.

Accordingly, in order to interpret the significant solvent shift incurred by both syn and anti proton resonances (see Table 1), a model of dipolar interaction between solvent and solute molecules, which does not involve any important change in the structure of the solute, will be preferred to a true coordination interaction. In this prospect, we will consider a loose and time-averaged organisation of solvent molecules around the $(ANiTFA)_2$ binuclear complexes, representing the cumulative effect of all the encounters taking place [11]. The solvent shifts can then be interpreted as a result of the relative proximity of these nuclei and the solvent molecules in the solvation sphere.

The upfield shift observed in d^6-benzene and in d^8-toluene (the corresponding reference chemical shift was measured in d^{12}-cyclohexane *versus* TMS) is expected from the aromatic structure of these solvents; it can be interpreted in terms of an ASIS effect connected with the large magnetic anisotropy of the aromatic rings close to the allylic ligand [11].

However, the downfield shifts observed in d^2-methylene chloride seem to be the result of Van der Waals interactions arising from the relative proximity of the chlorine nuclei and the allylic protons [12]. This interpretation should be preferred to the well-known Reaction-Field effect [13]. In this last case, solvent shifts are strongly anisotropic [12], in contrast to our observations (syn and anti proton signals incur equivalent solvent shifts despite the difference in orientation of the C–H$_{syn}$ and C–H$_{anti}$ bonds relative to the mean dipolar moment of the whole binuclear complex (Fig. 2).

Analysis of low temperature NMR spectra

Solvent effect on the chemical shift

At lower temperatures, the apparent ^{1}H NMR equivalence of the η^3-allyl ligands of one $(ANiTFA)_2$ molecule is removed and two overlapping A_2M_2X patterns corresponding to the symmetric and asymmetric binuclear species are observed [1]. These two isomeric forms of the complex appear in d^8-toluene at −40 °C and 0 °C for the syn and the anti protons signals, respectively (this order being expected from the related line separations; see Fig. 3 which shows the overlapping spectra of the symmetrical and asymmetrical h^3-allyl-nickel complexes), and at −25 °C and −10 °C for the corresponding resonances in d^2-methylene chloride.

When the temperature is lowered, all these signals are progressively shifted towards higher field in d^8-toluene and towards lower field (if significant) in d^2-methylene chloride; this means in each case an enhancement of the corresponding solvent shift (see Fig. 4). In fact, such a temperature effect would be expected from dipolar-type interactions, the energy of which is known to be inversely proportional to the square of the temperature and it may even be considered as additional support for this type of phenomenon.

An analysis of this temperature dependence of the chemical shift pointed out another more subtle effect of the solvent. In d^2-methylene chloride experiments, the temperature shifts $\Delta\delta(T)$ have the same intensity for both

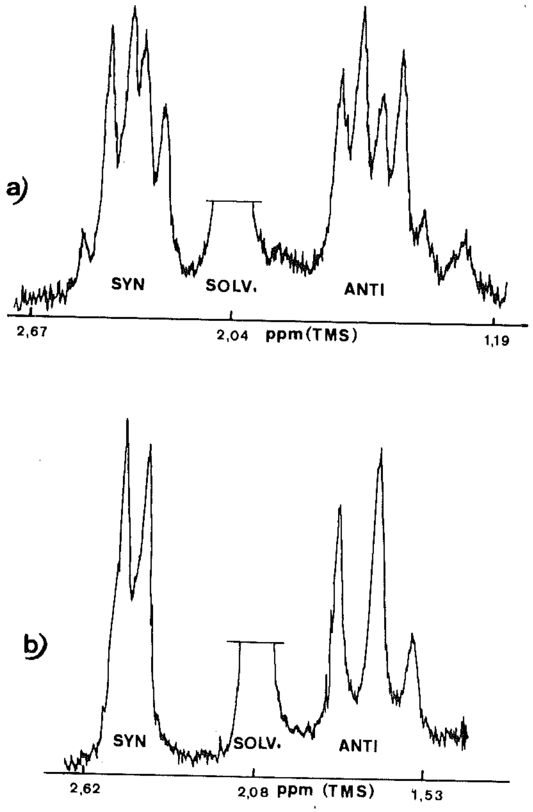

Fig. 3. ^{1}H NMR spectra of symmetric and asymmetric isomers of $(ANiTFA)_2$ in d^8-toluene: (a) at −55 °C; (b) at −10 °C.

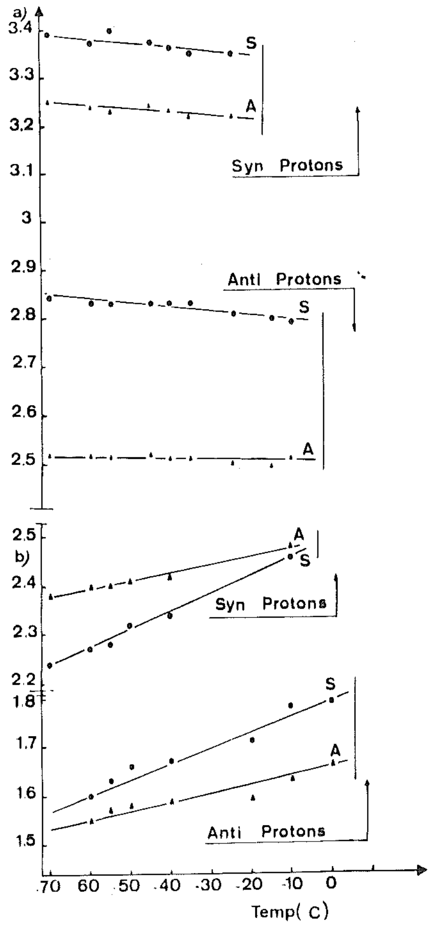

Fig. 4. Influence of temperature on the chemical shift of η^3-allylic protons (A for asymmetric isomer, S for symmetric isomer): (a) in d^2-methylene chloride; (b) in d^8-toluene.

symmetric and asymmetric binuclear complexes (see Fig. 4). In contrast, in d^8-toluene, the resonances characteristic of the symmetric* species are more shifted than the corresponding resonances of the asymmetric species within the same temperature interval. This higher sensitivity of the symmetric resonances positions probably involves a difference in the mean solvation energy of the two binuclear isomers. Further experiments are now in progress to define better this interesting selective effect in the solvent solute interactions.

---

*The η^3-allylic patterns were assigned by considering the relative proximity of the anti protons in the symmetric isomer: this situation implies important Van der Waals type electronic cloud distortions and, accordingly, higher chemical shifts (in the δ scale) than in the asymmetric species. It is obvious that, for steric reasons, only one symmetric isomer can exist (tail-to-tail).

Solvent effect on the relative concentrations of the symmetric and asymmetric isomers

In d^2-methylene chloride, as in chlorobenzene [1], the two overlapping A_2M_2X patterns are of almost equal intensity at any temperature, indicating a constant equivalence in the proportions of the different binuclear isomers. In contrast, in d^8-toluene these relative proportions are strongly temperature-dependent: below −55 °C the asymmetric species are more abundant than the symmetric species, and conversely at higher temperature (see Fig. 3).

From a thermodynamic standpoint, these observations mean that the value of ΔH°_{a-s} for the exchange reaction between symmetric and asymmetric binuclear isomers (*i.e.* following Van't Hoff's law, the parameter controlling the temperature dependence of the equilibrium constant) is zero in d^2-methylene chloride and positive in d^8-toluene.

Conclusions

In order to interpret the striking solvent influence on the butadiene 1,4-polymerization process initiated by $(ANiTFA)_2$ (see Introduction), we have attempted to define the nature of the solvent–solute interactions and their implications for the catalyst structure and dynamic behaviour.

The conservation of the η^3-allyl-ligand symmetry and of the complex square planar geometry in all of the solvents investigated, prevents us from considering these solvents as playing the role of ligands in the coordination sphere.

Furthermore, no fundamental structural changes in the complex have been detected which could lead to a meaningful interpretation of the striking solvent effect on the polymerization process. More precisely, these results show that the observed solvent–solute interactions lead to specific displacements of the equilibrium between the asymmetric and symmetric complex diastereoisomers, and determine the temperature-sensitivity of the related chemical shifts.

Undoubtedly, these interactions are strong enough to induce significant variations of the polarizability of the Ni–TFA bonds and to control accordingly the microstructure of the resulting polymer, to the extent where that microstructure will depend on the mode of cleavage of the bonds.

However, the results of ^{1}H NMR studies are in agreement with the existence of a random solvation sphere of solvent molecules around the organometallic complex, thus accounting for the similar overall dynamical behaviour of the binuclear species in each solvent.

In conclusion, the effect of the solvents on the polymerization process is to be interpreted in terms of bond reactivity modifications, rather than to structural changes in the initiator coordination sphere.

New experiments, including a quantitative analysis of the isomer distribution in the resulting polymer chains, are in progress to support these conclusions.

Acknowledgment

One of us (M.J.) is indebted to IRSIA for a fellowship; we are also grateful to the Fonds de la Recherche Fondamentale et Collective and the Services de Programmation de la Politique Scientifique (Belgium) for financial support.

References

1 R. Warin, M. Julemont and Ph. Teyssié, *J. Organometal. Chem.*, in press.
2 F. Dawans and Ph. Teyssié, *J. Polym. Sci., B*, 7 (1969) 111.
3 P. Bourdauducq and F. Dawans, *J. Polym. Sci., A*, 10, (1972) 2527.
4 J. C. Marechal, F. Dawans and Ph. Teyssié, *J. Polym. Sci., A*, 8 (1970) 1993.
5 M. Julemont, E. Walckiers, R. Warin and Ph. Teyssié, *Makromol. Chem.*, 175 (1974) 1673.
6 (a) M. Julemont, *Ph. D. Thesis*, Liège, 1976.
(b) M. Julemont, P. Hadjiandreou, R. Warin and Ph. Teyssié, in preparation.
7 Ph. Teyssié, M. Julemont, J. M. Thomassin, E. Walckiers and R. Warin, in J. Chien (ed.), *Coordination Polymerization, A Memorial to Karl Ziegler*, Academic Press, New York, 1975, p. 327.
8 M. Julemont, R. Warin and Ph. Teyssié, in preparation.
9 C. Sourisseau and B. Pasquier, *Can. J. Spectrosc.*, 19 (1974) 11.
10 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley–Interscience, New York, 1972.
11 E. M. Engler and P. Laszlo, *J. Am. Chem. Soc.*, 93 (1971) 1317.
12 A. D. Buckingham, T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, 32 (1960) 1227.
13 C. J. F. Böttcher, *Theory of Electric Polarisation*, Elsevier Publ. Comp., Amsterdam, 1952.

Journal of Molecular Catalysis, 7 (1980) 531 - 534
© Elsevier Sequoia S.A., Lausanne — Printed in the Netherlands

THE USE OF (—)DIOP AND THE CLUSTER Rh_6CO_{16} AS A CATALYST PRECURSOR IN ASYMMETRIC HYDROGENATION

G. BALAVOINE, T. DANG*, C. ESKENAZI and H. B. KAGAN
Laboratoire de Synthèse Asymétrique, Laboratoire associé au C.N.R.S. L.A. no 040255-02, Université de Paris-Sud, 91405, Orsay (France)

(Received July 27, 1979)

Summary

The cluster Rh_6CO_{16} was used in the presence of the chiral diphosphine (—)DIOP ([2,2-dimethyl 1,3-dioxolane 4,5-diyl bis methylene] bis diphenylphosphine) as a catalytic complex for various types of asymmetric hydrogenation under mild conditions. Enantiomeric excesses of up to 40% were observed and are compared with the results obtained with mononuclear rhodium-(—) DIOP** complexes.

Introduction

The use of organometallic clusters as catalysts has undergone rapid development over the past several years. At least part of this interest derives from the hope that well-identified clusters will provide a link between homogeneous catalysts and the active metal surfaces of heterogeneous catalysts [1]. Despite the wide variety of cluster compounds used as catalysts it appears that in no case has it been firmly established that the actual catalyst is the cluster itself and not a mononuclear species. For these reasons it was of interest to check the potential of clusters containing chiral ligands in asymmetric catalysis both from a synthetic point of view and also to obtain mechanistic information. The use of clusters in asymmetric catalysis is still in its infancy. Ruthenium clusters with (—)DIOP as ligand, catalyze asymmetric reductions of ketones, ketoximes [2] or α,β-unsaturated carboxylic acids [3, 4]. Enantiomeric excesses up to 68% were observed in spite of harsh experimental conditions (80 °C, 3 atm H_2).

Our investigations into the behaviour or Rh_6CO_{16} in the presence of (—)DIOP were begun following the publication of results showing that Rh_6CO_{16} treated with various phosphines was able to catalyze hydrogenations [5, 6]. Preliminary results [7] established that Rh_6CO_{16} and an excess of DIOP gave a new catalytic system. We present here results obtained using this type of system for asymmetric reductions.

---

*Present address: Rhône-Poulenc Centre de Recherches des Carrières, 69190 - Saint Fons (France).

**DIOP stands for [2,2-dimethyl 1,3-dioxolane 4,5-diyl bis methylene] bis diphenylphosphine.