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[(Ph)$_2$nacnac]MCl$_2$(THF)$_2$ (M = Ti, V, Cr): A New Class of Homogeneous Olefin Polymerization Catalysts Featuring *β*-Diiminate Ligands

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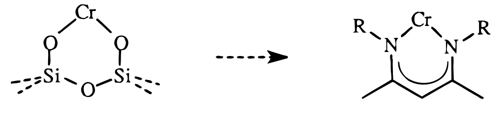
*Summary: [(Ph)$_2$nacnac]MCl$_2$(THF)$_2$ ([(Ph)$_2$nacnac] = N,N-diphenyl-2,4-pentanediimine anion; M = Ti (**1a**), V (**1b**), Cr (**1c**)) were prepared and their structures determined by X-ray diffraction. In the presence of excess methylaluminoxane (MAO), **1a−c** catalyzed the homopolymerization of ethylene and the copolymerization of ethylene with α-olefins.*

Heterogeneous catalysts containing early transition metals (Ti, V, Cr) are widely used for the polymerization of small olefins (ethylene, propene, etc.). The discovery of homogeneous model systems has substantially improved our understanding of the underlying organometallic chemistry and is fueling the current round of innovation hailed as "metallocene technology".[1] Despite their commercial importance, chromium catalysts have inspired less modeling activity,[2] owing possibly to the paramagnetism of relevant organometallic complexes. We have previously created a homogeneous model system for the so-called "Union Carbide catalyst" (i.e. Cp$_2$Cr/SiO$_2$),[3] which suggests that the active sites of this catalyst are coordinatively unsaturated cyclopentadienylchromium(III) alkyls.[4] A notable feature of this system is its extreme selectivity between ethylene and α-olefins, making homopolymerizations of and copolymerizations with the latter impractical. In a bid to overcome this limitation, we have now turned to modeling the "Phillips-catalyst" (i.e. CrO$_3$/SiO$_2$);[5] which is known to incorporate α-olefins. The ligand system we have chosen to mimic the hard coordination environment of the silica surface (**A**) is a class of *β*-diiminates (**B**); sterically demanding substituents on the nitrogen should allow preservation of coordinatively unsaturated mononuclear metal complexes, and the flexibility in the choice of substituents (R, R′) will be useful to modify the local symmetry of the catalytic sites. *β*-Diiminates have been used as ligands before,[6] but by comparison with the analogous *β*-diketonates ("acac" complexes), their chemistry is largely undeveloped. Herein we describe our initial foray into the organometallic chemistry of "nacnac"-complexes of early transition metals, which has yielded a novel class of homogeneous olefin polymerization catalysts.



A **B**

Reaction of [(Ph)$_2$nacnac]Li ([(Ph)$_2$nacnac] = *N,N*-diphenyl-2,4-pentanediimine anion with MCl$_3$(THF)$_3$ (M = Ti, V, Cr) in THF yielded the chlorides [(Ph)$_2$nacnac]-MCl$_2$(THF)$_2$ (**1a−c**; see Scheme 1). Their molecular structures have been determined by X-ray diffraction;[7] all three are isomorphous, and the representative chromium complex (**1c**) is depicted in Figure 1 with selected interatomic distances and angles for all three compounds listed in Table 1. The coordination environment of the metals is octahedral, with the oxygen atoms of the THF ligands in the same plane as the nitrogen atoms of the bidentate ligand. The nacnac moiety is coordinated in the η^2 mode, and the structural parameters show the expected gradual decrease in the size of the metal atom with increasing atomic number. **1a−c** are paramagnetic, with effective magnetic moments

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[7] **1a**: orthorhombic, $Pna2_1$, $a = 19.5601(8)$ Å, $b = 9.4959(4)$ Å, $c = 13.5555(5)$ Å, $V = 2517.8(2)$ Å^3, $Z = 4$, $T = 223(2)$ K, $D_{calcd} = 1.352$ g cm^{-3}, $R(F) = 4.15\%$ for 3912 observed independent reflections ($4 \leq 2\theta \leq 57°$). **1b**: orthorhombic, $Pna2_1$, $a = 19.5215(4)$ Å, $b = 9.5341(2)$ Å, $c = 13.4898(3)$ Å, $V = 2510.72(9)$ Å^3, $Z = 4$, $T = 218(2)$ K, $D_{calcd} = 1.363$ g cm^{-3}, $R(F) = 3.75\%$ for 4948 observed independent reflections ($4 \leq 2\theta \leq 57°$). **1c**: orthorhombic, $Pna2_1$, $a = 19.6220(4)$ Å, $b = 9.5971(2)$ Å, $c = 13.4509(3)$ Å, $V = 2533.00(9)$ Å^3, $Z = 4$, $T = 218(2)$ K, $D_{calcd} = 1.354$ g cm^{-3}, $R(F) = 5.35\%$ for 2408 observed independent reflections ($4 \leq 2\theta \leq 57°$).

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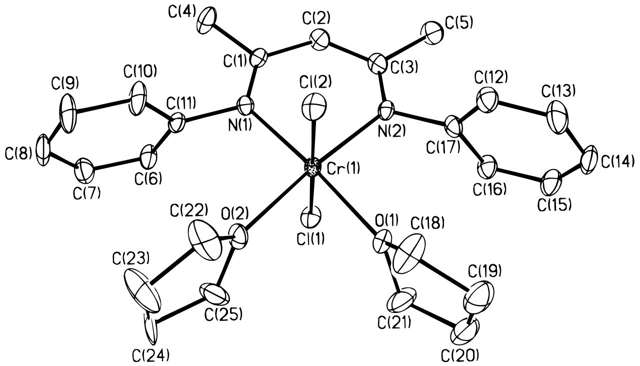

Figure 1. Molecular structure of $(Ph)_2nacnacCrCl_2(THF)_2$ (**1c**). The titanium and vanadium analogues (**1a** and **1c**) are isomorphous. See Table 1 for selected distances and angles.

Scheme 1

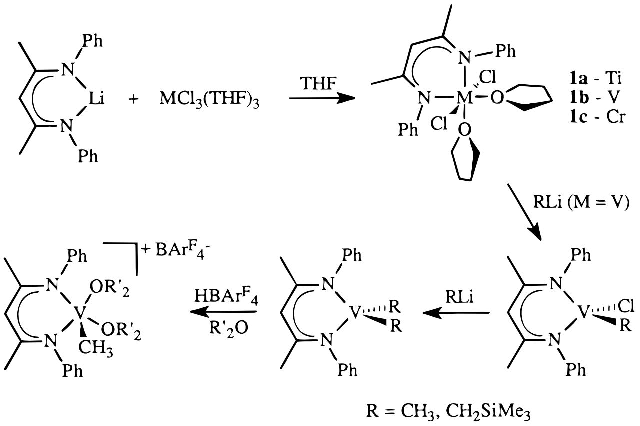

Table 1. Comparison of Average Interatomic Distances (Å) and Angles (deg) of $(Ph)_2nacnacMCl_2(THF)_2$ (M = Ti, V, Cr)

	M = Ti (**1a**)	M = V (**1b**)	M = Cr (**1c**)
M−N	2.087	2.027	2.033
M−O	2.211	2.215	2.143
M−Cl	2.395	2.362	2.346
N−C	1.331	1.341	1.319
C−C	1.401	1.398	1.413
N−M−N	87.5	90.9	91.7

Table 2. Characterization of Polymers Prepared with $(Ph)_2nacnacMCl_2(THF)_2$/MAO Mixtures (Al/M = 130) in Toluene

catalyst	yield (g)	M_w	M_n	M_w/M_n	branches[a]
(a) Ethylene Homopolymerization					
M = Ti (**1a**)	10.5	818 850	28 651	28.6	
$TiCl_3(THF)_3$	3.4	1 479 060	9 660	153.1	
M = V (**1b**)	4.7	1 958 584	1 121 628	1.75	
$VCl_3(THF)_3$	8.0	2 042 158	1 177 308	1.73	
M = Cr (**1c**)	10.5	1 157 039	15 892	72.8	
$CrCl_3(THF)_3$	0.5	1 319 817	34 847	37.9	
(b) Ethylene/Propene Copolymerization					
M = V (**1b**)	0.8	1 659 000	478 300	3.46	14.9
M = Cr (**1c**)	0.3	209 900	2 050	53.9	9.7

[a] Number of side chains per 1000 carbon atoms.

consistent with one (**1a,** $\mu_{eff} = 2.0(1)\ \mu_B$), two (**1b**, $\mu_{eff} = 3.2(1)\ \mu_B$), and three (**1c**, $\mu_{eff} = 4.1(1)\ \mu_B$) unpaired electrons per metal ion, respectively. However, the intraligand bond distances provide no structural evidence for any differences in degree of π-bonding.

Solutions of **1a**−**c** (or **1a**−**c**-$\boldsymbol{d_{10}}$) in CD_2Cl_2 exhibit isotropically shifted and broadened ^1H and ^2H NMR resonances.[8] The numbers of resonances observed exceeded those expected on the basis of the solid-state structures; however, addition of THF to the CD_2Cl_2 solution greatly simplified the spectra, allowing assignment of the resonances of **1a**−**c**. These observations indicate that solutions of **1a**−**c** contain equilibrium mixtures of complexes with various numbers of coordinated THF molecules—i.e., $[(Ph)_2nacnac]MCl_2(THF)_n$ (n = 2, 1, 0). The metals' affinity for THF is further reduced by alkylation. For example, treatment of **1b** with lithium alkyls yielded complexes of the type $[(Ph)_2nacnac]V(R)Cl$ and $[(Ph)_2nacnac]VR_2$ ($R = CH_3$, CH_2SiMe_3);[9] these tetrahedral molecules exhibited no tendency to coordinate THF.

In the presence of excess methylaluminoxane (MAO), **1a**−**c** catalyzed the polymerization of ethylene. In a typical experiment, toluene solutions (ca. 50 mL) of **1a**−**c** (0.30 mM) and MAO (40 mM, 130 equiv of "$[Al(CH_3)O]$") at room temperature were exposed to ethylene at 300 psig. In all cases an immediate exotherm indicated polymerization; reaction temperatures were kept below 60 °C by cooling with ice water. After ca. 1 h the reactor was opened and the polymer was filtered off, washed with acidic methanol and water, and dried in vacuo at 60 °C. Yields and polymer characterization data are listed in Table 2; dramatic differences in molecular weights and molecular weight distributions are apparent. One of the interesting features of this set of homogeneous catalysts is the direct comparison of the commercially relevant metals in an isostructural setting.

Also listed in Table 2, for comparison, are the results of ethylene polymerizations catalyzed by mixtures of $MCl_3(THF)_3$ (M = Ti, V, Cr) and MAO under comparable reaction conditions. While distinct in the detailed characteristics of the polymers produced, these results serve as a reminder of the potent activation effect of MAO, the detailed structure and function of which are still unclear.[10] Under these circumstances we felt it important to demonstrate that $[(Ph)_2nacnac]M$ complexes were indeed responsible for the catalytic activity of **1a**−**c**/MAO mixtures. ^2H NMR spectra of a mixture of $[(Ph\text{-}d_5)_2nacnac]VCl_2(THF)_2$ with excess MAO showed only isotropically shifted and broadened resonances characteristic of a ligand bound to paramagnetic V(III); the absence of any ^2H NMR resonances of diamagnetic species ruled out transfer of the nacnac ligand to aluminum and hence indicated that all vanadium remains coordinated by a $(Ph)_2nacnac$ ligand. Second, MAO is not necessary for polymerization activity. To wit, addition of $B(C_6F_5)_3$ to $[(Ph)_2nacnac]V(CH_3)_2$ yielded an active catalyst, and the cationic alkyl $[[(Ph)_2nacnac]V(OEt_2)(THF)CH_3]B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4$ catalyzed the polymerization of ethylene in the absence of any cocatalyst.[9]

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1a−**c**/MAO also catalyzed the copolymerization of ethylene with α-olefins (see Table 2). Under the present conditions the levels of incorporation of comonomer (determined by ^{13}C NMR) are still relatively low, and the molecular weights of the polymers are significantly lowered. However, we believe that structural modification of the catalysts will improve these characteristics.

Nacnac ligands represent a promising class of monoanionic ligands for use in organometallic chemistry. They offer a unique combination of hard, bidentate nitrogen coordination and variable steric protection of the metal, providing an interesting contrast to the ubiquitous cyclopentadienyl ligation. In keeping with our interest in "metallaradicals", we have initiated an exploration of the synthesis and reactivity of paramagnetic organometallics of early transition metals coordinated by nacnac ligands. The results reported herein suggest that such compounds will be useful as homogeneous catalysts.

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Supporting Information Available: Text and tables giving experimental details of the synthesis, characterization, and X-ray structural determination of **1a**−**c** (19 pages). See any current masthead page for ordering information and Web access instructions.

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