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In Search of the Elusive Open-Faced Triangulo Nickel Cluster: Insertion of Thallium(I) into a μ_3-I Capping Ligand

Marc J. A. Johnson, Peter K. Gantzel, and Clifford P. Kubiak*

*Department of Chemistry and Biochemistry, University of California, San Diego,
La Jolla, California 92093-0358*

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Summary: Thallium(I) inserts into the Ni−I bonds on one face of the 52e triangulo cluster $[\mathrm{Ni_3}(\mu_3\text{-I})_2(\mu\text{-dppm})_3]$ *to form the new electron-deficient cluster cation* $[\mathrm{Ni_3}(\mu_3\text{-TlI})(\mu_3\text{-I})(\mu\text{-dppm})_3]^+$*. A single-crystal X-ray diffraction study revealed a triangulo cluster containing a symmetrically face-capping TlI ligand and having average Ni−Ni, Ni−Tl, and Ni−I distances of 2.509(14), 2.580(16), and 2.624(14) Å, respectively. Thallium ion can be removed from this cationic cluster by various reagents to regenerate the starting cluster but will not eliminate as TlI and yield an open-faced cluster.*

Cationic trinuclear nickel clusters of the type $[\mathrm{Ni_3}(\mu_3\text{-CNR})(\mu_3\text{-I})(\mu\text{-dppm})_3]^+$ (R = alkyl, aryl; dppm = $\mathrm{Ph_2PCH_2PPh_2}$) catalyze the reduction of carbon dioxide in aprotic solvents at potentials near −1.2 V vs SCE.[1,2] These clusters are derived from the diamagnetic, neutral 52e cluster $[\mathrm{Ni_3}(\mu_3\text{-I})_2(\mu\text{-dppm})_3]$ (**1**)[3,4] by treatment with 1 equiv of RNC.[4] Further advances in catalysis of CO_2 reduction with this system would be facilitated by new clusters of the form $[\mathrm{Ni_3}(\mu_3\text{-CNR})(\mu_3\text{-X})(\mu\text{-dppm})_3]^+$, where X is a bifunctional anion. Puddephatt and coworkers have prepared trinuclear clusters that contain $[\mathrm{M_3}(\mu\text{-dppm})_3]^{2+}$ (M = Pd, Pt) cores and various capping ligands.[5−12] Several clusters exhibited one open face.[5,6,13−15] Open-face clusters are not known for the $\mathrm{Ni_3(dppm)_3}$ class, but they could be extremely useful. Since the isocyanide-capped clusters $[\mathrm{Ni_3}(\mu_3\text{-CNR})(\mu_3\text{-I})(\mu\text{-dppm})_3]^+$ proved inert to both iodide abstraction and nucleophilic displacement, synthetic efforts focused on modification of cluster **1**. In addition to isocyanides, various other π-acids, including CO and NO^+, displace iodide from **1** to form 48e clusters,[4] but various nucleophiles do not. Furthermore, known synthetic routes to **1** are not amenable to replacement of I by other elements except Br[4] and Te.[16] Removal of iodide ion appeared an attractive option, but common halide abstraction reagents such as Ag^+ ion and $AlCl_3$ resulted in oxidation to the paramagnetic 51e cation $\mathbf{1}^+$ in a variety of solvents. The half-wave potential for the $\mathbf{1}^{+/0}$ couple in acetonitrile is −0.68 V vs SCE.[4] Consequently, Tl^+ was investigated as a potential iodide ion abstractor.

Treatment of a suspension of **1** in MeCN with 1 equiv or more of TlOTf led to rapid dissolution of dark green **1**, with concomitant formation of a dark orange-brown solution (Scheme 1).[17] ^{1}H and ^{31}P NMR spectra of aliquots from this mixture in CD_3CN were revealing. A broad doublet centered at δ 3.96 (J = 510 Hz) in the ^{31}P NMR spectrum could be explained by unresolved coupling to both naturally occurring isotopes of Tl (both $I = {}^1/_2$) in a cluster containing one symmetrically bridging Tl atom. Appearance of an AB pattern for the dppm methylene protons in the ^{1}H NMR spectrum confirmed a face-differentiated cluster. A single-crystal X-ray diffraction study of crystals grown from an acetonitrile/toluene/hexane mixture (1/4/4) revealed a cationic cluster in which a thallium ion had inserted into the Ni−I bonds on one face of cluster **1**, forming an approximately symmetrically μ_3-capping Tl−I moiety.[18] The opposite cluster face remained capped by iodide. A thermal ellipsoid plot of one of the two

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(17) **Synthesis of** $\mathbf{[Ni_3(\mu_3\text{-}TlI)(\mu_3\text{-}I)(\mu\text{-}dppm)_3]^+OTf^-}$ **(2(OTf)).** A powder of complex **1** (1.014 g, 0.6405 mmol) was dissolved in 120 mL of toluene, affording a dark green solution. Next, a clear, colorless solution of TlOTf (226.0 mg, 0.6394 mmol, 0.9983 equiv) in 20 mL of MeCN was added rapidly via pipet and rinsed in with an additional 10 mL of MeCN. The reaction mixture became a rich dark brown color during the addition process. Following addition, the mixture was stirred an additional 20 min, at which point 120 mL of hexane was added. The resulting dark brown solution was then placed in a freezer at −30 °C. After 2 days, a mixture of brown crystals and powder had formed. This was isolated by vacuum filtration and dried in vacuo to yield **2**(OTf) (970.4 mg, 0.5011 mmol, 78.37%). ^{1}H NMR (CD_3CN, 22 °C): δ 7.00 (m, 60H, phenyls), 4.05 (dd, 6H, $\mathrm{PC}H_2\mathrm{P}$). ^{31}P NMR (CD_3CN, 22 °C): δ 3.96 (^2J(Tl−P) = 510 Hz). Anal. Calcd for $\mathrm{C_{76}H_{66}F_3I_2Ni_3O_3P_6STl}$: C, 47.14; H, 3.44. Found: C, 47.57; H, 3.69.

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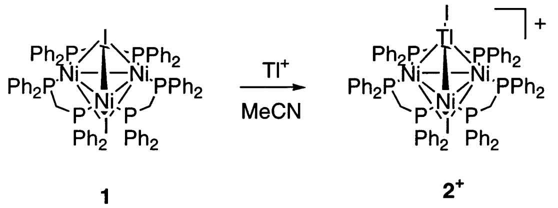
Scheme 1. Synthesis of the Cluster Cation $[Ni_3(\mu_3\text{-}TlI)(\mu_3\text{-}I)(\mu\text{-dppm})_3]^+$ (2^+)



chemically equivalent cluster ions $[Ni_3(\mu_3\text{-}TlI)(\mu_3\text{-}I)(\mu\text{-dppm})_3]^+$ present in the unit cell is depicted in Figure 1.

Examples of clusters that coordinate Tl^+ are rare. Nevertheless, several *triangulo*-Pt_3 clusters that have one open face react with added thallium(I) reagents to form Pt−Tl bonds. The well-known Chatt−Chini triplatinum clusters $Pt(\mu\text{-}CO)_3(PR_3)_3$ add a variety of metal fragments, including Tl^+ salts of weakly coordinating anions.[12,19−22] The related *triangulo*-triiridium clusters $Ir_3(\mu\text{-}CO)(\eta^5\text{-}C_9H_7)_3$ behave similarly.[23] In these complexes, thallium is coordinated solely to the three metal atoms as a face-capping ligand. In contrast, the rhenium−platinum cluster cation $[Pt_3(ReO_3)(\mu\text{-dppm})_3]^+$ simply adds molecular Tl(acac) to form $[Pt_3\{\mu_3\text{-}Tl(acac)\}(ReO_3)(\mu\text{-dppm})_3]^+$.[12] Cluster $\mathbf{2}^+$ can be regarded as a 46e system, at least to the extent that the "inert pair" of Tl^+ really is inert. An average Ni−Ni distance of 2.509(14) Å is found for $\mathbf{2}^+$. This is similar to the average Ni−Ni distances of 2.49(2) and 2.518(13) Å for the 52e cluster **1** and 51e cluster $\mathbf{1}^+$, respectively, but significantly longer than the average Ni−Ni distance of 2.402(6) Å in the 48e cluster $[Ni_3(\mu_3\text{-}CO)(\mu_3\text{-}I)(\mu\text{-dppm})_3]^+$ ($\mathbf{3}^+$). The longer Ni−Ni distances of **1** and $\mathbf{1}^+$ are attributed to an electronic structure in which cluster valence electrons above 48 in number occupy molecular orbitals that are partly Ni−Ni antibonding.[4] It would appear that the longer Ni−Ni distances of $\mathbf{2}^+$ arise from the partial depopulation of the a_1 Ni_3 dπ-bonding level that is occupied in a 48e cluster.[4]

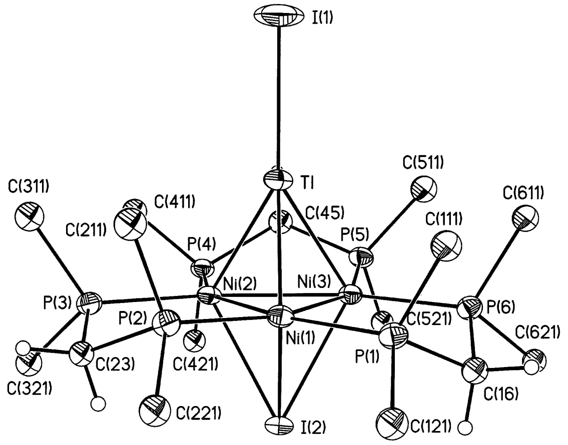


Figure 1. ORTEP diagram of the core of cluster $\mathbf{2}^+$ in the solid state. Only one of the two crystallographically independent cluster ions is shown. Ellipsoids are evaluated at the 35% probability level. Selected bond lengths (Å) and angles (deg): Ni(1)−Tl = 2.559(2), Ni(2)−Tl = 2.569(2), Ni(3)−Tl = 2.598(3), Ni(1)−Ni(2) = 2.520(3), Ni(1)−Ni(3) = 2.518(3), Ni(2)−Ni(3) = 2.491(3), Ni(1)−I(2) = 2.602(2), Ni(2)−I(2) = 2.624(2), Ni(3)−I(2) = 2.642(2), Tl−I(1) = 2.788(2); Ni(1)−Ni(2)−Ni(3) = 60.32(8), Ni(1)−Ni(3)−Ni(2) = 60.41(8), Ni(2)−Ni(1)−Ni(3) = 59.27(8), Ni(1)−Tl−I(1) = 149.63(7), Ni(2)−Tl−I(1) = 144.29(6), Ni(3)−Tl−I(1) = 142.97(7), Tl−Ni(1)−I(2) = 113.42(8), Tl−Ni(2)−I(2) = 112.36(8), Tl−Ni(3)−I(2) = 110.84(8), P(1)−Ni(1)−P(2) = 107.8(2), P(3)−Ni(2)−P(4) = 106.8(2), P(5)−Ni(3)−P(6) = 106.2(2).

The electronic deficiency implied by a 46e configuration for $\mathbf{2}^+$ is evident in its reactivity. Cluster ion $\mathbf{2}^+$ appears to be unstable in most solvents other than acetonitrile, often undergoing conversion to paramagnetic $\mathbf{1}^+$ and elemental Tl. In contrast to the clean and reversible electrochemistry observed for **1** and **3** at negative potentials (vs SCE),[4] cluster $\mathbf{2}^+$ exhibits only irreversible reduction at positive potentials to afford **1**. Similarly, $Co(Cp)_2$, $NaBH_4$, and NaI all chemically reduce $\mathbf{2}^+$ to **1** with loss of thallium. We are continuing our synthetic efforts in attempts to access the open-face clusters $[Ni_3(\mu_3\text{-}I)(\mu\text{-dppm})_3]^+$ via nucleophilic displacement of TlI from $\mathbf{2}^+$, or alternately via removal of I or I^- concurrently with or followed by reduction in the presence of appropriate trapping agents. To date, such open-face triangulo nickel clusters continue to elude us.

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Supporting Information Available: Text detailing the synthesis, characterization, and selected reactions of **2**(OTf) and tables of crystal data collection and refinement parameters, positional and thermal parameters, and bond distances and angles for **2**(OTf). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) **X-ray Crystal Structure of 2OTf.** A dark brown crystal of **2**(OTf) of approximate dimensions 1.20 × 0.50 × 0.20 mm grown from an acetonitrile/toluene/hexane mixture at −35 °C was coated with Paratone-N oil (Exxon). Crystal data: chemical formula $C_{76}H_{66}F_3I_2Ni_3O_3P_6STl$, triclinic, $a = 15.583(11)$ Å, $b = 17.541(8)$ Å, $c = 35.060(12)$ Å, $\alpha = 98.88(3)°$, $\beta = 96.22(5)°$, $\gamma = 90.38(5)°$, $V = 9410(9)$ Å^3, $Z = 4$, space group $P\bar{1}$, $\rho_{calcd} = 1.565$ g cm^{-3}, $\mu = 3.133$ mm^{-1}, $F(000) = 4362$, R1 = 0.0758 ($I > 2\sigma(I)$), wR2 = 0.1694. Data were collected at −88 °C with a Siemens R3m/V four-circle diffractometer using Mo Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2 (SHELXTL PLUS, version 3.4). Non-hydrogen atoms were located on a series of difference Fourier maps. Phenyl rings, including toluene, were treated as regular hexagons of D_{3h} symmetry with C−C = 1.395 Å and C−C−C = 120°. Hydrogen atoms were calculated and fixed in idealized positions (d(C−H) = 0.96 Å). Unit cell dimensions and standard deviations were obtained by a least-squares fit to 25 reflections ($14 < 2\theta < 24°$). A rigid-body n-hexane was smeared to fit a string of residual electron density. One CF_3SO_3 ion and three toluene molecules were disordered, and each was modeled with two rigid 50% molecules.

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