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Carbon monoxide poisoning as a probe for the active site(s) of a nickel-based olefin oligomerization catalyst

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The interaction of the olefin oligomerization catalyst system derived from [Ni(sacsac)(PBu$_3$)Cl] (sacsac = pentane-2,4-dithionate = dithioacetylacetonate) with carbon monoxide (CO) has been examined by a combination of ^{31}P NMR and FTIR spectroscopy. The catalyst is rapidly and completely inhibited by CO; however, removal of the CO restores catalytic activity. A CO-adduct of the active catalyst has a characteristic CO stretching frequency of 2042 cm^{-1}, and δ ^{31}P 9.9 ppm. Carbon monoxide does not react with [Ni(sacsac)(PBu$_3$)Cl], but [Ni(sacsac)(PBu$_3$(Cl] reacts with any of Et$_2$AlCl, BuLi, Li[Et$_3$BH] or K[s-Bu)$_3$BH] under an atmosphere of carbon monoxide in the presence or absence of olefin to produce [Ni(PBu$_3$)(CO)$_3$], which has been identified by FTIR and ^{31}P NMR. [Ni(sacsac)(PBu$_3$)Cl] reacts completely with BuLi or K[(s-Bu)$_3$BH] to form catalytically inactive species which yield active catalysts on addition of Et$_2$AlCl.

Keywords: Olefin, oligomerization, isomerization, catalysis, poisons, carbon monoxide, NMR spectra, infrared spectra

INTRODUCTION

We have reported previously on the very high olefin oligomerization activity of catalysts derived by combining [Ni(R^2—R^{1}sacR^{3}sac) (PL^{1}L^{2}L^3)X] (R^j, L^j = alkyl, aryl; X = halide; R^2—R^{1}sacR^{3}sac = dithio-β-diketonate) and Et$_2$AlCl in a suitable solvent in the presence of an olefin.[1-3] These catalysts are extremely active: 1000 mol of ethylene per mol of nickel are dimerized per second at 1 atmosphere of ethylene and at room temperature.[4] The catalyst must therefore be used at very low concentrations (*ca* 10^{-7}M) to maintain manageable reaction rates, and to avoid undesirable temperature excursions ($\Delta H°$ for ethylene dimerization = -104.1 kJ mol^{-1}). Identification and/or isolation of the active species is therefore difficult.

We have, however, shown that two catalytic species appear to be produced in solution during the dimerization of butenes,[5] and that an excess of alkyl aluminium is required for maximum activity.[6] The conventional mechanism of nickel-catalysed olefin oligomerization[7] is illustrated in Scheme 1. According to this mechanism, any alkylating or hydric reagent should act as a co-catalyst, only one equivalent of co-catalyst should be required, and the co-catalyst does not participate in the catalytic cycle.

Our investigations into the effects of potential poisons on the oligomerization of ethylene suggested that, although an excess of water completely deactivates the catalyst, low concentrations of water appear to increase the catalytic activity. In addition, carbon monoxide appears to be a reversible inhibitor of the catalyst, rather than an irreversible poison.[8] Accordingly, we wished to examine the interaction of carbon monoxide with the catalyst, in the hope that a more CO-resistant catalyst might be developed. Moreover, if CO does indeed reversibly inhibit the catalyst, then the nature of the catalytic active site(s) might be deduced from a chemical or spectrophotometric examination of the CO-poisoned catalyst. The CO-poisoned catalyst might also be more stable than the active catalyst, and might therefore be isolated and characterized.

The objectives of the present study were threefold: (i) to ascertain the nature of the major product(s) consequent upon poisoning the catalyst with CO; (ii) to establish whether CO poisoning of the catalyst is reversible, and, if so, to

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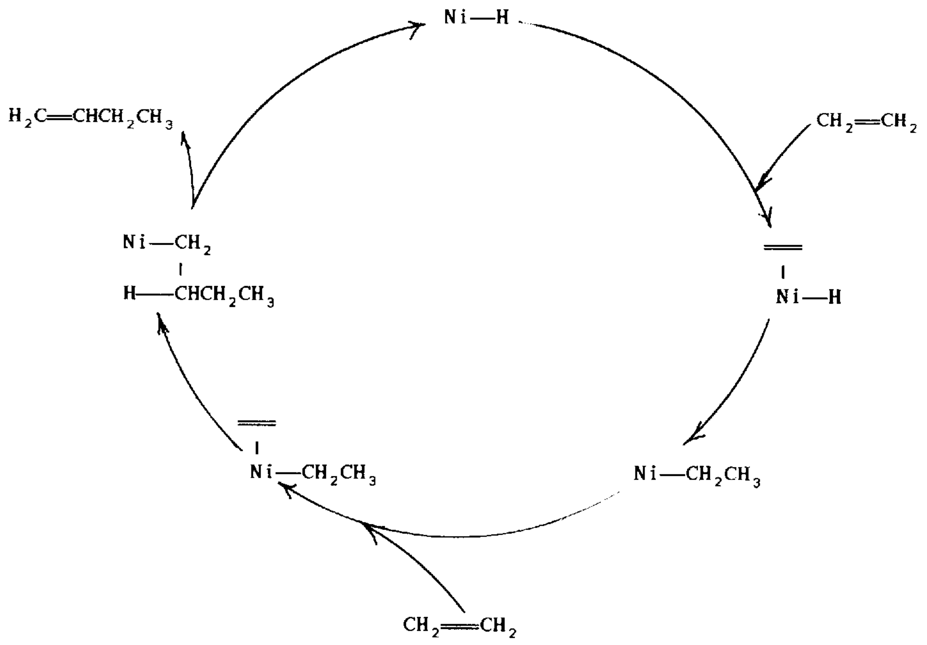

Scheme 1

investigate the viability of trapping the catalytically active species as a carbonyl-containing derivative, so as to identify the active catalyst(s) spectroscopically; and (iii) to investigate the role of the co-catalyst.

We report here a combination of FTIR, NMR and chemical investigations on the catalyst system in the presence of olefins and CO, and on the use of other potential co-catalysts.

EXPERIMENTAL

Chemicals

All manipulations were performed under an inert atmosphere of dry argon using conventional Schlenk techniques.[9] Analytical-grade solvents used in the preparations were dried and freshly distilled under argon, immediately prior to use, unless otherwise stated. Diethyl ether (BDH), benzene (Merck spectroscopic grade) and tetrahydrofuran (Merck) were distilled from sodium benzophenone ketyl. Toluene (Univar) was distilled from sodium wire. Chlorobenzene (Univar and Ajax) was distilled from diphosphorus(V) pentoxide, and dichloromethane from calcium hydride. Diethylaluminium chloride (Merck), diisobutylaluminium hydride (Aldrich), trimethylaluminium (Aldrich), lithium triethylborohydride (Superhydride, Aldrich), n-butyllithium (Aldrich) and potassium tri(s-butyl)borohydride (Selectride, Aldrich) were used as received. Ethylene, carbon monoxide (high-purity) and *trans*-2-butene (all Matheson) were used as received. 1-Hexene (97%, Aldrich) was distilled from sodium under argon before use. 3,3′-Dimethyl-1-butene (Aldrich) was used as received. [Ni(sacsac)$_2$] was prepared by the method of Barraclough *et al.*[10] The species [Ni(sacsac)(PBu$_3$)Cl], [Ni(sacsac)(P(C$_6$H$_5$)$_3$)Cl] and [Ni(sacsac)(P(C$_6$H$_5$)$_2$Me)Cl] were all prepared from [Ni(sacsac)$_2$] and the corresponding [Ni(PR$_3$)$_2$Cl$_2$] as described previously.[11]

Instrumentation

Fourier Transform infrared (FTIR) spectra were obtained from solutions in spectroscopic-grade benzene (Aldrich) using a Digilab 20/80 FTS spectrometer. The samples were contained in a potassium bromide solution cell with an optical pathlength of 0.2 mm. The concentration of [Ni(sacsac)(PBu$_3$)Cl] in the test solution was 0.014 M, and that of the alkylating or hydridic reagents was 0.28 M or 0.20 M (Superhydride). Proton-decoupled ^{31}P NMR spectra were recorded from solutions which were 0.064 M in [Ni(sacsac)(PBu$_3$)Cl] and 0.64 M in Et$_2$AlCl, or 0.15 M in BuLi or LiEt$_3$BH, on a Bruker WM 400

NMR spectrometer using a 5-mm tube at a probe temperature of 27 °C. A capillary of a triethyl phosphate solution (20%, w/w, in benzene) was inserted in the NMR tube and used as an integration standard for ^{31}P NMR. The ^{31}P NMR chemical shifts are referenced to neat external trimethyl phosphite taken to be 140.85 ppm. Gas-chromatographic analyses were performed on a Hewlett–Packard 5790A gas chromatograph with an SGE 25 m QC2/BP1 0.25 mm capillary column as described previously.[3,5] The olefin products were identified from their retention times by comparison with authentic samples of each.

Reactions

Carbon monoxide was reacted with the nickel substrates in a Schlenk tube connected to a vacuum/argon manifold, and fitted with a septum through which CO or gaseous olefins could be introduced via a catheter, and other reagents and solvents via syringe. A solution of [Ni(sacsac)(PBu_3)Cl] in benzene was injected into the Schlenk tube maintained under an atmosphere of argon. For liquid olefins, a 2 ml aliquot of olefin was injected into the Schlenk tube. For gaseous olefins or CO, the gas was bubbled through the catalyst solution for 5 min and then passed over the reaction mixture. The total pressure was slightly greater than 1 atm. A known amount of co-catalyst was injected through the septum. Whenever the CO gas was removed, this was done by flushing the system with argon. Samples were drawn from the Schlenk tube by a syringe at regular time intervals for analysis by GC and FTIR and ^{31}P NMR spectroscopy.

The FTIR spectra in the CO stretching region contained several overlapping absorptions and also peaks due to dissolved CO. To resolve overlapping carbonyl absorptions, the IR absorption spectra were processed by the program 'Fitgauss',[12] a deconvolution and analysis program, and the peaks due to dissolved CO subtracted from the spectra.

The oligomerization of butenes was conducted in a stainless-steel tubular reactor with Swagelok™ fittings, a magnetic stirrer and a thermocouple. The temperature of the cold junction was maintained at 0 °C in a Dewar flask filled with an ice–water mixture. The reactor pressure and solution temperature were monitored by a transducer and thermocouple, respectively, which were linked to a Datataker™ for data storage. The empty reactor was assembled hot and cycled with argon/vacuum several times and then weighed. The reactor was cooled to a temperature of -5 °C and butenes condensed into the reactor. Excess butene was slowly vented until the exact amount of 7.50 ± 0.05 g of butene remained in the reactor. A chlorobenzene solution (10 ml) of [Ni(sacsac)(PBu_3)Cl] (0.015 g, 3.5×10^{-5} mol) was then injected into the stirred reactor. Once the temperature and pressure had stabilized, the reaction was initiated by the injection of either Et_2AlCl or BuLi through the septum at the head of the reactor. Variations of temperature and pressure were then monitored at regular time intervals. In the initial stages of the reaction, readings were recorded every 10 s; and after 20 min, readings were acquired once each minute. After the test period had elapsed, the mass of the reactor was checked, and the gaseous and liquid products were analysed by GC. The other olefin oligomerization and isomerization reactions were performed as described previously.[4,13]

RESULTS AND DISCUSSION

We have reported previously that the oligomerization of butenes in a batch reactor at *ca* 2 atm is completely inhibited if the reactor is pressurized with carbon monoxide either before or after catalyst activation.[2] In the presence of carbon monoxide, the normally red–brown catalyst solution becomes orange in colour. In the present work, we have detected no oligomerization of ethylene, 2-butene, or 1-hexene, nor any isomerization of 2-butenes or 1-hexene, when diethylaluminium chloride (Et_2AlCl) is added to benzene solutions of the olefin and [Ni(sacsac)(PBu_3)Cl] under a carbon monoxide atmosphere. Under the conditions of these experiments, but in the absence of carbon monoxide, ethylene and butenes are oligomerized, and butenes and 1-hexene are isomerized.

Under an atmosphere of carbon monoxide, Et_2AlCl was added to benzene solutions of Ni(sacsac)(PBu_3)Cl and either ethylene, 2-butenes, 1-hexene, 3,3-dimethyl-1-butene, or no olefin, and the resultant solutions assayed by FTIR in the CO-stretching region. Equivalent spectra were obtained in all cases. Three peaks, at ν(CO) 2062, 2042 and 1985 cm^{-1}, were observed.

The Ni—H moiety is the putative catalytic active site for both olefin oligomerization and olefin isomerization.[7,14–17] Certainly, olefin isomerization (where possible and detectable) has always been observed to accompany olefin oligomerization in the present system. We have found olefin isomerization to be a convenient test reaction to assay for catalytic activity.

A variety of alkylating or hydridic reagents was investigated as potential co-catalysts. When added to a benzene solution of [Ni(sacsac)(PBu$_3$)Cl] and 1-hexene, Et$_2$AlCl, Me$_3$Al or (i-Bu)$_2$AlH formed effective olefin isomerization catalysts. By contrast, the use of BuLi, K[(s-Bu)$_3$BH] or Li[Et$_3$BH] as potential co-catalysts did not result in the generation of olefin isomerization catalysts. Similarly, the dimerization of 2-butene in chlorobenzene is catalysed by a combination of Et$_2$AlCl and [Ni(sacsac)(PBu$_3$)Cl], but not by a combination of BuLi and [Ni(sacsac)(PBu$_3$)Cl].

When any of BuLi, s-BuLi, t-BuLi, EtMgCl, AlCl$_3$, LiEt$_3$BH or Et$_3$Al is combined with [Ni(sacsac)(PBu$_3$)Cl] in toluene no isomerization of 1-hexene is detected.

These potential co-catalysts were added to benzene solutions of [Ni(sacsac)(PBu$_3$)Cl] under carbon monoxide. and the solutions examined by FTIR. Peaks at 2062 and 1985 cm^{-1} were observed in the IR spectra of all these potential co-catalysts; however, a peak at 2042 cm^{-1} was observed only when effective co-catalysts [Et$_2$AlCl or (i-Bu)$_2$AlH or Me$_3$Al] were combined with [Ni(sacsac)(PBu$_3$)Cl] under carbon monoxide (Table 1).

Carbon monoxide does not appear to react with either [Ni(sacsac)(PBu$_3$)Cl] or Et$_2$AlCl in benzene at room temperature and atmospheric pressure. Thus, the only peaks due to CO-stretching vibrations observed in the FTIR spectra of benzene solutions of [Ni(sacsac)(PBu$_3$)Cl] or Et$_2$AlCl are coincident with those due to dissolved CO. Similarly, the only ^{31}P NMR resonance detected from benzene solutions of [Ni(sacsac)(PBu$_3$)Cl] in the presence or absence of CO is a peak at δ 9.0 ppm, due to the coordinated PBu$_3$.

Table 1 Relationships between catalytic activity and the IR spectra for a variety of potential co-catalysts interacting with [Ni(sacsac)(PBu$_3$)Cl] and 1-hexene in benzene under a carbon monoxide atmosphere

Reagent	ν(CO) (cm^{-1})			Catalytic activity
Et$_2$AlCl	2062	2042	1985	Yes
i-Bu$_2$AlH	2062	2042	1985	Yes
Me$_3$Al	2062	2042	1985	Yes
BuLi	2062		1985	No
K[(s-Bu)$_3$BH]	2062		1985	No
Li[Et$_3$BH]	2062		1985	No
BuLi + Et$_2$AlCl	2062	2042	1985	Yes

Attempts to examine the active catalyst by ^{31}P NMR at room temperature were unsuccessful. Activation of [Ni(sacsac)(PBu$_3$)Cl] in chlorobenzene by Et$_2$AlCl in the presence of 1-hexene resulted in an approximately ten-fold loss of ^{31}P NMR signal intensity. Accordingly, carbon monoxide poisoning was used in an attempt to trap reactive intermediates.

[Ni(sacsac)(PBu$_3$)Cl] was reacted with Et$_2$AlCl in benzene under carbon monoxide. The ^{31}P NMR spectrum of the resultant solution contained two resonances at δ 12.2 (assigned to [Ni(PBu$_3$)(CO)$_3$]; *vide infra*) and 9.9 ppm. Absorptions assigned to ν(CO) at 2062 and 1985 cm^{-1} ([Ni(PBu$_3$)(CO)$_3$]; *vide infra*) and at 2042 cm^{-1} were observed in the FTIR spectrum of this solution. The FTIR absorption at 2042 cm^{-1} is initially more intense than those assigned to [Ni(PBu$_3$)(CO)$_3$]. However, the intensity of the absorption at 2042 cm^{-1} slowly decreases with time, and there is a concomitant increase in the intensities of the absorptions assigned to [Ni(PBu$_3$)(CO)$_3$] at 2062 and 1985 cm^{-1}. This same time-dependence of the ν(CO) absorptions in the FTIR spectrum is observed whether the catalyst is activated under carbon monoxide, or poisoned with carbon monoxide after approximately one hour of operation. If argon is passed through the solution for 10 min, the FTIR absorption at 2042 cm^{-1} disappears, leaving the [Ni(PBu$_3$)(CO)$_3$] absorptions ast 2062 and 1985 cm^{-1}, and the resultant solution isomerizes added 1-hexene.

[Ni(sacsac)(PBu$_3$)Cl] was reacted with butyllithium (BuLi) in benzene under argon. The ^{31}P NMR spectrum established that all of the [Ni(sacsac)(PBu$_3$)Cl] had reacted. Three new ^{31}P NMR resonances were observed at δ 12.1, 9.7 and 7.5 ppm. 1-Hexene was added to the solution. No 1-hexene isomerization was detected. The ^{31}P NMR spectrum was unchanged. Carbon monoxide was then passed through the solution for 5 min and the ^{31}P NMR and FTIR spectra were recorded. Three ^{31}P NMR resonances, at δ 12.3 (minor), 12.2 and 7.5 ppm, and two FTIR ν(CO) absorptions at 2062 and 1985 cm^{-1} were observed. The intensity of the ^{31}P NMR absorption at δ 7.5 ppm decreased with time, whilst that of the absorption at δ 12.2 ppm increased with time at the same rate.

The ^{31}P NMR resonance at δ 12.2 ppm, and FTIR absorptions at 2062 and 1985 cm^{-1}, are coincident with those of [Ni(PBu$_3$)(CO)$_3$].[18-24] Moreover, the frequencies of the FTIR ν(CO) absorptions are dependent on the nature of the coordinated phosphine {with [Ni(sacsac)(PBu$_3$)Cl] and 1-hexene reacted with Li[Et$_3$BH] or BuLi under CO, ν(CO) = 2070(m), 1996(s), and with [Ni(sacsac)(PPh$_2$Me)Cl] and 1-hexene reacted with Li[Et$_3$BH] or BuLi under CO, ν(CO) = 2068(m), 1995(s)}. Accordingly, the ^{31}P NMR resonance at δ 12.2 ppm, and FTIR absorptions at 2062(m) and 1985(s) cm^{-1}, are assigned to [Ni(PBu$_3$)(CO)$_3$].

[Ni(sacsac)(PBu$_3$)Cl] was reacted with BuLi in an identical manner. The same ^{31}P NMR spectrum was obtained. Carbon monoxide was then passed through the solution for 5 min. The ^{31}P NMR and FTIR spectra exhibited absorptions at δ 12.2 and 7.5 ppm, and ν(CO) = 2062 and 1985 cm^{-1}, respectively. The resonances at δ ^{31}P 12.2 ppm and ν(CO) = 2062, 1985 cm^{-1}, are assigned to [Ni(PBu$_3$)(CO)$_3$] as discussed above. Thus, the resonance at δ ^{31}P 7.5 ppm must be derived from a species with no coordinated CO. Diethylaluminium chloride was added to this solution. The ^{31}P NMR spectrum of the resultant solution exhibited resonances at δ 12.2 (assigned to [Ni(PBu$_3$)(CO)$_3$]) and 9.9 ppm. The FTIR spectrum contains absorptions assigned to ν(CO) at 2062 and 1985 cm^{-1} (due to [Ni(PBu$_3$)(CO)$_3$]) and a new ν(CO) absorption at 2042 cm^{-1}.

[Ni(sacsac)(PBu$_3$)Cl] was reacted with BuLi in benzene in the presence of 1-hexene. No olefin isomerization activity was detected. Et$_2$AlCl was added to the solution and the 1-hexene was rapidly isomerized. The catalyst was poisoned with carbon monoxide and the FTIR spectrum of the resultant solution exhibited absorptions at 2062, 2042 and 1985 cm^{-1}.

[Ni(sacsac)(PBu$_3$)Cl] was reacted with K[(s-Bu)$_3$BH] in benzene. 1-Hexene was added to the solution and no isomerization was observed. Carbon monoxide was then passed through the solution. The ^{31}P NMR spectrum of this solution exhibited a resonance at δ 12.2 ppm. The FTIR spectrum exhibited absorptions assigned to ν(CO) at 2062 and 1985 cm^{-1} ([Ni(PBu$_3$)(CO)$_3$]). The carbon monoxide was removed and 1-hexene was added to the solution. No 1-hexene isomerization could be detected in the presence or absence of Et$_2$AlCl.

[Ni(sacsac)(PBu$_3$)Cl] was reacted with K[(s-Bu)$_3$BH] in benzene in the presence of 1-hexene. No olefin isomerization activity was detected. Et$_2$AlCl was added to the solution and the 1-hexene was isomerized. Carbon monoxide was bubbled through the solution and the FTIR spectrum showed absorptions assigned to ν(CO) at 2062, 2042 and 1985 cm^{-1}.

These data suggest that [Ni(sacsac)(PBu$_3$)Cl] and Et$_2$AlCl react in benzene under carbon monoxide to form a carbonyl-containing product, **A** (with ν(CO) = 2042 cm^{-1} and δ ^{31}P 9.9 ppm), which slowly reacts to form catalytically inactive [Ni(PBu$_3$)(CO)$_3$]. The carbon monoxide can be removed from the species **A** to produce an active catalyst.

[Ni(sacsac)(PBu$_3$)Cl] appears to react quantitatively with BuLi to give, amongst other products, a compound, **B** (δ ^{31}P 7.5 ppm), which slowly forms compound **C** (δ ^{31}P 9.7 ppm), and compound **D** (δ ^{31}P 12.1 ppm). Compound **C** can also be prepared by the reaction of [Ni(sacsac)(PBu$_3$)Cl] with hydridic reagents. Compound **B** does not react with either 1-hexene or CO. Compounds **B** and **C** react with Et$_2$AlCl to produce an active 1-hexene isomerization catalyst, which reacts reversibly with carbon monoxide to form the CO-adduct, **A**.

Compound **D** (and possibly compound **C**) react(s) rapidly and irreversibly with carbon monoxide to form [Ni(PBu$_3$)(CO)$_3$], which is catalytically inactive for 1-hexene isomerization under the conditions of our experiments.

The conventional mechanism for olefin oligomerization/isomerization invokes nickel–hydride and nickel–alkyl species as catalytic intermediates. Nickel–alkyl compounds can react reversibly with carbon monoxide to form acyl derivatives.[25,26] However, we have not detected a characteristic coordinated acyl ν(CO) absorption (between 1620 and 1650 cm^{-1}) in the FTIR spectra.[27,28] The reversible carbon monoxide poisoning is therefore unlikely to be the result of an equilibrium

$$\text{Nickel–acyl} \rightleftharpoons \text{nickel–alkyl} + \text{CO}$$

Despite the implications of the conventional mechanism, the production of a nickel–alkyl (or presumably Ni–H) species may be a necessary, but is not a sufficient, requirement for the generation of the olefin oligomerization or isomerization catalyst. Thus, all of the [Ni(sacsac)(PBu$_3$)Cl] is consumed on reaction with BuLi, but none of the species produced in this reaction is catalytically active. However, an active catalyst is generated by the addition of Et$_2$AlCl to the solution. Since the solution contains no [Ni(sacsac)(PBu$_3$)Cl], the catalyst must be produced from the interaction of Et$_2$AlCl with one or more of the products of the [Ni(sacsac)(PBu$_3$)Cl]/BuLi reaction. Perhaps significantly, the complex [Ni(acac)(PPh$_3$)Et] does not isomerize 1-butene.[29]

CONCLUSIONS

This work has shown that the activation of [Ni(sacsac)(PBu$_3$)Cl] by Et$_2$AlCl consumes all of the [Ni(sacsac)(PBu$_3$)Cl]. Similarly, [Ni(sacsac)(PBu$_3$)Cl] is quantitatively converted on raction with BuLi, K[(s-Bu)$_3$BH] or Li[Et$_3$BH]. The products of these reactions are catalytically inactive, but may be converted to an active catalyst by reaction with Et$_2$AlCl. Moreover, these reaction products (possibly Ni–hydrides or Ni–alkyls) only react with CO or olefins in the presence of Et$_2$AlCl. These results support our earlier suggestion that the active catalyst is a dimetallic Ni–Al species, and not a simple Ni–hydride or Ni–alkyl. Accordingly, therefore, although many alkylating or hydridic reagents react with [Ni(sacsac)(PBu$_3$)Cl], only some of these reagents form active catalysts.

The ultimate product of the reaction of the catalyst with carbon monoxide appears to be [Ni(PBu$_3$)(CO)$_3$], which is catalytically inactive under the conditions described herein. Poisoning of the catalyst with carbon monoxide can be reversed if the carbon monoxide is removed.

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REFERENCES

1. Cavell, K J and Masters, A F *J. Chem. Res.*, 1983, 72
2. Chin, V W L, Masters, A F, Tyler, R J and Vender, M *Studies Surf. Sci. Catal.*, 1988, 36: 421
3. Brown, S J, Masters, A F and Vender, M *Polyhedron*, 1988, 7: 2009
4. Brown, S J and Masters, A F *J. Organomet Chem.*, 1989, 367: 371
5. Brown, S J, Masters, A F, Sachinidis, J I and Tregloan, P A *Polyhedron* (in the press)
6. Brown, S J, Clutterbuck, L M, Masters, A F, Sachinidis, J I and Tregloan, P A *Appl. Catal.*, 1989, 48: 1
7. Bogdanovic, B *Adv. Organomet. Chem.*, 1979, 17: 105
8. Brown, S J and Masters, A F *Erdöl & Kohle Erdgas Petrochemie* 1990, 43: 15
9. Shriver, D F, *The Manipulation of Air Sensitive Compounds*, McGraw-Hill, New York, 1969
10. Barraclough, C G, Martin, R L and Stewart, I M, *Aust. J. Chem.*, 1969, 22: 891
11. Masters, A F and Fackler, J P, Jr *Inorg. Chim. Acta*, 1980, 39: 111
12. Reimers, J Fitgauss program, University of Sydney
13. Clutterbuck, L M B.Sc.(Hons) Thesis, University of Sydney, 1987
14. Jolly, P W and Wilke, G *The Organic Chemistry of Nickel*, vol 2, Academic Press, New York, 1975
15. Jolly, P W *Comprehensive Organometallic Chemistry*, vol 8, Wilkinson, G, Stone, F G A and Abel, E W (eds), Pergamon Press, Oxford, 1982, p 615
16. Keim, W, Behr, A and Roper, M in *Comprehensive Organometallic Chemistry*, vol 8, Wilkinson, G, Stone, F G A and Abel, E W (eds), Pergamon Press, Oxford, 1982, p 371
17. Onsager, O and Johansen, J E in *Chemistry of the Metal Carbon Bond*, vol 3, Hartley, F R and Patai, S (eds), Wiley, New York, 1985, p 205
18. Tolman, C A, *Chem. Rev.*, 1977, 77: 343
19. Bigorgne, M *Mem. Soc. Chem.*, 1960, 326: 1986
20. Tolman, C A *J. Am. Chem. Soc.*, 1970, 92: 2953
21. Edgell, W F and Dunkle, M P *Inorg. Chem.*, 1965, 4: 1629
22. Meriwether, L S and Fiene, M L *J. Am. Chem. Soc.*, 1959, 81: 4200
23. Mathieu, R, Lenzi, M and Poilblanc, R *Inorg. Chem.*, 1970, 9: 2030
24. Chatt, J and Hart, F A *J. Chem. Soc.*, 1960, 1378
25. Carmona, E, Gonzalez, F, Poveda, M L, Atwood, J L and Rogers, R D *J. Chem. Soc., Dalton Trans.*, 1980, 2108
26. Coronas, J M, Muller, G, Rocamora, M, Miravitiles, C and Solans, X *J. Chem. Soc., Dalton Trans.*, 1985, 2333
27. Yamamoto, T, Kohara, T and Yamamoto, A *Bull. Chem. Soc. Jpn*, 1981, 54: 2161
28. Corain, B and Favero, G *J. Chem. Soc., Dalton Trans.*, 1975, 283
29. Yamamoto, A, Yamamoto, T, Saruyama, T and Nakamura, Y *J. Am. Chem. Soc.*, 1973, 95: 4073