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Nickel(0) Addition to a Disulfide Bond

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Abstract Ni(IMes)₂ (IMes = N,N'-(2,4,6-trimethylphenyl)imidazole) was prepared and reacted with dimethyldisulfide. A novel trinuclear product (IMes)(SMe) Ni(μ -SMe)₂Ni(μ -SMe)₂Ni(SMe)(IMes) (1) was obtained containing both bridging and non-bridging methylsulfido groups. The crystal of 1 belongs to triclinic space group *P*-1 with unit cell dimensions a = 9.6664(5) Å, b =12.8304(6) Å, c = 16.1842(8) Å, $\alpha = 70.0370(10)^{\circ}$, $\beta =$ 73.0050(10)°, $\gamma = 86.7240(10)^{\circ}$, V = 1802.20(15) Å³, $Z = 1, D_{calcd} = 1.294$ Mg m⁻³, and F(000) = 730.

Keywords Structural study · *N*-Heterocyclic carbene · Trimetallic complex

Introduction

N-Heterocyclic carbine (NHC) ligands have found their way into a wide variety of transition metal complexes that are useful in catalysis [1]. These ligands serve as phosphine replacements, and are typically found to be better σ -donors than their phosphorus-containing counterparts. Examples of reactions that can be carried out a palladium–NHC centers include aryl chloride amination [2], cyclization of anilides [3], ester enolate arylation to afford α -aryl esters

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J. Morris · W. W. Brennessel · W. D. Jones (🖂) Department of Chemistry, University of Rochester, Rochester, NY 14627, USA e-mail: jones@chem.rochester.edu [4], Sonogashira reactions of unactivated alkyl bromides [5], and the ruthenium-catalyzed RCM reaction [6].

Attachment of NHC ligands to nickel(0) has been demonstrated in the work of Radius, who reported the preparation of $Ni_2(iPr_2Im)_4(COD)$ as a reactive nickel precursor to the fragment $[Ni(iPr_2Im)_2]$ [7]. This fragment was reported to insert into the C–CN bonds of aryl nitriles, giving stable Ni(II) *trans*-square planar products (Eq. 1) [8]. Other reactions include insertions into the C–S bonds of sulfoxides [9] and the C–C bond of biphenylene [7, 10], the stabilization of phosphaalkynes [11], and Suzuki couplings of aryl fluorides [12]. These reactions parallel the earlier reports of similar C–CN [13], C–S [14], and C–C [15] insertions by the nickel(0) phosphine fragment [Ni(dippe)].



Radius also reported the reaction of $Ni_2(iPr_2Im)_4(COD)$ with Me_2S_2 and Ph_2S_2 . The products obtained were simple, mononuclear, square planar nickel(II) addition products (Eq. 2) [16].

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Results and Discussion

We have investigated the related chemistry of the NHC ligand IMes with nickel(0) (IMes = N,N'-(2,4,6-trimethylphenyl)imidazole). Reaction of the NHC with Ni(cod)₂ in 2:1 ratio leads to Ni(IMes)₂ as a purple solid. Reaction with excess dimethyl sulfide results in an immediate change in color to dark yellow. Over the course of several days at room temperature, the ¹H NMR spectrum shows the formation of a major product identified as **1**. Two products were isolated from this solution by crystallization (Eq. 3), the second being S = IMes (**2**).



The single crystal structure of **1** was obtained, showing 3 square planar nickel(II) centers bridged by pairs of μ -methylthiolate ligands (Fig. 1; Table 1). The terminal nickel centers possess one IMes ligand and one terminal methylthiolate ligand. The molecule sits on an inversion center, and the Ni1–Ni2 distance is 2.9697(2) Å. The



Fig. 1 Plot of 1. Hydrogens have been omitted for clarity. Ellipsoids are shown at the 50 % level

Table 1 Crystal data and structure refinement for 1

Identification code	CCDC #951112
Empirical formula	$C_{72}H_{66}D_{24}N_4Ni_3S_6$
Formula weight	1404.11
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	a = 9.6664(5) Å; $\alpha = 70.0370(10)^{\circ}$
	b = 12.8304(6) Å; $\beta = 73.0050(10)^{\circ}$
	c = 16.1842(8) Å; $\gamma = 86.7240(10)^{\circ}$
Volume	1802.20(15) Å ³
Ζ	1
Density (calculated)	1.294 mg/m^3
Absorption coefficient	0.991 mm^{-1}
<i>F</i> (000)	730
Crystal color, morphology	Dark red-orange, block
Crystal size	$0.40 \times 0.36 \times 0.32 \text{ mm}^3$
Theta range for data collection	1.691°-37.784°
Index ranges	$-16 \le h \le 16, -22 \le k \le 22, \\ -27 \le l \le 27$
Reflections collected	67254
Independent reflections	19045 [$R(int) = 0.0331$]
Observed reflections	12950
Completeness to theta = 25.242°	99.9 %
Absorption correction	Multi-scan
Max. and min. transmission	0.7476 and 0.6830
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	19045/0/394
Goodness-of-fit on F^2	1.014
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0387, wR2 = 0.0979
R indices (all data)	R1 = 0.0683, wR2 = 0.1128
Extinction coefficient	n/a
Largest diff. peak and hole	$0.857 \text{ and } -0.495 \text{ e/}\text{\AA}^3$

nickel- μ -methylthiolate distances are slightly longer (2.2183(3), 2.2130(3) Å) than the nickel-terminal methylthiolate distance (2.1895(4) Å). The adjacent square planes are folded at an angle of 125.9°, which is substantially smaller than that seen in [Ni(dippe)(μ -S)]₂ (140.2°) and [Ni₂(dippe)₂(μ -S)(μ -SMe)]⁺ (136.5°) [17]. The nickel-IMes carbon distance is 1.8926(11) Å. The methyl groups on the bridging methylthiolates take on an 'bent/*anti*' mixed geometry as seen in [Rh(dippe)(μ -SMe)₂]₂ [18].

A search of the Cambridge Database for molecules containing a $Ni(\mu$ -S)₂Ni(μ -S)₂Ni core produces 100 hits, many of which contain this unit as part of a larger cyclic structure containing 6 or more nickels. Only ~30

Fig. 2 Cocrystallized benzene solvent molecule encase 1



Fig. 3 Edge-to-face arrangement of benzene molecules

structures contain similar trinuclear moieties, and none were found to have NHC ligands.

Crystals of the minor product S = IMes (2) were also obtained. A preliminary X-ray structure determination confirmed that this was indeed the compound, which cocrystallized with benzene. The structure of 2 has been previously reported in the literature [19].

Fig. 4 Benzene molecule relative to the IMes ligand

The cocrystallized benzene solvent molecules, of which there are four per tri-nickel species, essentially encase the nickel molecule (Fig. 2). Sets of four benzene molecules, related by inversion symmetry, are oriented edge-to-face, which is reminiscent of the structure of benzene itself (Fig. 3) [20]. While there are no close contacts in which atoms are within the van der Waals radii of other atoms,

there are some suggestive orientations like the edge-to-face orientation of the benzene molecules, which may have played a role in the particular packing. For instance, one benzene molecule (C25–C30) appears to have an orientation relative to an IMes phenyl arm that suggests that pistacking and C–H··· π interactions may have dictated the arrangement (Fig. 4). The closest contact between the rings is 3.5–3.6 Å, which is reasonable for pi-stacking, but the rings have almost no eclipsed regions and the angle between the planes is a rather canted 32.19(9)°, thus minimizing any potential overlap. Atom H5 is directed toward the pi-system of the benzene ring, yet the closest (H5···C29) distance of 2.86 Å is larger than the sum of the van der Waals radii, 2.79 Å.

Experimental Section

General Procedures

Unless otherwise stated, all reactions and manipulations were carried out in dry glassware using standard Schlenk and glovebox techniques under a nitrogen atmosphere. Deuterated solvent C_6D_6 (Cambridge Isotope Laboratories) for NMR experiments and dimethyl disulfide were purchased from Aldrich, dried over CaH₂, and distilled under vacuum. All other reagent grade chemicals were used without further purification. All NMR spectra were recorded on Bruker Avance 400 and 500 MHz spectrometers. IMes was prepared as described in the literature [21].

Synthesis of Ni(IMes)2

A suspension of IMes (4.4 mg, 14 μ mol) in benzene (0.1 mL), Ni(cod)₂ (2 mg, 7.3 μ mol) in benzene(0.1 mL), and 0.3 mL benzene were added to a J-Young NMR tube. The resulting free cod and solvent were removed under vacuum, leaving a violet solid. ¹H NMR (400 MHz, C₆D₆): δ 6.82 (s, 8H), 6.01 (s, 4H), 2.30 (s, 12H), 2.08 (s, 24H).

Reaction of Ni(IMes)₂ with Me₂S₂

Dimethyl sulfide $(10\mu L, 110 \mu mol)$ was added to Ni(IMes)₂ (5 mg, 7 µmol) dissolved in 0.5 mL benzene in a J-Young NMR tube. The color changed from violet to yellow brown instantly and the solution was maintained at room temperature for 10 days. The excess dimethyl disulfide and solvent were removed under vacuum. The reaction was monitored by ¹H NMR spectroscopy. Crystals of complex **1** and **2** were grown by slow evaporation from C₆D₆ solution. For [(IMes)(MeS)Ni(µ-SMe)₂]₂Ni (**1**), ¹H NMR (400 MHz, C₆D₆): δ 6.77 (s, 8H), 5.93 (s, 4H), 2.15 (s, 24H), 2.11 (s, 12H), 1.80 (s, 6H), 1.74 (s, 12H).

¹³C{¹H} NMR (500 MHz, C₆D₆): δ 165.16 (s), 138.74 (s), 136.19 (s), 134.75 (s), 129.37 (s), 117.34 (s), 21.10 (s), 18.13 (s). NMR yield, 90 %. For free IMes: ¹³C NMR (500 MHz, C₆D₆): δ 219.45 (s), 139.31 (s), 137.25 (s), 135.45 (s), 128.14 (s), 120.56 (s), 21.06 (s), 18.09 (s). For S = IMes (**2**), a crystal provided cell data that matched that in the literature for this compound (as a benzene solvate) [19]. 200 frames of data allowed solution of the structure, confirming it to be S = IMes.

X-ray Structure Determination of [(IMes)(MeS)Ni (µ-SMe)₂]₂Ni (1)

A crystal $(0.40 \times 0.36 \times 0.32 \text{ mm}^3)$ was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 173(2) K. The full data collection was carried out using Mo K α radiation (graphite monochromator) with a frame time of 30 s and a detector distance of 4.01 cm. The structure was solved using SIR97 [22] and refined using SHELXL-2012 [23]. The structure is similar to the one suggested. The asymmetric unit contains one tri-nickel molecule in a crystal-lographic inversion center that is coincident with atom Ni2 and two independent cocrystallized deuterated benzene solvent molecules in general positions.

Supplementary Material

CCDC 951112 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk.

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