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A Strange Nickel(I)−Nickel(0) Binuclear Complex and Its Unexpected Ethylene Oligomerization

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Summary: The unusual heterovalent bimetallic Ni^I-Ni^0 *complex* $\{[\eta\text{-}C_5H_4CH{=}N(C_6F_5)]Fe[\eta\text{-}C_5H_4PPh_2]\}_2Ni_2(Cl)$ (**2**) *was isolated from the reaction between* $[\eta\text{-}C_5H_4CH{=}N(C_6F_5)]Fe[\eta\text{-}C_5H_4PPh_2]$ (**1**) *and* $Ni(COD)_2$ *in the presence of* $AlEtCl_2$ *or* $AlCl_3$*. Complex* **2** *has been crystallographically characterized and theoretically analyzed; it is catalytically active (TOF 90 500) and selective (91%) toward the formation of* C_4 *oligomers from ethylene (300 psi) at 30 °C, the only other significant isomer formed being* C_6*.*

Nickel is the "disturbing" element in Ziegler's Nobel-winning work in ethylene polymerization.[1] Its salt is the source of the "nickel effect" that accounts for the premature polymer termination.[2] Today, five decades later, research in this area has led to the development of Ni-based systems that catalyze the growth of the C_6-C_{20} linear α-olefin (LAO) industry.[3] Inspired by the SHOP process,[4] different teams (e.g., Brookhart,[5] DuPont,[6] Grubbs,[7] Braunstein,[8] etc.) have designed a number of elegant olefin oligomerization catalysts. Notable challenges remain, however, such as activity under ambient conditions, selectivity over specific oligomers (e.g., C_6 LAO), ambiguous mechanistic details, etc. Interestingly, virtually all known Ni-based LAO catalysts are Ni^{II} systems. The role of low-valent nickel in this technologically significant process is virtually unknown. Our objective is to design and synthesize suitable low-valent Ni model complexes that could help in the promotion and understanding of Ni-based ethylene oligomerization.

We have recently isolated the rare three-coordinate Ni^I complex $[\eta\text{-}C_5H_4CH{=}N(C_6H_5)]Fe[\eta\text{-}C_5H_4P(t\text{-}Bu)_2]Ni^ICl$ and the unusual bimetallic Ni^0-Al^{III} complex $[\eta\text{-}C_5H_4CH{=}N(C_6F_5)]Fe[\eta\text{-}C_5H_4PPh_2]Ni(AlMe_3)$.[9] These successes have encouraged us to extend the use of unsaturated metals carrying a hybrid ligand[8] to design new low-valent Ni catalysts. In this communication, we report the isolation of an intriguing Ni^I-Ni^0 bimetallic complex that is more active than its Ni^{II} and Ni^0 counterparts. Although bimetallic catalysts have exhibited some advantages in certain systems such as selective hydrogenation,[10] asymmetric epoxide opening reactions,[11] and copolymerization,[12] the use of such a system in ethylene oligomerization is still less developed.[13]

Reaction between $Ni^0(COD)_2$ (COD = 1,5-cyclooctadiene) and the hybrid ligand $[C_5H_4CH{=}N(C_6F_5)]Fe(\eta\text{-}C_5H_4PPh_2)$ (**1**) in toluene in the presence of a polymerization promoter such as $AlEtCl_2$ or $AlCl_3$ gives 57% yield of an air- and moisture-sensitive red solid formulated as $\{[\eta\text{-}C_5H_4CH{=}N(C_6F_5)]Fe[\eta\text{-}C_5H_4PPh_2]\}_2Ni_2Cl$ (**2**) (eq 1). The solid form is fairly stable (for days) under an inert atmosphere at room temperature, while its solution shows minimum decomposition after 2 days at −30 °C. Complex **2** is unusual. The oxidation self-selects to stop at the stage of a binuclear Ni^I-Ni^0 species. We also could not detect any binuclear Ni^I or any major Ni^{II} or Ni^0 products under the experimental conditions. Its paramagnetism frustrates any reasonable NMR analyses. In view of its unusual formulation,

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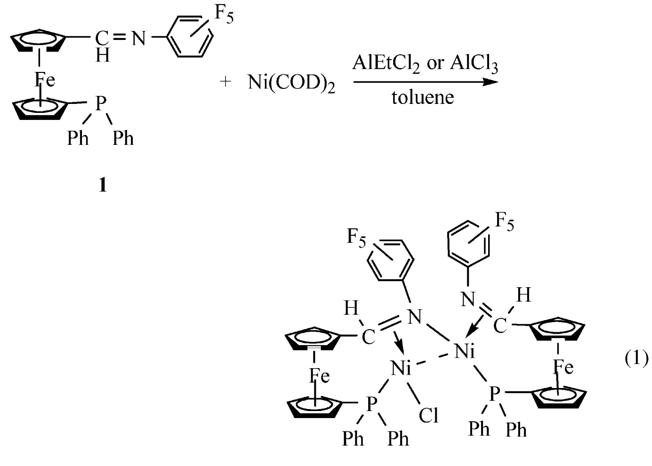

we carried out an X-ray single-crystal diffraction to establish its structure.[14] Suitable single crystals were obtained by diffusion of *n*-hexane into its CH_2Cl_2 or toluene solution under argon. The structure (Figure 1) shows a dinickel core with a CNπ,P-iminophosphine chelate on one nickel and terminal chloride on another. The two metals are brought into close proximity (Ni−Ni = 2.9607(13) Å) by a second iminophosphine that shows its maximum donation capacity as a 6e donor (2e P + 2e π CN on one metal and 2e σ N on the other) that bridges the metals. Ignoring the Ni−Ni bond, both metals adopt a distorted-square-planar geometry (the dihedral angle between Ni(1)−C(1)−N(1) and Ni(1)−N(2)−P(1) is 6°, and that between Ni(2)−C(2)−N(2) and Ni(2)−Cl(1)−P(2) is 1.9°). The two C_6F_5 substituents are oriented on the top half of the molecule, showing some degree of $\pi\cdots\pi$ stacking (interplanar distance 3.34 Å). The two phosphines of **2** show good donicity, giving two strong Ni−P bonds (2.148 and 2.141 Å) which are shorter than the usual Ni−P bonds (2.151−2.169 Å).[8d,9,15] The Ni−Cl bond (2.265 Å), on the other hand, is unexpectedly weak, being longer than the regular Ni^I−Cl bonds (2.192−2.231 Å).[8,9a,15] This appears to be a common feature of the complexes formed from the iminophosphine.[9a] The Ni−Ni separation (2.9607(13) Å) is closer to the nonbonding interactions found in many binuclear Ni(II) structures (2.973−3.064 Å)[16] than to the conventional metal−metal-bonded Ni^I−Ni^I (2.30−2.52 Å),[17] Ni^0−Ni^0 (2.572−2.603 Å),[18] and Ni^{II}−Ni^{II} dimers (2.281−2.7527 Å).[19]

With two formally neutral iminophosphines and a chloride, this is formally a Ni^I−Ni^0 binuclear complex, which is unusual. The presence of unsaturated and paramagnetic metal centers in a complex that depends so much on ligand support from a seemingly weak donor (imine) is also surprising. To gain some insights into these structural anomalies, we have performed density functional theory (DFT)[20] calculations. To analyze complex **2**, it is dissected into two fragments: (a) Ni^ICl-**1** and (b) Ni^0-**1**. Interestingly, the calculations revealed that the standalone Ni^0-**1** and Ni^ICl-**1** are also stable, with fully optimized structures similar to their counterparts in complex **2**. The coupling of Ni^ICl-**1** with Ni^0-**1** will gain energy by 1.47 eV, indicating that the binuclear structure is more stable than the mononuclear forms. The HOMO of binuclear **2** is singly occupied, which is found to be antibonding between the Ni halves but bonding within the Ni^0-**1** moiety. This implies that adding an electron to **2** would destabilize the binuclear structure, whereas extracting an electron would weaken the internal bond of the Ni^0-**1** portion. Therefore, it appears that the presence of Ni^INi^0 instead of Ni^0Ni^0 or $Ni^{II}Ni^0$ is due to the bifunctionality of the HOMO of **2**: a half-occupation in this orbital is most thermodynamically favored.

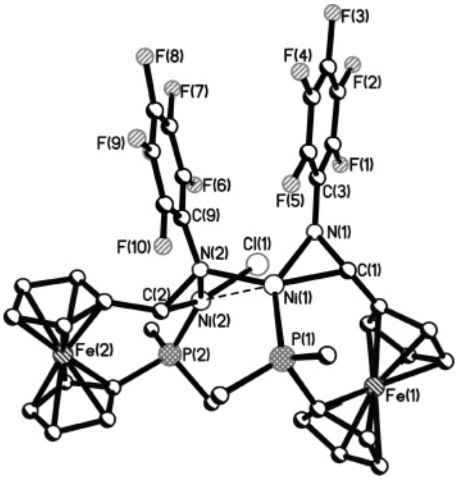

Figure 1. Molecular structure of complex **2** (phenyl rings on the P and H atoms are omitted). Selected bond lengths (Å) and angles (deg): Ni(1)···Ni(2) = 2.9607(13), Ni(1)−C(1) = 1.901(7), Ni(1)−N(2) = 1.934(6), Ni(1)−N(1) = 1.959(6), Ni(1)−P(1) = 2.141(2), Ni(2)−C(2) = 1.904(7), Ni(2)−N(2) = 1.940(6), Ni(2)−P(2) = 2.148(2), Ni(2)−Cl(1) = 2.265(2), N(1)−C(1) = 1.453(9), N(2)−C(2) = 1.455(9); C(1)−Ni(1)−N(1) = 44.2(3), C(2)−Ni(2)−N(2) = 44.5(3).

We now turn to determining how the neutral ligand **1** bonds with Ni and how the “weak” imine holds the two metals together and stabilize both. Our calculations revealed that **1** is a metallo ligand with a large LUMO−HOMO gap of 1.89 eV. Its LUMO is a C=N antibonding state, while the HOMO, HOMO-1, and HOMO-2 are all d orbitals of Fe. The HOMO-3 and HOMO-4 are related to the nonbonding 2p orbital of P and the π bonding state of C=N. For the formation of the Ni^0-**1** fragment, we

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[14] Crystal data for $\mathbf{2}\cdot C_6H_{14}\cdot CH_2Cl_2$: M_r = 1450.51, triclinic, space group $P\bar{1}$, a = 12.867(2) Å, b = 14.027(2) Å, c = 17.800(3) Å, α = 100.472(3)°, β = 106.307(3)°, γ = 90.936(4)°, V = 3024.2(8) Å^3, Z = 2, ρ = 1.593 Mg m^{-3}, $F(000)$ = 1474, λ(Mo Kα) = 0.710 73 Å, μ = 1.343 mm^{-1}, T = 223(2) K, crystal dimensions 0.34 × 0.20 × 0.18 mm. A Siemens SMART diffractometer, equipped with a CCD detector, was used. Of 25 829 reflections measured, 9040 unique reflections were used in the refinement. Final R = 0.0695 (R_w = 0.1598). CCDC 627879.

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Table 1. Activities toward Oligomerization of Ethylene[a,b]

				oligomer[d]		
entry	cat.	activator	TOF[c]	C_4/ ΣC	C_6/ ΣC	α-olefin (C_4)
1	**2**	MAO	90 500	91.2	8.8	27.3
2[e]	$NiBr_2$(DME) + **1**	MAO	65 300	90.1	9.9	26.4
3	$Ni(COD)_2$ + **1**	MAO	64 800	93.4	6.6	26.4
4	**2**[f]	$EtAlCl_2$	87 300	78.8	21.2	22.2
5	$Ni(COD)_2$ + **1**	$EtAlCl_2$	58 000	91.3	8.7	24.5

[a] Average of two runs. [b] Conditions: 0.2 μmol of catalyst (based on Ni), 4 mL of toluene, 30 °C, 300 psi of ethylene, Al/Ni = 500, 1 h. [c] TOF = (mol of ethylene consumed)/((mol of Ni) h)$^{-1}$. [d] In units of mol %. [e] Prepared in CH_2Cl_2. [f] 2 h.

observe that the d orbitals of Ni are split into two groups: group I, d_{z^2}, d_{xz}, and d_{yz}, which are largely nonbonding states, with d_{z^2} being the HOMO; group II, d_{xy} and $d_{x^2-y^2}$, which form covalent bonds with the empty LUMO of **1** and the occupied p states of P, respectively. Consistently, as Ni bonds with CN, the CN bond is lengthened from ~1.30 to ~1.40 Å, indicating the weakening of the C═N bond and π bonding. In the Ni^0-**1** molecular fragment, the Ni is three-coordinated (with P, N, and C). It is expected that the Ni can still bond with one extra electron-rich ligand to complete the typical square-planar four-coordination. This could be achieved by species such as Cl^- and imine (the lone-pair electron of N), which are able to donate an electron to the empty 4s state of the Ni.

Cationic species have been proposed to be the active components in olefin polymerization/oligomerization catalysis.[21] Our calculations of the ionization energy and electron affinity of **2** gave 6.01 and 2.13 eV, respectively. Interestingly, this indicates that the conversion of **2** to ionic species is facile. The calculation results also suggested that the ethylene molecule does not promote the cleavage of the binuclear species into the separated mononuclear form, as such a dissociation would require 1.46 eV, which is more than the energy gain from ethylene adsorption on separated monomers. Thus, DFT appears to support the binuclear **2** to function as an intact molecular cationic entity upon Cl dissociation and subsequent ethylene adsorption and oligomerization.

Complex **2** was then examined for ethylene oligomerization (300 psi) activity in toluene at 30 °C in the presence of MAO as coactivator (Al/Ni = 500).[22] There is no apparent formation of α-oligomers in the absence of MAO. Some comparisons of the catalytic activities of **2** with those of its Ni(II) and Ni(0) counterparts are summarized in Table 1. Preliminary experiments showed that when it is activated by excess MAO under similar conditions, the bimetallic Ni^I−Ni^0 complex **2** gives activities (TOF 90 500) somewhat higher than for its related Ni^{II} and Ni^0 counterparts, such as $NiBr_2$(DME) + **1** in situ (65 300), $Ni(COD)_2$ + **1** in situ (64 800), and the Ni(0) tris(isocyanide) complex $[\{[\eta\text{-}C_5H_4CH{=}N(C_6F_5)]Fe[\eta\text{-}C_5H_4PPh_2]\}Ni^0(CNtBu)_3]$[9a] (75 000). It is still unclear if such higher activity could be related to the metal cooperative effect or to the ability of **2** to dissociate into its catalytically active mononuclear forms that are coordinatively unsaturated. Further experiments using MAO or $AlMe_3$ as activator also gave inconclusive evidence on its exact role. We should add also that the differences are less significant compared to those in the chromium system, in which the Cr(II) tripyrrolide is more active than its Cr(III) counterpart.[23] Our systems show good and similar selectivities toward C_4 oligomer formation (90−93%), with C_6 being the only other notable isomers (7−10%). Selectivities toward α-C_4 (26−27%) are also similar (Table 1, entries 1−3). These could suggest similar active species. The preference for C_4 and C_6 over other oligomers or polymers is consistent with the facile β-elimination being the key chain termination step. Use of $AlEtCl_2$ as an activator does not improve the activity of this Ni^I−Ni^0 complex (entries 4 and 5). These results are inconsistent with those observed for our previous Ni^I and Ni^0−Al complexes as well as the [P,N]-chelating Ni catalytic systems,[8] possibly due to the differences in the Ni−alkyl species formed that precede the active Ni−hydride.

Although we are unable to pinpoint how a bimetallic heterovalent Ni_2 species can promote olefin oligomerization, it is clear that its performance is at least comparable with those of its Ni^0 and Ni^{II} analogues. There is no experimental or theoretical evidence that the bimetallic **2** must undergo fragmentation for it to be catalytically active. Current work is focused on the study of the role of its hybrid ligand and the associated hemilability in determining the catalytic efficacy. The present and earlier studies suggested that this ligand shows different dimensions of coordination and donor flexibilities: namely, 2e ↔ 4e ↔ 6e donor, P only ↔ P + CN(π) ↔ P + CN(π) + N(σ) coordination, unidentate ↔ chelating ↔ chelate-bridging mode, and low ↔ intermediate ↔ normal metal valency stabilization. This is achieved by balancing its σ and π donation with π acceptance behaviors. Such multidimensional flexibility could help the ligand support and stabilize not only the precatalyst but also the different intermediates along the catalytic pathway. The isolation of **2** and other unusual Ni complexes suggested that more unexpected structures can be expected.

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Supporting Information Available: Text, tables, figures, and a CIF file giving experimental details and X-ray structural data for **2** and LUMO and HOMO orbitals of ligand **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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