

Figure 1. Isotopic-label-directed NOE experiment on 50 mM $[1,3-^{15}\text{N}_2]$ uracil in dimethyl sulfoxide. (a) A control proton NMR experiment with no heteronuclear irradiation; the signals at 7.44 and 5.49 ppm are from the unlabeled protons at C6 and C5, respectively. (b) A ^1H - ^{15}N INDOOR experiment; in contrast to (c), there is no proton preirradiation, and strong ^{15}N decoupling is applied on and off resonance during the free induction decay. Residual features at C5H and C6H come from the small coupling between these protons and $^{15}\text{N}1$. (c) The isotopic-label-directed experiment for the proton at $\text{N}1$; a total of 320 scans were acquired with alternate on- and off-resonance ^{15}N preirradiation combined with ^1H preirradiation at 10.90 ppm for 1 s.

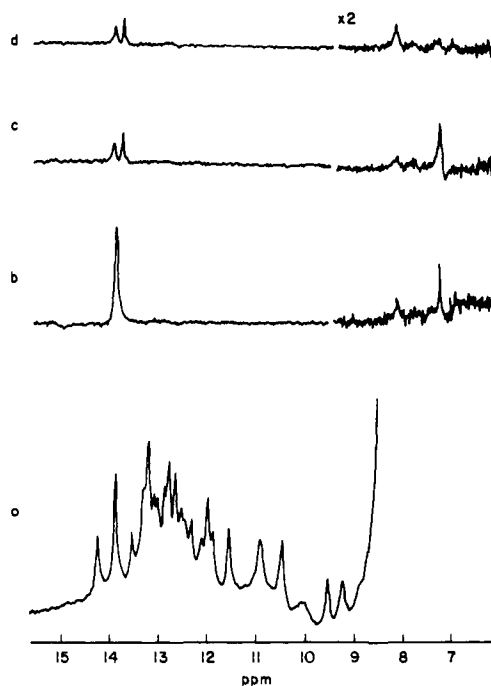


Figure 2. Isotopic-label-directed NOE experiment with *E. coli* tRNA^{Gln}. (a) A control spectrum of unlabeled tRNA^{Gln} at 20 °C. (b) Preirradiation of the peak at 13.88 ppm for 100 ms. (c) ^1H preirradiation of ^{15}N -enriched tRNA^{Gln} at 13.88 ppm with ^{15}N preirradiation on resonance at 163.2 ppm. (d) ^1H preirradiation at 13.88 ppm with ^{15}N preirradiation on resonance at 160.4 ppm. A total of 2000 scans were acquired with on- and off-resonance ^{15}N preirradiation. Both tRNA samples were dissolved in a 10 mM sodium phosphate buffer containing 100 mM sodium chloride, 10 mM magnesium chloride, 1 mM sodium thiosulfate, and 5% deuterium oxide.

demonstrated the method for ^{15}N -enriched molecules, but it will prove of equal benefit with ^{13}C -labeled compounds, where the one-bond scalar coupling is 140–200 Hz.

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Registry No. $[1,3-^{15}\text{N}_2]$ Uracil, 5522-55-4.

Syntheses and X-ray Structures of $[\text{Li}(\text{THF})_4][\text{Ni}(\text{NPh}_2)_3] \cdot 0.5\text{C}_7\text{H}_8$, $[\text{Ni}(\text{NPh}_2)_2]_2$, and $[\text{Co}(\text{NPh}_2)_2]_2$: Structural Characterization of Three Coordinate First-Row d^7 and d^8 Complexes

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The synthesis of $\text{Ti}(\text{NPh}_2)_4$, the first transition-metal amide, was reported in 1935.¹ However, it was only recently that Fröhlich et al. extended the application of the interesting diphenylamido group to other d-block elements.²⁻⁵ In the interim, other transition-metal amides, especially complexes of the NMe_2 and $\text{N}(\text{SiMe}_3)_2$ groups, have been intensively investigated.⁶⁻⁸ These studies suggest that, apart from a few $\text{N}(\text{SiMe}_3)_2$ derivatives, it is difficult to prepare stable homoleptic⁹ amido complexes of the later ($\text{Fe} \rightarrow \text{Cu}$) transition metals. The sole, structurally characterized, exceptions are the closed-shell complex $[(\text{CuNET}_2)_4]^{10}$ and $[\text{Co}(\text{NPh}_2)_2]_2$, which was reported to have a unique unsupported Co-Co bond.³ In this paper we will show that the cobalt complex exists rather as an amido-bridged dimer. Here we also report the first structures of two homoleptic diaryl amides of Ni(II) which have a first-row d^8 metal in the unreported trigonal-planar geometry.

The nickel complexes $[\text{Li}(\text{THF})_4][\text{Ni}(\text{NPh}_2)_3] \cdot 0.5\text{PhMe}$ (**1**) and $[\text{Ni}(\text{NPh}_2)_2]_2$ (**2**) were synthesized by treating a -78°C THF slurry of anhydrous NiCl_2 with 2 equiv of a THF/hexane solution of LiNPh_2 . The reaction mixture became navy blue on warming to 25°C and was stirred for an additional 2 h. The volatiles were removed in vacuo and the residue redissolved in hot toluene, filtered, and cooled to give ca. 50% yield of **2** as dark green crystals. Alternatively a mixture comprised of equal volumes of ether/hexane/toluene may be added to the original blue reaction mixture. Filtration followed by slow cooling to -20°C gave **1**, as navy blue crystals in 40% yield.¹¹ Substitution of CoCl_2 for NiCl_2 under similar conditions yielded a green complex which analyzed as $[\text{Li}(\text{THF})_4][\text{Co}(\text{NPh}_2)_3] \cdot 0.5\text{PhMe}$ (**3**) (25% yield) and the brown-red complex $[\text{Co}(\text{NPh}_2)_2]_2$ (**4**) in 45% yield.¹²

The structures of **1**, **2**, and **4** were determined by X-ray diffraction¹³ and are illustrated in Figures 1 (anion only) and 2. The structure of $[\text{Ni}(\text{NPh}_2)_3]^-$ consists of a roughly trigonal-planar NiN_3 array with an approximate D_{3h} field at the metal leading to two unpaired electrons in the e' orbitals. This is supported by a μ at 298 K of $2.6 \mu_B$. The average Ni-N distance of 1.89 Å is close to that expected from published covalent radii.¹⁴ The

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- (13) Anal. Calcd for **1**: C, 73.68; H, 7.35; N, 4.64. Found: C, 74.2; H, 7.73; N, 4.4. Mp 115°C . Anal. Calcd for **2**: C, 72.95; H, 5.10; N, 7.09. Found: C, 72.8; H, 5.1; N, 7.0. Mp 140°C .
- (14) Anal. Calcd for **3**: C, 73.66; H, 7.35; N, 4.64. Found: C, 74.1; H, 7.4; N, 4.4. Mp 138°C . Anal. Calcd for **4**: C, 72.91; H, 5.10; N, 7.09. Found: C, 72.8; H, 5.1; N, 6.9.
- (15) Crystal data: $[\text{Li}(\text{THF})_4][\text{Ni}(\text{NPh}_2)_3] \cdot 0.5\text{C}_7\text{H}_8$ (**1**) $P\bar{1}$, $T = 140\text{ K}$, $a = 9.948$ (2) Å, $b = 13.640$ (2) Å, $c = 18.237$ (3) Å, $\alpha = 95.84$ (1)°, $\beta = 92.83$ (2)°, $\gamma = 102.10$ (1)°, $R = 0.044$ for 698 parameters, 4289 unique observed reflections; $[\text{Ni}(\text{NPh}_2)_2]_2$ (**2**) Pc , $T = 140\text{ K}$, $a = 9.372$ (2) Å, $b = 10.122$ (2) Å, $c = 20.648$ (4) Å, $\beta = 102.31$ (2)°, $R = 0.060$ for 245 parameters, 2185 unique observed reflections; $[\text{Co}(\text{NPh}_2)_2]_2$ (**4**) $P2_1/n$, $T = 140\text{ K}$, $a = 9.040$ (3) Å, $b = 21.351$ (7) Å, $c = 9.927$ (3) Å, $\beta = 95.62$ (3)°, $R = 0.067$ for 125 parameters, 1221 unique observed reflections.

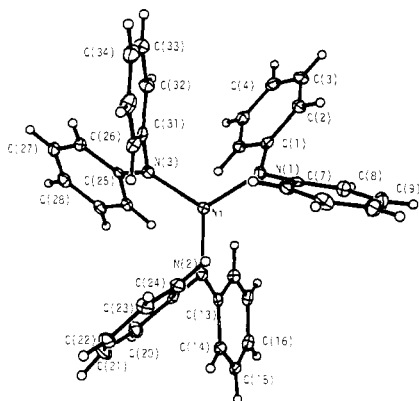


Figure 1. Computer-generated drawing of the anion $[\text{Ni}(\text{NPh}_2)_3]^-$. Important bond distances and angles: Ni-N(1), (2), (3) 1.889 (3), 1.895 (3), 1.877 (3) Å; N(1)NiN(2) 122.9 (1)°, N(1)NiN(3) 115.0 (1)°, N(2)NiN(3) 121.7 (1)°.

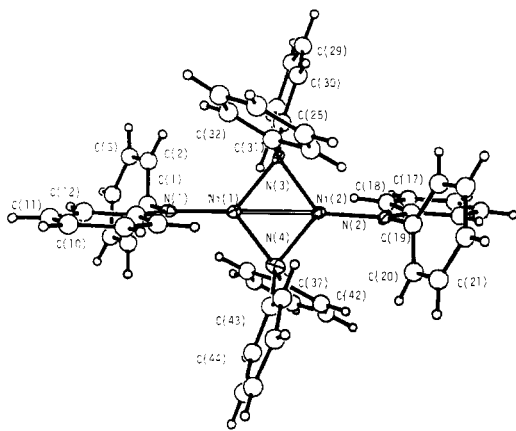


Figure 2. Computer-generated drawing of **2**; **4** has a similar structure but possesses an inversion center. Important bond distances and angles for $[\{\text{M}(\text{NPh}_2)_2\}_2]$: M = Ni[Co]; M...M 2.327 (2) [2.566 (3)] Å, M-N (terminal) 1.837 (9), 1.819 (8) [1.889 (8)] Å, M-N (bridging) 1.916 (9), 1.924 (8), 1.907 (9), 1.898 (9) [2.004 (7), 1.993 (8)] Å; NMN 104.3 (4)°, 105.7 (4)° [100.1 (3)°]; MNM 75.0 (3)°, 75.0 (3)° [79.9 (3)°].

structure of **2** consists of dimers of the $\text{Ni}(\text{NPh}_2)_2$ unit with the diphenylamides behaving as both a bridging and a terminal ligand. The Ni-N (terminal) distances average 1.83 Å and are somewhat shorter than those in **1** possibly due to the lower negative charge density in **2**. The bridging Ni-N distances have the somewhat longer value of 1.91 (av) Å. The Ni-Ni distance of 2.327 (2) Å is extremely short and implies a significant Ni-Ni interaction. Short Ni-Ni distances have also been seen in a small number of other nickel complexes.¹⁵⁻¹⁸ So far as we are aware **1** and **2** are the first reported structures of three-coordinate nickel(II).

The complexes **2** and **4** (Figure 2) are structurally similar to $[\{\text{Co}(\text{N}(\text{SiMe}_3)_2)_2\}_2]$.⁷ The dimeric configurations of **2** and **4**, with bridging NPh_2 groups, are in sharp contrast to the published structure of $[\{\text{Co}(\text{NPh}_2)_2\}_2]$, which was reported to be associated through a Co-Co interaction without amido bridges.³ The complex **4** has two cobalt atoms separated by 2.566 (3) Å. The average Co-N distances range from 1.89 (terminal) to 2.00 Å (bridging). The magnetic susceptibility of **4** at 298 K is 1.72 μ_B . It is interesting to note that while $[\{\text{Co}(\text{N}(\text{SiMe}_3)_2)_2\}_2]$ and $[\{\text{Co}$

$(\text{NPh}_2)_2\}_2]$ have similar metal-metal distances they have different degrees of magnetic couplings.^{3,7} The magnetic moment of $[\{\text{Co}(\text{N}(\text{SiMe}_3)_2)_2\}_2]$ at 296 K is 4.83 μ_B .²⁰

Information on multiple metal-metal bonding in late transition metals is somewhat sparse. However, we hope that a series of formula $[\{\text{M}(\text{NPh}_2)_2\}_2]$, M = Mn-Ni, can be crystallized which will give magnetic and structural data to yield valuable information on the M-M interactions in the d^{5-9} metals. More comprehensive magnetic and spectroscopic studies on complexes **1** → **4** are under way.²¹

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances and angles, and data collection and refinement summaries (15 pages). Ordering information is on any current masthead page.

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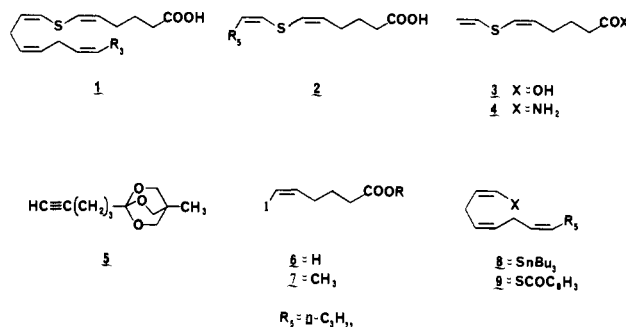
A New Class of Irreversible Inhibitors of Leukotriene Biosynthesis

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Effective inhibitors of leukotriene^{1,2} biosynthesis are of interest for both the understanding and control of various inflammatory and allergic diseases.³ Recent papers from this laboratory have described rationally devised inhibitors of the first step of leukotriene biosynthesis (a 5-lipoxygenase, 5-LO reaction) which are of competitive⁴ and irreversible types.⁵ Reported herein is a novel class of potent irreversible 5-LO inhibitors (**1-4**) whose activity also provides insight regarding the mechanism of the LO reaction.



The synthesis of 7-thiaarachidonic acid (**1**) was accomplished as follows. The OBO ester of 5-hexynoic acid⁶ (**5**) was transformed into the *Z*-iodo olefin methyl ester **7** by the following sequence: (1) metalation with 1 equiv of *n*-butyllithium in tetrahydrofuran (THF) at -10 °C, cooling to -78 °C, and reaction with 1 equiv of iodine to form the iodo acetylene, mp 77-78 °C,

(14) Covalent radii for four-coordinate Ni are 1.21 Å (Td) and 1.16 Å (Sq); Kilburn, B. T.; Powell, H. M. *J. Chem. Soc. A* **1970**, 1688. For *N*, values of 0.70-0.75 Å are commonly quoted.

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