A Proton Directly Attacks 1,5-Cyclooctadiene in Bis(1,5-cyclooctadiene)nickel(0) in the Formation of a Keim Type Oligomerization Catalyst

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Full proton and carbon assignments have been obtained for ((1,4,5-η)-cyclooctenyl)-(1,1,1,5,5,5-hexafluoro-2,4-pentadionato)nickel(II) (**1**), a Keim type ethylene oligomerization catalyst, which is afforded by treatment of bis(1,5-cyclooctadiene)nickel with 1,1,1,5,5,5-hexafluoroacetylacetone. The larger metallacycle formed by nickel and the (1,4,5-η)-cyclooctenyl ligand in **1** is shown to be in a "nickela chair" conformation. The reaction of bis(1,5-cyclooctadiene)nickel with 1,1,1,5,5,5-hexafluoroacetylacetone-d_2 at low temperature shows a 70% incorporation of a deuterium atom *anti* to nickel at a β-carbon. This observation is incompatible with a hydride migration path for the formation of **1** but fully consistent with a direct protonation of an alkene coordinated to an electron-donating nickel.

Introduction

In a particular respect nickel is a remarkable member of the triad composed of the well-known catalyst metals nickel, palladium, and platinum. Although palladium has recently been found to be able to polymerize ethylene,[1] nickel is the only metal long known to be able to catalyze the oligomerization of ethylene.[2,3] This property of nickel is taken advantage of industrially in the Shell higher olefin process (SHOP), which has a capacity to convert 10^6 tons/year (1990) of ethylene to statistical mixtures of linear medium-length terminal olefins.[2a] A manifold of nickel compounds, among them
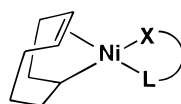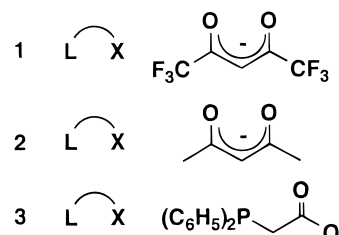
Chart 1

1−3 (the last is used as an industrial catalyst), are "unicomponent" homogenous catalysts (Chart 1). It should, however, be noted that these so-called Keim catalysts (after the inventor), although unicomponent, are not the true catalysts. These are formed *in situ* and are most probably hydrides.[2a−e,l]

The catalysts **1−3** can be prepared by treating bis-(1,5-cyclooctadiene)nickel, Ni(COD)$_2$, with the appropriate acid; i.e., in the preparation of **1** ((1,4,5-η)-cyclooctenyl)(1,1,1,5,5,5-hexafluoro-2,4-pentadionato)nickel(II), the acid is 1,1,1,5,5,5-hexafluoropentane-2,4-dione (trivial name hexafluoroacetylacetone), H(hfacac).[2,4]

To elucidate the mechanism for this formation, we have performed (a) an NMR study affording full assignments of the protons (and carbons) of **1**, (b) a deuterium-labeling study, and (c) DFT calculations at the B3LYP level of two reasonable conformers of **1**, **1a** and **1b**. As the interpretation is dependent of NMR assignments, some of the NMR observations have to be discussed in certain detail.

Results

DFT Calculations. (1,4,5-η)-Cyclooctenyl ligands can form two conformationally different complexes with

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(1) (a) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.*, **1995**, *117*, 1137. (b) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (c) Brookhart, M.; Johnson, L. K.; Killian, C. M.; Mecking, S.; Tempel, D. *J. Polym. Prep.* **1996**, *37*, 254.

(2) (a) Keim, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 235. (b) Müller, U.; Keim, W.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1011. (c) Keim, W. *J. Mol. Catal.* **1989**, *52*, 19. (d) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594. (e) Keim, W.; Behr, A.; Kraus, G. *J. Organomet. Chem.* **1983**, *251*, 377. (f) Peuckert, M.; Keim, W.; Storp, S.; Weber, R. S. *J. Mol. Catal.* **1983**, *20*, 115. (g) Keim, W. *Chimia* **1981**, *35*, 344. (h) Keim, W.; Hoffmann, B.; Lodewick, R.; Peuckert, M.; Schmitt, G.; Fleischhauer, J.; Meier, U. *J. Mol. Catal.* **1979**, *6*, 79. (i) Keim, W.; Kowald, F. H.; Goddard, R.; Krüger, C. *Angew. Chem.* **1978**, *90*, 493. (j) Keim, W.; Behr, A.; Limbäcker, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 503. (k) Keim, W.; Appel, R.; Storeck, A.; Krüger, C.; Goddard, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 116. (l) Keim, W.; Behr, A.; Röper, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 371.

(3) (a) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 186. (b) Al-Jarallah, A. M.; Anabtawi, J. A.; Siddiqui, M. A. B.; Aitani, A. M.; Al-Sa'doun, A. W. *Catal. Today* **1992**, *14*, 1. (c) Johnson, L. K.; Killian, C. M.; Brookhart, M. *Organometallics* **1997**, *16*, 2005. (d) Brookhart, M. Eur. Pat. Appl. 0454231A2, 1991. (e) Johnson, L.; Killian, C. M.; Arthur, S. D.; Feldman, J.; McCord, E. F.; McLain, S. J.; Kreutzer, K. A.; Bennett, M, A.; Coughlin, E. B.; Ittel, S. D.; Parthasarathy, A.; Tempel, D. J.; Brookhart, M. Patent WO 96/23010, 1996.

(4) Bogdanovic, B.; Kröner, M.; Wilke, G. *Justus Libigs Ann. Chem.* **1966**, *699*, 1.

Table 1. ^{1}H NMR Data of Compound 1

proton	shift[a]	obsd or calcd coupling constant[b]			
1	−0.37	$J_3 = -16$	$J_4 = 4.2^c$	$J_6 = 7.1^c$	$J_8 = 3.4^c$	
2	0.32	$J_5 = 10^c$	$J_8 = 2^c$	$J_9 = 2.5^c$	$J_{10} = -15^c$	
3	1.52	$J_1 = -16$	$J_4 = 12.1^c$	$J_6 = 3.5^c$	$J_8 = 3.5^c$	
4	1.85	$J_1 = 4.2^c$	$J_3 = 12.1^c$	$J_6 = -13.1^c$	$J_7 = 4.5^c$	$J_{11} = 12.9^c$
5	2.03	$J_2 = 10^c$	$J_9 = -17^c$	$J_{10} = 2^c$	$J_{13} = 7.3^c$	
6	2.05	$J_1 = 7.1^c$	$J_3 = 3.5^c$	$J_4 = -13.1^c$	$J_7 = 4.5^c$	$J_{11} = 5.3^c$
7	2.14	$J_4 = 4.5^c$	$J_6 = 4.5^c$	$J_{11} = -17$	$J_{12} = 2.2^c$	$J_{13} = -1.9^c$
8	2.34	$J_1 = 3.4^c$	$J_2 = 2^c$	$J_3 = 3.5^c$	$J_{10} = 7.5^c$	
9	2.43	$J_2 = 2.5^c$	$J_5 = -17^c$	$J_{10} = 10^c$	$J_{13} = 6.2^c$	
10	2.47	$J_2 = -15^c$	$J_5 = 2^c$	$J_8 = 7.5^c$	$J_9 = 10^c$	
11	2.66	$J_4 = 12.9^c$	$J_6 = 5.3^c$	$J_7 = -17$	$J_{12} = 6.4^c$	
12	5.16	$J_7 = 2.2^c$	$J_{11} = 6.4^c$	$J_{13} = 8.3^c$		
13	5.63	$J_5 = 7.3^c$	$J_7 = -1.9^c$	$J_9 = 6.2^c$	$J_{12} = 8.3^c$	

[a] The spectra are recorded in CDCl$_3$ at 298.3 K. Shifts are given in ppm downfield from Me$_4$Si, as calculated from the solvent signal at δ 7.24. The singlet from the hexafluoroacetylacetonate proton is observed at 6.07 ppm. [b] Coupling constants in Hz. [c] All nonoverlapping NMR signals are simulated by the program NMR II 1.0 by Calleo Scientific Software Publishers.
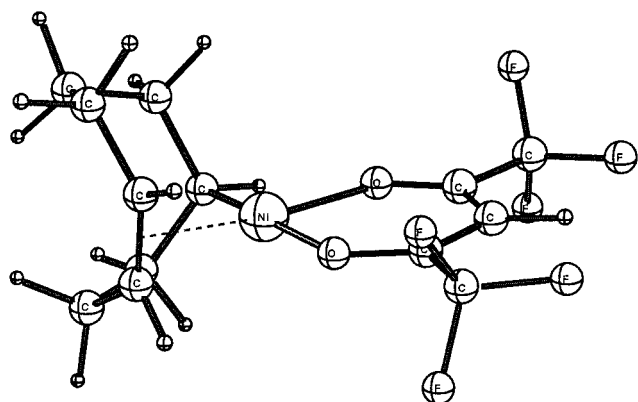
1a
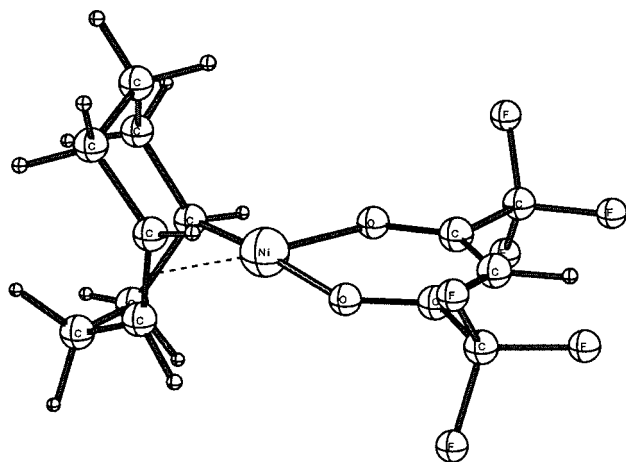
1b

Figure 1. Two conformations of compound **1**: a "metalla-chair" (**1a**) and a "metalla-boat" (**1b**).

transition metals (*vide infra*). The difference is easily seen in the larger metallacycle, which may adopt a metalla-chair structure of type **1a** or a metalla-boat structure of type **1b** (Figure 1). The DFT calculations show **1a** to be energetically favored by approximately 1 kcal/mol, calculated at the B3LYP level using a double-ζ-quality basis set.[5] If the exchange is slow at room

(5) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

Table 2. ^{13}C NMR Data of Compound 1

carbon	shift[a]	proton correl[b]
A	26.3	4; 6
B	26.5	5; 9
C	29.0	7; 11
D	36.0	1; 3
E	37.1	2; 10
F	46.4	8
G	95.1	12
H	96.7	13

[a] The values are obtained from proton-decoupled spectra in CDCl$_3$ at 298.3 K. Shifts are given in ppm downfield from Me$_4$Si as calculated from the solvent signal at δ 77.0. Carbon signals from hexafluoroacetylacetonate are observed at δ 90.6 ppm (C,H-COSY correlation with proton signal at δ 6.07 ppm), 117.7 (q, J_{CF} = 284 Hz, CF$_3$) 175.3 (q, J_{CF} = 35 Hz, CO). [b] Observed by COSY-heteronuclear correlation.

temperature, this rather small value should correspond to two sets of signals in the NMR spectrum, with an intensity ratio of 85:15.[6] In fact, we only detect a single set of signals in ^{1}H NMR and ^{13}C NMR at various temperatures. A possible interpretation is that the calculations underestimate the energy difference between the two conformers. Another possibility is a fluxional situation, even at lower temperatures. However, the lack of intermediate-sized couplings (*vide infra*) shows one conformation to be clearly dominating.

NMR Assignments and Conformational Analysis. The shifts of the 13 protons of the cyclooctadienyl ligand are numbered from high field to low field in the first column of Table 1. In a similar order the ^{13}C NMR signals are labeled as letters and their shifts displayed in Table 2. The spectra do not change with temperature; the coupling patterns of the signals appear the same in different solvents (CDCl$_3$, benzene-d_6, toluene-d_8), although some shift changes are noticed in aromatic solvents. However, the ^{1}H NMR spectrum is extremely sensitive to impurities; even tiny amounts of impurities remaining from the preparation cause extensive line broadening.

From a brief look at the spectrum few assignments are obvious. A C−H COSY study afforded correlations between carbons and the attached protons (see Table 2). The low-field carbon signals G and H correlate with low-field proton signals 12 and 13, respectively. Hence, G and H are caused by the two olefinic carbons, and 12

(6) Juaristi, E. *Introduction to Stereochemistry & Conformational Analysis*; Wiley: New York, 1991; p 242.
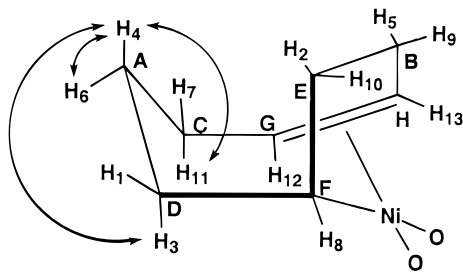
Figure 2. Simplified view of the "metalla-chair" **1a**, showing proton assignments and the three large couplings of proton 4.

and 13 (which are coupled) originate from the olefinic protons (in accordance with previously suggested assignments of these proton[2e,h]). As only one carbon signal, F, related to a single proton signal, 8, remains, these signals belong to the σ-bonded carbon and its hydrogen. (This proton assignment contradicts some literature suggestions.[2e,h,7]) Assignments of coupling constants (as shown in the second column of Table 1) and connectivity within the cyclooctenyl ligand were unambiguously established by extensive decoupling experiments, simulations of nonoverlapping ^{1}H signals, and a homonuclear COSY study.[8]

Spatial relationships are more intricate to establish. A published X-ray study of the closely related **2** shows the larger (six-and-a-half-membered) nickelacycle to be in a chair-like conformation.[9] With this conformation as a model, we have made the total assignments according to numbers and labels on complex **1** in Figure 2.

The shifts for geminal protons show a pleasantly consistent pattern: the low-shift proton of a geminal pair resides uniformly at the face of the octenyl ring opposite to the nickel–hfacac part. Furthermore, the shift differences within a pair of two geminal protons become larger as the pair is positioned more closely to nickel. Thus, proximity to nickel does not necessarily imply lower shifts and, accordingly, the relatively high shifts for the σ-carbon (46.4 ppm) and its proton (2.34 ppm) seem easy to accept.

A convincing reason for the spatial assignments is that, as seen in Figure 2, there should exist only one proton with three large couplings, i.e. the axial proton on the carbon most remote to nickel in the nickela-chair. This proton should have one large geminal coupling and two axial–axial couplings. The only signal in the ^{1}H NMR spectrum that fits is the well-resolved multiplet 4. Decoupling of multiplet 4 shows that (a) the well-resolved multiplets 3 and 11 lose one large coupling each, confirming axial–axial relationships toward 4 and (b) multiplets 1 and 7 lose only small couplings, compatible with axial–equatorial relations. A check simulation of multiplet 4 gives an excellent fit. The large axial–axial couplings and lack of intermediate-sized couplings also prove that one conformation is dominating.

In Figure 3 another simplified projection of a model of the nickela-chair, **1a**, is shown. In this projection it
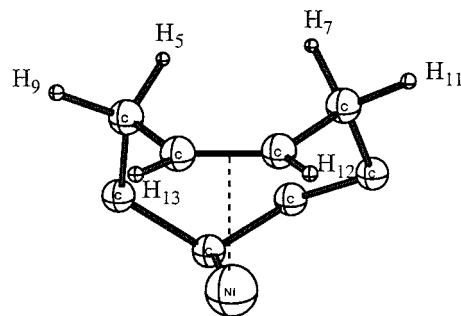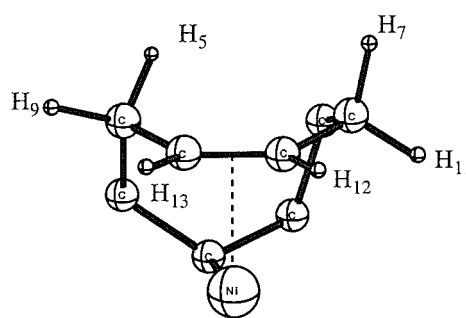

Figure 3. (a, top) View of **1a** from nickel toward a simplified octenyl ligand, illustrating the unsymmetrical constellations of the methylene groups in a nickela-chair. (b, bottom) View of **1b** from nickel toward a simplified octenyl ligand, illustrating the semisymmetrical constellations of the methylene groups in a nickela-boat.

appears that the proton previously assigned as signal 7 should exhibit an allylic bond with a nearly perpendicular dihedral angle toward the alkene plane.[10] Indeed, the only allylic coupling found ($J_{7-13} = -1.9$ Hz) supports such an angular relation.[11a] Further support for a dihedral angle close to 90° (calculated 74°) is found in the rather small coupling to the vicinal alkene proton ($J_{7-12} = 2.2$ Hz).[11b] The proton previously assigned to multiplet 11 has a coupling constant ($J_{11-12} = 6.4$ Hz) which is reasonable for a small dihedral angle (calculated 38.0°). The small J_{2-8} (2 Hz) and the larger (7.5 Hz) indicate the facial assignments shown, with a dihedral angle between protons 2 and 8 around 90° (calculated 81.0°) and a more cisoid relation (35.6°) between protons 10 and 8. The rather large couplings $J_{2-5} \approx J_{9-10} \approx 10$ Hz are compatible with approximately cisoid relations between protons 2 and 5 and, on the opposite face, protons 9 and 10. This suggestion receives further support from the small couplings $J_{5-10} \approx 2$ Hz and $J_{2-9} = 2.5$ Hz, which obviously cannot result from cisoid dihedral angles. Furthermore, the coupling between protons 5 and 13 (7.3 Hz) is slightly too large to be accepted as the result of a cisoid relation; the dihedral angle between protons 5 and 13 should be around 130° (calculated 126.4°). The coupling between

(7) Chow, Y. L.; Li, H.; Yang, M. S. *J. Chem. Soc., Perkin Trans. 2* **1990**, 17.

(8) The system is overdetermined. Simulations of all nonoverlapping signals showed excellent fits.

(9) Mills, O. S.; Paulus, E. F. *J. Chem. Soc., Chem. Commun.* **1966**, 738.

(10) Due to π-back-donation from nickel, a back-bending of the alkene protons is expected. The back-bending of coordinated ethylene has been recently calculated for the metals in oxidation state II in the nickel triad: Strömberg, S.; Svensson, M.; Zetterberg, K. *Organometallics* **1997**, *16*, 3165. The calculations show the angle between the plane formed by Ni alkene carbons and the plane formed by the alkene carbons and the alkene hydrogens to be 98°, a rather modest deviation from a perpendicular geometry.

(11) (a) Becker, E. D. *High Resolution NMR*, 2nd ed.; Academic Press: New York, 1980, p 103. (b) Coupling constants are similar and small for vicinal protons when dihedral angles are between 60 and 120°, whether both of the carbons are considered sp^3 or one of them is sp^2.

protons 9 and 13 (6.2 Hz) is very likely for a small dihedral angle (calculated 9.6°).

NOESY shows, as expected, strong correlations between all protons geminally related. Conformationally it is interesting to find that protons assigned 4 and 5 in the six-membered ring and the five-membered ring respectively correlate. This correlation is expected for conformation **1a** only, where the distance between the two proximate protons is calculated to be 2.06 Å.

For rather similar palladium compounds coordinating substituted (1,4,5-η)-cyclooctenyl ligands, the metal and the ligand can form six-and-a-half-membered rings of both chair and boat conformations.[12–15] (In some of the references "chair" and "boat" refer to the shape of the whole cyclooctenyl ligand and not to the largest metallacycle.) The spectra reported in the literature have a coarse appearance similar to our spectrum of **1a**, but those of metalla-boat conformations exhibit a significant difference which deserves comment: in the pallada-boats the signals corresponding to olefinic protons 12 and 13 have very similar patterns; in our case these signals differ substantially in both pattern and total width. A characteristic in common for our case and the reported pallada-chair cases is that the couplings within the five-and-a-half-membered ring between both of the allylic protons and the olefinic protons, corresponding to J_{13-5} and J_{13-9}, are rather close (our case 7.3/6.2 Hz compared to 7.4/7.4 Hz[11] and 8.8/8.8 Hz[12]). The corresponding couplings in the larger ring should be similar in the metalla-boat, as the allylic protons nearly mirror each other in a plane perpendicular to the carbon–carbon double bond (see Figure 3, bottom view). Indeed, this is also reported for complexes favoring this conformation; the mirroring allylic protons have exactly the same couplings toward their vicinal olefinic protons.[12,13] In a chair conformation this pseudosymmetry is completely lost (Figure 3, top view), consistent with our very different coupling constants mentioned previously.

Why do some (1,4,5-η)-cyclooctenyl ligands exist in a metalla-boat form and others, like **1** and **2**, in a metalla-chair form? It does not seem likely that electronic factors alone present a complete answer, as pallada-cycles exist in both chair and boat forms. However, from a view of steric factors, a consistent pattern appears. It is pointed out by Rettig and Espinet that the pallada-boats discussed above have larger groups in equatorial positions: chloride[12] and pentafluorophenyl.[13] An X-ray study of bis(μ-chloro)bis[(1,4,5-η)-8-(α-chloroethyl)cyclooctenyl]dipalladium displays a pallada-chair and the chloroethyl substituent in an equatorial position.[13] Some β-alkoxy-substituted ((1,4,5-η)-cyclooctenyl)palladium compounds are in pallada-chair forms and have their alkoxy groups in equatorial positions.[15] The same situation, metalla-chair and the bulky substituent in an equatorial position at the β-carbon, is found by X-ray diffraction for platinum[16] and nickel complexes.[17] It seems reasonable to suggest that bulky substituents

Scheme 1. Potential Hydride Route to 4
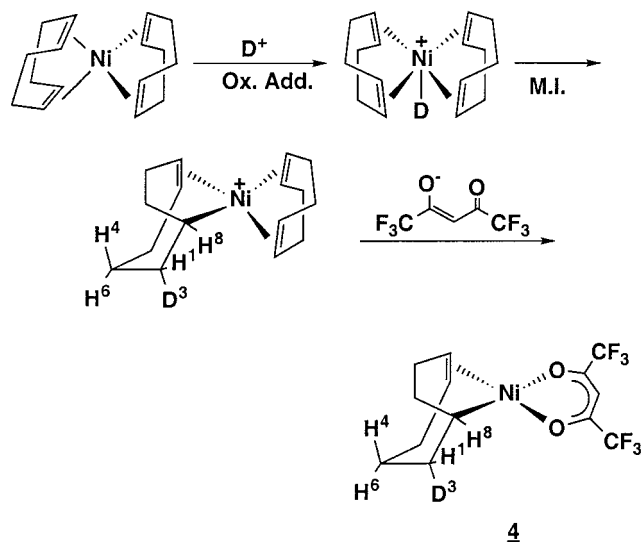
experience ((1,4,5-η-cyclooctenyl)metals as rather congested and by preferring the least sterically demanding conformation determine whether the metallacycle should be chair or boat.

Considering the X-ray structure for **2**, the caclulated preference, and the NMR observations presented above, we conclude that our compound exists in a nickela-chair conformation, **1a**.

Deuterium Labeling. At the outset of this study we felt that a very reasonable mechanism for the formation of **1** from Ni(COD)$_2$ and H(hfacac) would be the following (Scheme 1): H(hfacac), which mainly exists in the enol form and is a proton donor (pK_a = 4.2[2e]), initially protonates nickel (i.e. formally an oxidative addition); the cationic nickel hydride that is formed undergoes a migratory insertion (MI); subsequent ligand displacement of cyclooctadiene from the cationic ((1,4,5-η)-cyclooctenyl)nickel compound affords neutral **1**.

Accordingly, if hexafluroacetylacetone-d_2 is used, we would expect **4**, as migratory insertion proceeds with *cis* stereochemistry.[18] Such a compound should produce a ^{13}C {^{1}H} NMR with carbon D signal as a deuterium-coupled triplet, and in ^{1}H NMR the signal corresponding to proton 3 should be absent. However, treatment of Ni(COD)$_2$ with H(hfacac)-d_2 afforded, after regular workup, a product with an NMR spectrum indistinguishable from the spectrum of **1**. The use of toluene-d_8 as solvent in the preparation did not change the result, ruling out solvent as a source of hydrogen.

Complex **3** exists in equilibrium with its ((1,2,3-η)-cyclooctenyl)nickel isomer, and we therefore suspected that our isolation and purification procedures (involving sublimation at +40 °C) caused hydrogen–deuterium scrambling within the cyclooctenyl ring. Such scrambling may be envisaged as double-bond migrations due to β-hydride elimination–insertion steps.

To avoid scrambling, the deuteration procedure was repeated at −30 °C, and the volatiles were evaporated

(12) Albelo, G.; Wiger, G.; Rettig, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 4510. The structure was elucidated by ^{1}H NMR.

(13) Albéniz, A. C.; Espinet, P.; Jeannin, Y.; Philoche-Levisalles, M.; Mann, B. E. *J. Am. Chem. Soc.* **1990**, *112*, 6594. The article contains both X-ray and ^{1}H NMR evidence for the structure.

(14) Parra-Hake, M.; Rettig, M. F.; Wing, R. M.; Woolcock, J. C. *Organometallics* **1982**, *1*, 1478 (an X-ray structure).

(15) Grennberg, H. Dissertation, Uppsala University, Uppsala, Sweden, 1992.

(16) Fallis, S.; Anderson, G. K.; Rath, N. P. *Organometallics* **1991**, *10*, 3180.

(17) Fisher, B.; Boersma, J.; Kojić-Prodić, B.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1966**, 738.

(18) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; p 383.

to a cold trap at this temperature. The nickel compound was analyzed, without further purification, by NMR at low temperature. ^{13}C {^1H} NMR now revealed the expected deuterium triplet, previously mentioned, and only a minor part of the original singlet D remained. When the temperature was increased to 25 °C, the triplet gradually disappeared while the singlet of carbon D increased.

The initial ^1H NMR spectrum (very broadened signals due to impurities) did not show any reduction of integration of signal 3. Instead, the high-field signal 1 was dramatically reduced; only 30% of the expected integration remained. GC−MS analysis of the trapped volatiles showed that the cyclooctadiene liberated in the reaction had a 25% incorporation of deuterium.

In situ generation of the deuterated catalyst in toluene-d_8 in an NMR tube at low temperatures also showed a 70% decrease of the integration of proton signal 1. In no case could total extinction of signal 1 be observed. When these types of NMR experiments were repeated with ordinary H(hfacac), no high-field protons indicative of nickel hydrides were observed.

Discussion

Upon coordination to a transition metal, an alkene may change its reactivity in quite a complex way. Some of these changes may be nontrivial to predict (e.g. propensity toward migratory insertion). However, the metal can be considered as either net electron-withdrawing or net electron-releasing, and within this oversimplified picture predictability is achieved.[19] With an electron-withdrawing metal the alkene undergoes an umpolung; the weak original nucleophilicity is exchanged for a more or less pronounced electrophilicity, and the alkene may now be the target for a nucleophilic attack, *anti* to the metal (eq 1).

$$Nu^- \quad \overset{\delta+}{||} \longrightarrow M \longrightarrow \quad \overset{Nu}{\underset{M^+}{}} \tag{1}$$
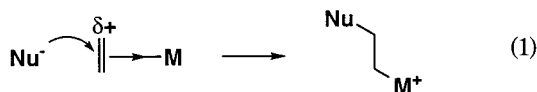
This umpolung constitutes an established methodology in organic synthesis.[20−23] In a similar manner an alkene coordinated to an electron-releasing metal should show an enhanced nucleophilicity and, accordingly, more easily react with electrophiles such as a proton, also here in an *anti* stereochemical mode (eq 2).

$$E^+ \quad \overset{\delta-}{||} \longleftarrow M \longrightarrow \quad \overset{E}{\underset{M^+}{}} \tag{2}$$

However, this phenomenon is very uncommon when the electrophile is a proton.[24−26] By far the most common path for protonation of a coordinated alkene consists of an initial protonation of the metal and a consecutive migratory insertion proceeding in a *syn* fashion to afford the product (eq 3).[27−30]

$$H^+ \quad || \quad \overset{..}{M} \quad \overset{Ox. Add.}{\longrightarrow} \quad || \overset{H}{\underset{M^+}{}} \quad \overset{M.I.}{\underset{\beta-EL}{\rightleftarrows}} \quad \overset{H}{\underset{M^+}{}} \tag{3}$$

Our stereochemical result is clearly incompatible with the common type of proton addition and leaves us with little doubt that we observe a direct protonation of the π-alkene ligand.

It seems reasonable to assume that direct protonation of π-alkene complexes, even when the metal is electron-rich, is the less general path, but in those cases where the stereochemistry of the reaction is unknown and transient hydrides defy detection, direct protonation has to be, at least, considered.[30−32]

(19) This situation can be expressed in more detail within the framework of the classical Dewar−Chatt−Duncanson model. When σ-donation from the alkene dominates the alkene−metal interaction, the metal is electron-withdrawing, and when π-back-donation is prevailing, the metal is electron-releasing. (a) Reference 18, p 156. (b) Chatt, J. *J. Chem. Soc.* **1949**, 3340. (c) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2933. (d) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79.
(20) (a) Reference 17, p 826. (b) Bäckvall, J. E. In *Reaction of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, p 679. (c) Pearson, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 964. (d) Hosokawa, T.; Murahashi, S.-I. *Acc. Chem. Res.* **1990**, *23*, 49.
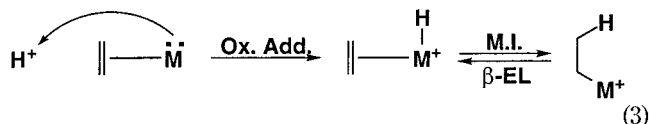(21) Hegedus, L. S. *Tetrahedron* **1984**, *40*, 2415.
(22) (a) Bäckvall, J. E.; Andersson, P. G. *J. Am. Chem. Soc.* **1992**, *114*, 6374. (b) Turnbull, M. M.; Foxman, B. F.; Rosenblum, M. *Organometallics* **1991**, *10*, 3180.
(23) Hydrides can be added as external nucleophiles: (a) McConnel, W. W.; Nelson, G. O.; Wright, M. E. *Inorg. Chem.* **1983**, *22*, 1689. (b) Florio, S. M.; Nicholas, K. M. *J. Organomet. Chem.* **1976**, *112*, C17.

(24) If a (π-alkene)metal has organic ligands with heteroatoms, these atoms can constitute the preferred site of protonation instead of the metal: (a) Chizhevsky, I. T.; Rastova, N. V.; Kolobova, N. E.; Petrovskii, P. V.; Vinogradova, L. E. *J. Organomet. Chem.* **1987**, *335*, 109. (b) Tóth, I.; Hanson, B. E.; Davis, M. E. *J. Organomet. Chem.* **1990**, *396*, 363.
(25) In the case of bis(π-alkene)rhodium(I) coordinating different acetylacetonates, an oxygen is the kinetically preferred site of protonation. A succesive direct proton transfer via a non-hydride path to an alkene carbon, the thermodynamically favored site of protonation, may ultimately afford (σ-alkyl)rhodium(III) compounds: Öhrström, L.; Strömberg, S.; Glaser, J.; Zetterberg, K. Manuscript in preparation.
(26) For the direct protonation of π-alkene transition metal complexes, see: (a) Henderson, R. A.; Oliglive, K. E. *J. Chem. Soc., Chem. Commun.* **1991**, 584. (b) Henderson, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 946.
(27) In the following publications hydrides as well as the insertion products are shown: (a) Werner, R.; Werner, H. *Chem. Ber.* **1983**, *116*, 2074. (b) Canestrari, M.; Green, M. L. H.; Izquierdo, A. *J. Chem. Soc., Dalton* **1984**, 2795. (c) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton* **1974**, 1324.
(28) In the following cases the alkene is 1,5-cyclooctadiene; hydrides as well as insertion products are shown: (a) Bennett, M. A.; Neumann, H.; Thomas, M.; Wang, X. *Organometallics* **1991**, *10*, 3237. (b) Sowa, J. R., Jr.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2537. (c) Bouachir, F.; Chaudret, B.; Dahan, F.; Agbossou, F.; Tkatchenko, I. *Organometallics* **1991**, *10*, 455. (d) Bouachir, F.; Chaudret, B.; Tkatchenko, I. *J. Chem. Soc., Chem. Commun.* **1986**, 94.
(29) The following articles illustrate protonations that initially afford (π-alkene)hydridometals, which eventually turn into (σ-alkyl)metals where agostic interactions are noticed: (a) Brookhart, M.; Hauptman, E.; Lincoln, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 10394. (b) Bennett, M. A.; McMahon, I. J.; Pelling, S.; Brookhart, M.; Lincoln, D. M. *Organometallics* **1992**, *11*, 127. (c) Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634. (d) Brookhart, M.; Lincoln, D. M.; Volpe, A. F., Jr.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212. (e) Brookhart, M.; Lincoln, D. M. *J. Am. Chem. Soc.* **1988**, *110*, 8719. (f) Mole, L.; Spencer, J. L.; Carr, N.; Orpen, A. G. *Organometallics* **1991**, *10*, 49. (g) Carr, N.; Dunne, B. J.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 926. (h) Conroy-Lewis, F. M.; Mole, L.; Redhouse, A. D.; Litster, S. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1601. (i) McNally, J. P.; Cooper, N. J. *Organometallics* **1988**, *7*, 1704. (j) Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Chem. Commun.* **1988**, 677.
(30) Sometimes protonation of (π-alkene)metals affords (σ-alkyl)-metals without any hydrides beeing observed. Still, such intermediates seem most likely. (a) Casey, C. P.; Yi, C. S. *Organometallics* **1991**, *10*, 33. (b) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 326. (c) Chicote, M. T.; Green, M.; Spencer, J. L.; Stone, F. G. A.; Vicente, J. *J. Chem. Soc., Dalton Trans.* **1979**, 536. (d) Seiwell, L. P. *Inorg. Chem.* **1976**, *15*, 2560.

Scheme 2
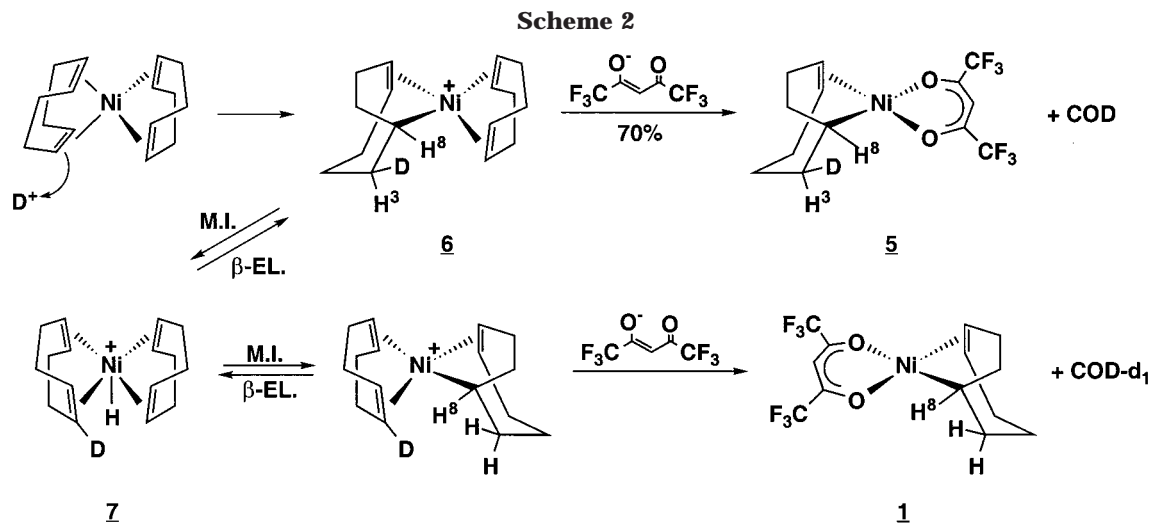
In this case the metal-induced increase of basicity of 1,5-cyclooctadiene in Ni(COD)$_2$ is substantial; a rather weak acid as H(hfacac) (pK_a = 4.2) affords protonation.[33]

Why is there still a 30% ^{1}H appearance in the low-temperature deuterium labeling experiments? One simple explanation could comprehend a competition between a direct protonation and a reaction via hydride. However, we could not detect any hydrides and, more importantly, we did not observe any decrease in integration of proton 3, the likely result of migratory insertion of a hydride. Furthermore, a clean competition between the two paths could not account for the 25% incorporation of deuterium in displaced COD.

A mechanism compatible with all our observations is depicted in Scheme 2.

The direct deuteronation of the COD ligand forms an initial, cationic, rather labile complex **6** which follows two paths: (1) immediate ligand exchange, affording the deuterium-labeled nickel compound and COD, or (2) β-hydride elimination, giving the hydride **7**. Reinsertion of a double bond of the non-deuterated COD ligand and subsequent ligand exchange are responsible for formation of **1** and the incorporation of deuterium into the free COD.

Conclusion

A very general route to form σ-alkyl transition metals, either as crucial intermediates in catalysis or for preparative purposes, is to add a proton to a π-alkene complex. It is generally believed, e.g. as the result of

many observations of *syn* stereochemistry in such "hydrometalations" of alkenes, that these reactions proceed via an intermediate hydride as shown in eq 2. Our study of an ethylene oligomerization catalyst, **1**, illustrates that protonation of a π-alkene transition-metal complex can display *anti* stereochemistry and, accordingly, takes place by direct protonation of the coordinated alkene. The basicity of the alkene is enhanced by the net electron-releasing effect of the (low-valent) metal, and in our case 1,5-cyclooctadiene is activated by nickel(0) to be protonated by hexafluoroacetylacetonate (pK_a = 4.2).

Experimental Section

All manipulations were carried out under a dry, oxygen-free argon atmosphere, using standard vacuum line/Schlenk tube techniques.[34] Solvents and reagents were distilled under argon and used after freeze−pump−thaw degassing. Deuterated solvents were stored over Linde 4 Å molecular sieves under argon and thoroughly degassed (freeze−pump−thaw technique) prior to use.

Bis(1,5-cyclooctadiene)nickel(0) and (η^1:η^2-cyclooctenyl)-(hexafluoroacetylacetonato)nickel(II) were prepared according to published procedures.[35,36] Deuterated (η^1:η^2-cyclooctenyl)-(hexafluoroacetylacetonato-d_1)nickel(II) was prepared in the same way as the nondeuterated analogue in the reaction of Ni(COD)$_2$ with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione-d_2 (preparation of ligand described below).[34]

Nuclear magnetic resonance spectra were run on a Bruker AM-400 or AMX-500. Chemical shifts are reported in units of parts per million (δ) with residual protons in the solvent as an internal standard (CDCl$_3$, 7.24 ppm; toluene-d_8, 2.09 ppm; methylene-d_2 chloride, 5.32 ppm). The ^{13}C spectra are referenced by using the ^{13}C resonance of the solvent as an internal standard (CDCl$_3$, 77.0 ppm; toluene-d_8, 20.4 ppm; methylene-d_2 chloride, 53.8 ppm). Two-dimensional NMR spectrometry in the form of homonuclear and heteronuclear correlation spectroscopy (^{1}H,^{1}H- and ^{1}H,^{13}C-COSY) and phase-sensitive NOESY (mixing time 0.500 s) was carried out to find correct assignments of proton and carbon resonances. Simulation of ^{1}H NMR spectra was achieved by using the program NMR II 1.0 by Calleo Scientific Software Publishers. Mass spectra were obtained with a Finnigan 4500 GC−MS spectrometer connected to a Varian 3400 GC chromatograph.

(31) Direct protonations have been previously suggested: (a) Evans, J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. D* **1971**, 1252. (b) Green, M.; Grove, D. M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 2228.

(32) It has been suggested that Os(CO)$_4$(C$_2$H$_4$) is directly attacked by a proton: Norton, J. R. Personal communication. In this case the ethylenic ligand is better viewed as the two-carbon part of a metalla-cyclopropane than a (π-alkene)metal species. Bender, B. R.; Norton, J. R.; Miller, M. M.; Anderson, O. P.; Rappé, A. K. *Organometallics* **1992**, *11*, 3427.

(33) (a) Transformation of alkenes via secondary carbocations usually requires mineral acids and semi-brutal conditions. Thus, one of the industrial processes for production of 2-propanol is run in 70% H$_2$-SO$_4$ at 60−65 °C under propene (25 bar). As these parameters are optimized for production purposes, they are probably in the mild range. Weissermel, K.; Arpe, H.-J. *Industrial Organic Chemistry*, 2nd ed.; VCH: New York, 1993; p 195. (b) Alkenes may also be protonated under mild conditions with superacids. See: Olah, G. A. *Carbocations and Electrophilic Reactions*; Verlag Chemie: Weinheim, Germany, 1974; p 28.

(34) Schunn, R. A. *Inorg. Synth.* **1974**, *15*, 5.
(35) Bogdanovic, B.; Kröner, M.; Wilke, G. *Justus Liebigs Ann. Chem.* **1966**, *699*, 1.
(36) Shziver, D. F. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; McGraw-Hill: New York, 1987.

Preparation of 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione-d_2. Dry and freshly distilled hexafluoroacetylacetone (0.107 mol, 15.8 mL) was placed in the Schlenk type vessel (under Ar). A stoichiometric amount of NaOD (30% solution in D_2O 14.66 g) was slowly added (violent reaction and temperature rise close to boiling). The resulting solution was evaporated to dryness under vacuum, dissolved in D_2O, and then once again evaporated to dryness. A white sodium salt was obtained and treated with a large excess of concentrated D_2SO_4 (about 20 mL of deuterated sulfuric acid). The mixture was shaken for about 3 h and then left overnight under argon. Two layers of the resulting liquid mixture separated and the upper layer was transferred under argon to a round-bottom bulb and distilled at 80 °C under atmospheric pressure of argon, affording 11.6 g (50%) of product.

"In situ" Generation of Monodeuterated ((1,4,5-η)-Cyclooctenyl)(1,1,1,5,5,5-hexafluoro-2,5-pentadionato)-nickel(II) for NMR Determination and GCMS. $Ni(COD)_2$ (0.41 g, 1.5 mmol) was transferred to the Schlenk type vessel under dry Ar at −30 °C. Hexafluoroacetylacetone-d_2 (2.14 mL, 15 mmol) dissolved in 2 mL of toluene-d_8 was introduced via a cannula. After about $^1/_2$ h the solvent and the cyclooctadiene (evolved during reaction) were pumped off under vacuum (at −30 °C) and trapped at −196 °C. The deuterium content of the cyclooctadiene was analyzed by GC−MS. The residual solid material was dissolved in $CDCl_3$ at −30 °C and transferred to a cold NMR tube via a cannula furnished with a piece of paper as a filter.

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