Preliminary Communication

Synthesis and structure of the nickel A-frame complex Ni$_2$(μ-CNC$_6$H$_5$)(dppm)$_2$Cl$_2$
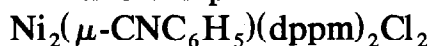
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Abstract

Oxidative addition of phenyl isocyanide dichloride (C$_6$H$_5$NCCl$_2$) to Ni(COD)$_2$ (COD = cycloocta-1,5-diene) in the presence of dppm (dppm = bis(diphenylphosphino)methane) in toluene is found to be a high yield procedure for the preparation of the new phenyl isocyanide-bridged A-frame complex, Ni$_2$(μ-CNC$_6$H$_5$)(dppm)$_2$Cl$_2$. The title complex crystallizes in the chiral space group $P4_32_12$ (a = 14.871(3), c = 25.790(7) Å, V = 5703.7 Å^3, Z = 4) and its structure was determined by X-ray diffraction.

In contrast to the many and varied A-frame complexes of platinum and palladium of the general type M$_2$(μ-L)X$_2$(dppm)$_2$ (M = Pt or Pd; dppm = Ph$_2$PCH$_2$-PPh$_2$; X = halide or pseudo-halide; L = small unsaturated molecules) [1–5], there are very few such complexes of nickel. Over the past several years, a series of dppm-bridged d^9–d^9 dinuclear nickel complexes have been reported [6–12]. With the exception of the μ-SO complex, Ni$_2$(μ-SO)Cl$_2$(dppm)$_2$ [11], and the μ-vinylidene complex, Ni$_2$(μ-C=CH$_2$)(SCN)$_2$(dppm)$_2$ [12], these have asymmetric, non-A-frame structures in the solid state [6–10]. These complexes generally exhibit a locally tetrahedral geometry at one metal center and a rectilinear geometry at the other. This class of complexes has thus been formulated as mixed oxidation state Ni^0/Ni^{II} species. The ligand-centered reactivity of bridging isocyanides in dinuclear nickel complexes can have important consequences. Thermal alklyations [13] and photochemical cycloadditions of carbon diox-

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ide [14] to μ-CNR complexes have been described. The cycloaddition of carbon dioxide, in particular, leads to multiple bond metatheses between the triple bonds of isocyanides and double bonds of carbon dioxide [15].

We report here the synthesis and structural characterization of a new dinuclear nickel complex, Ni$_2$(μ-CNC$_6$H$_5$)(dppm)$_2$Cl$_2$. The 'A-frame' complex was obtained by the reaction of [Ni(COD)$_2$] [16] (COD = cycloocta-1,5-diene) with dppm and phenyl isocyanide dichloride (2:2:1) in toluene. The mixture was stirred for 45 min at $-20°$C under nitrogen. The dark blue precipitate was filtered and washed with diethyl ether to obtain the complex in 90% yield. The IR (KBr) of the complex shows one ν(CN) band at 1633(s) cm^{-1}. The ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 85% H$_3$PO$_4$ external) spectrum is a singlet at δ = 16.5 ppm. The ^{1}H NMR (CD$_2$Cl$_2$) spectrum shows a second order multiplet at δ = 2.32 ppm, integrated as 4 protons for the methylene groups of the dppm ligands. There is also a broad multiplet between δ = 6.70–7.90 ppm integrated as 45 protons, 40 protons from the phenyl rings of the dppm ligands and 5 protons from the phenyl group of the bridging phenyl isocyanide. Satisfactory elemental
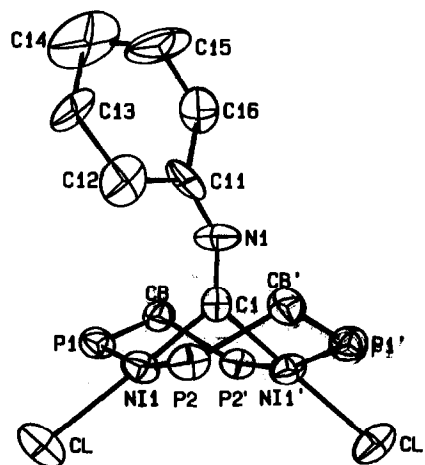

Fig. 1. ORTEP drawing of [Ni$_2$(μ-CNC$_6$H$_5$)(dppm)$_2$Cl$_2$] without dppm phenyl rings and hydrogen atoms. The atoms are depicted as 50% probability ellipsoids. Important bond distances (Å) and angles (°): Ni1–Ni1′, 2.917(4); Ni1–Cl, 2.261(5); Ni1–P1, 2.206(5); Ni1–P2, 2.240(5), Ni1–C1, 1.867(2); Ni1′–C1, 1.87(1); P1–CB, 1.81(2); C1–N1, 1.22(1); Ni1–Ni1′–Cl, 141.9(1); Ni1–Ni1′–P1, 92.7(2); Ni1–Ni1′–P2, 89.0(1); P1–Ni1–P2, 165.9(2); Ni1–C1–Ni1′, 102.7(6); Ni1–C1–N1, 128.6(8).

analyses (Galbraith Labs Inc.) were obtained (Calculated for $C_{57}H_{49}Cl_2Ni_2NP_4$: C, 60.78; H, 4.47; N, 1.22%. Found: C, 60.73; H, 4.50; N, 1.20%).

X-ray quality crystals were obtained by slow diffusion of diethyl ether into a methylene chloride solution. The structure of the title complex is presented in Fig. 1 *. The complex has crystallographically imposed two-fold symmetry. This results in two-fold disorder of the bridging isocyanide phenyl group. The complex $Ni_2(\mu\text{-}CNC_6H_5)(dppm)_2Cl_2$ is only the third structurally characterized dinuclear nickel 'A-frame' complex. The Ni1–Ni1' internuclear separation is 2.917(4) Å, which indicates the absence of a direct Ni–Ni bond. This is comparable to the Ni–Ni internuclear separation of 2.840(4) Å in the vinylidene complex, $Ni_2(\mu\text{-}C{=}CH_2)(SCN)_2(dppm)_2$ [12], but significantly shorter than the separation of 3.308(1) Å found in the μ-SO complex, $Ni_2(\mu\text{-}SO)Cl_2(dppm)_2$ [11]. Selected bond distances and angles are listed in Fig. 1.

The synthetic procedure leading to the preparation of the title complex is an effective way to synthesize d^9–d^9 dinuclear nickel complexes with various bridging ligands [10,11]. The complex $Ni_2(\mu\text{-}CNC_6H_5)(dppm)_2$-$Cl_2$ represents the third member of a series of structurally characterized $Ni_2(\mu\text{-}L)(dppm)_2Cl_2$ (L = CO [9,10], SO [11], $CNCNC_6H_5$) frameworks in which only the unsaturated bridging ligands differ. The μ-SO and title complex are of the A-frame type structure. The

μ-CO complex exhibits a tetrahedral/T-shaped mixed geometry in the solid state, but NMR data have been interpreted in terms of a more symmetrical A-frame structure in solution [9]. The factors which decide the delicate balance between symmetric A-frame and unsymmetric structures remain to be fully explained. The theoretical questions raised by this new complex as well as its reaction chemistry with Lewis acids are being investigated further.

Acknowledgments

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* Crystal Data for $C_{57}H_{49}Cl_2NP_4$, F.W. = 1060.25, space group $P4_32_12$, $a = 14.871(3)$ Å, $c = 25.790(7)$ Å, $V = 5703(4)$ Å^3, $Z = 4$. The structure was solved using the structure solution program SHELX-86. The remaining atoms were located in succeeding difference Fourier synthesis. The structure was refined to $R = 0.066$ and $R_w = 0.087$ for 2130 observations with $I > 3\sigma(I)$ with Mo-Kα radiation. The final selection of the space group as $P4_32_12$ was based on final refinements in this ($R = 0.066$, $R_w = 0.087$) and the enantiomorphous space group $P4_12_12$ ($R = 0.073$, $R_w = 0.094$). Data were corrected for absorption empirically, $\mu = 9.02$ cm^{-1}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the National Auxiliary Publication Service (NAPS). See NAPS document no. 05030 for 32 pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163, USA. Remit in advance in US funds only $4.00 for microfiche. Outside the US and Canada add $1.50 for microfiche postage.