Variation in crystallization conditions allows the isolation of trimeric as well as dimeric and monomeric forms of $[(\text{alkyl isocyanide})_4\text{Rh}^{\text{I}}]^+$

Ngon T. Tran, Jay R. Stork, David Pham, Marilyn M. Olmstead, James C. Fettinger and Alan L. Balch*

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Trimeric green $[(i\text{-PrNC})_{12}\text{Rh}^{\text{I}}_3]\text{Cl}_3\cdot4.5\text{H}_2\text{O}$, monomeric $[(\text{C}_6\text{H}_{11}\text{NC})_4\text{Rh}^{\text{I}}](\text{BPh}_4)$ and $[(i\text{-PrNC})_4\text{Rh}^{\text{I}}](\text{BPh}_4)$ (both yellow), and red, dimeric $[(\text{C}_6\text{H}_{11}\text{NC})_8\text{Rh}^{\text{I}}_2]\text{Cl}_2\cdot0.5\text{C}_6\text{H}_6\cdot2\text{H}_2\text{O}$ have been crystallized.

Numerous planar d^8 and linear d^{10} transition metal complexes undergo self-association with the formation of weak metal–metal bonds.[1] As a result, many of these complexes crystallize to form infinite stacks with metal–metal distances that are short, but not as short as found for the corresponding metal–metal single bonds. The anisotropic properties of these metal chain compounds have attracted considerable interest.[1,2] Cationic rhodium(I) isocyanide complexes of the type $[(\text{RNC})\text{Rh}^{\text{I}}]^+$ offer an unusual situation in which self-association is limited to the formation of dimers and trimers as shown in eqn (1) and (2).[3]

$$2[(\text{RNC})_4\text{Rh}^{\text{I}}]^+ \rightleftharpoons [(\text{RNC})_8\text{Rh}^{\text{I}}_2]^{2+} \qquad (1)$$

$$3[(\text{RNC})_4\text{Rh}^{\text{I}}]^+ \rightleftharpoons [(\text{RNC})_{12}\text{Rh}^{\text{I}}_3]^{3+} \qquad (2)$$

Several salts containing the dimeric dication, $[(\text{RNC})_8\text{Rh}^{\text{I}}_2]^{+2}$, have been isolated and crystallographically characterized. Typically these have Rh···Rh separations of *ca.* 3.2 Å (*e.g.* 3.193(1) Å for $[(\text{PhNC})_8\text{Rh}^{\text{I}}_2](\text{BPh}_4)_2$,[4] 3.207(2) Å for $[(p\text{-FC}_6\text{H}_4\text{NC})_8\text{Rh}^{\text{I}}_2]\text{Cl}_2\cdot\text{H}_2\text{O}$,[5] and 3.25(1) Å for $[(p\text{-O}_2\text{NC}_6\text{H}_4\text{NC})_8\text{Rh}^{\text{I}}_2]\text{Cl}_2$). A monomeric monocation has only been crystallographically characterized through the use of a bulky isocyanide in the salt $[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4\text{Rh}^{\text{I}}](\text{BPh}_4)$.[6] Crystallographic characterization of a trimeric form has not been available. Previously, we have shown that the degree and mode of self-association of two-coordinate gold(I) complexes can be altered in the solid state by changing the counter ion present.[7] Here we report that by varying the crystallization conditions, it is possible to obtain crystals of monomeric $[(\text{RNC})_4\text{Rh}^{\text{I}}]^+$, dimeric, $[(\text{RNC})_8\text{Rh}^{\text{I}}_2]^{2+}$ or trimeric $[(\text{RNC})_{12}\text{Rh}^{\text{I}}_3]^{3+}$. This is possible because crystallization from a complex mixture depends upon a number of variables including the relative solubilities of the different salts, the degree of solvation, and the rates of nucleation.

Samples of the salts of $[(\text{C}_6\text{H}_{11}\text{NC})_4\text{Rh}^{\text{I}}]^+$ and $[(i\text{-PrNC})_4\text{Rh}^{\text{I}}]^+$ were obtained through established methods.[4,8] Slow evaporation of yellow-orange solutions of $[(\text{C}_6\text{H}_{11}\text{NC})_4\text{Rh}^{\text{I}}](\text{BPh}_4)$ or $[(i\text{-PrNC})_4\text{Rh}^{\text{I}}](\text{BPh}_4)$ in ethanol produces bright yellow crystals.† Fig. 1 shows a drawing of the structure of $[(\text{C}_6\text{H}_{11}\text{NC})_4\text{Rh}^{\text{I}}](\text{BPh}_4)$. The cation has the expected planar geometry and is strictly monomeric; the shortest Rh-to-Rh distance in the crystal is 8.6390(7) Å. The structure of $[(i\text{-PrNC})_4\text{Rh}^{\text{I}}](\text{BPh}_4)$ is similar with a 8.5228(6) Å separation between nearest rhodium ions.

Red crystals of $[(\text{C}_6\text{H}_{11}\text{NC})_8\text{Rh}^{\text{I}}_2]\text{Cl}_2\cdot0.5\text{C}_6\text{H}_6\cdot2\text{H}_2\text{O}$ were obtained by diffusion of hexane into a moist benzene solution of the salt.† The structure of the cation in this salt is shown in Fig. 2. The two rhodium ions have a planar array of isocyanide ligands attached and are connected by a weak Rh···Rh bond. The Rh1···Rh2 distance is 3.287(2) Å. This distance is just slightly longer than the Rh···Rh distances in other dimers of this type. The Rh–C distances range from 1.893(13) to 1.981(11) Å as expected.

Deep green crystals of $[(i\text{-PrNC})_{12}\text{Rh}^{\text{I}}_3]\text{Cl}_3\cdot4.5\text{H}_2\text{O}$ were obtained by layering moist diethyl ether over a benzene solution of the salt.† A drawing of the structure of the cation is shown in Fig. 3. The trimer is situated on a crystallographic mirror plane that bisects each of the three rhodium ions. The Rh1···Rh2 distance is 3.1012(6) Å, and the Rh2···Rh3 distance is 3.0739(6) Å. Both of these distances are significantly shorter than the Rh1···Rh2 distances in related dimers, *e.g.* 3.287(2) Å in $[(\text{C}_6\text{H}_{11}\text{NC})_8\text{Rh}^{\text{I}}_2]\text{Cl}_2\cdot0.5\text{C}_6\text{H}_6\cdot2\text{H}_2\text{O}$ and 3.207(2) Å in $[(\text{PhNC})_8\text{Rh}^{\text{I}}_2](\text{BPh}_4)_2$.[4] The Rh1···Rh2···Rh3 angle is 168.05(2)°. Rh1 is displaced by 0.110 Å from the plane of the surrounding four carbon atoms toward Rh2. Similarly, Rh3 is

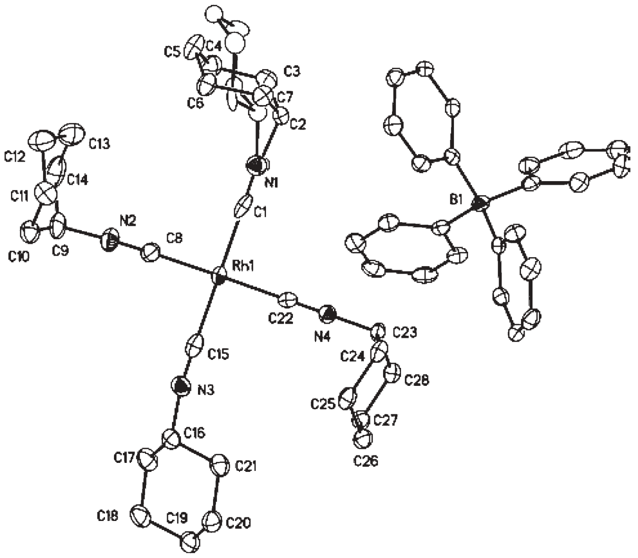


Fig. 1 A view of the structure of yellow, monomeric $[(\text{C}_6\text{H}_{11}\text{NC})_4\text{Rh}^{\text{I}}](\text{BPh}_4)$ with 30% thermal ellipsoids. The open ellipsoids show the minor orientation (site occupancy = 0.18) of one of the isocyanide ligands.

Department of Chemistry, University of California, One Shields Avenue, Davis, CA, USA. E-mail: albalch@ucdavis.edu; Fax: +1 (530) 752 8995; Tel: +1 (530) 752 0941

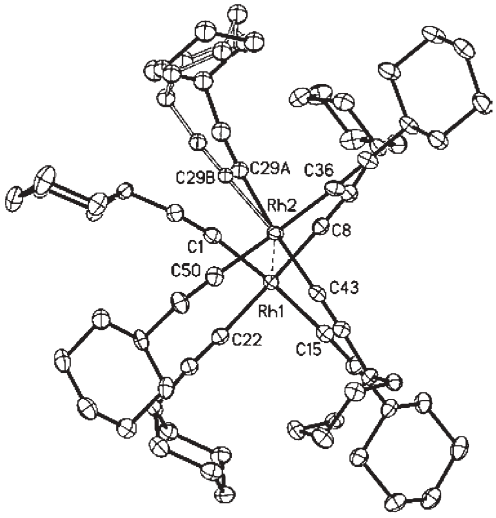


Fig. 2 A view of the structure of the cation in red, dimeric $[(C_6H_{11}NC)_8Rh^I_2]Cl_2{\cdot}0.5C_6H_6{\cdot}2H_2O$. The open lines show the position of the second orientation (occupancy = 0.4) of one of the isocyanide ligands with 50% thermal ellipsoids.

displaced by 0.124 Å towards Rh2 from its C_4 plane. In contrast Rh2 is only 0.002 Å away from its C_4 plane. The Rh1···Rh2 line is 3.7° from the normal to the C_4 plane surrounding Rh1, while the Rh3···Rh2 line is only 1.4° away from the normal to the C_4 plane surrounding Rh3. For Rh2 the displacements of the Rh2···Rh1 and Rh2···Rh3 bonds from the C_4 plane surrounding Rh2 are 8.0 and 4.0°, respectively.

The UV-Vis absorption spectra of these crystals show low-energy absorptions that are consistent with previous measurements of the spectra of concentrated solutions of the mono-, di-, and trimeric forms of these cations.[3,4,8] Thus, when dispersed in KBr yellow crystals of $[(C_6H_{11}NC)_4Rh^I](BPh_4)$ exhibit a lowest energy absorption at λ_{max} of 384 nm, while red $[(C_6H_{11}NC)_8Rh^I_2]Cl_2{\cdot}0.5C_6H_6{\cdot}2H_2O$ shows its lowest energy absorption at λ_{max} of 464 nm. Green crystals of $[(i\text{-PrNC})_{12}Rh^I_3]Cl_3{\cdot}4.5H_2O$ show a corresponding lowest energy absorption at λ_{max} of 684 nm. In comparison, the lowest energy absorption of $[(i\text{-PrNC})_4Rh^I]^+$ occurs at 383 nm, that of $[(i\text{-PrNC})_8Rh_2^I]^{2+}$ occurs at 495 nm , and that of $[(i\text{-PrNC})_{12}Rh_3^I]^{3+}$occurs at 610 nm in aqueous solution.[4]

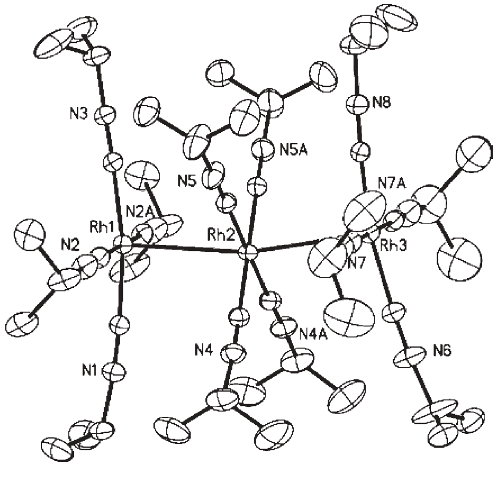
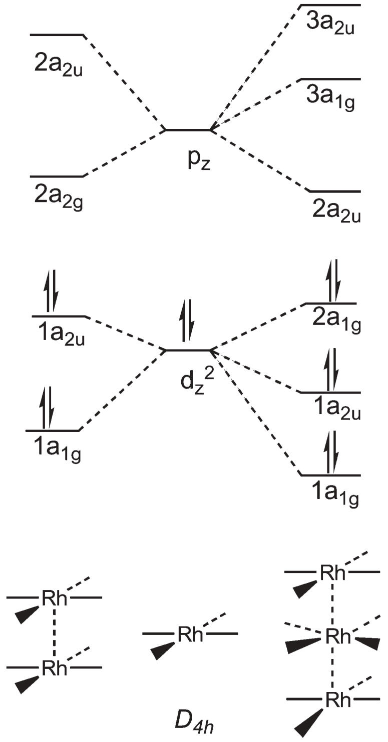


Fig. 3 The structure of the cation in green, trimeric $[(i\text{-PrNC})_{12}Rh^I_3]Cl_3{\cdot}4.5H_2O$ with 25% thermal elipsoids.



Scheme 1 Molecular orbital diagram for the overlap of the out-of-plane rhodium d_{z^2} and p_z orbitals.

The remarkable shortening of the Rh···Rh bonds in the trimer relative to the dimer is explained by the qualitative molecular orbital diagram for the overlap of the out-of-plane rhodium d_{z^2} and p_z orbitals shown in Scheme 1 using idealized D_{4h} symmetry.[4] In the trimer the key change involves the stabilization of the originally non-bonding $1a_{2u}$ orbital from mixing with the $2a_{2u}$ orbital. As a result, in the trimer there are two bonding and only one anti-bonding molecular orbitals that are filled, whereas in the dimer, one bonding and one anti-bonding MO are filled.

While the present work shows that different anions allow crystallization of three forms of $[(RNC)Rh^I]^+$, the process is not anion specific. Thus, tetraphenyl borate produces monomeric $[(C_6H_{11}NC)_4Rh^I](BPh_4)$, $[(i\text{-PrNC})_4Rh^I](BPh_4)$, and $[(2,6\text{-}Me_2C_6H_3NC)_4Rh^I](BPh_4)$[6] but dimeric $[(PhNC)_8Rh^I_2](BPh_4)_2$.[4] Chloride forms dimeric $[(C_6H_{11}NC)_8Rh^I_2]Cl_2{\cdot}0.5C_6H_6{\cdot}2H_2O$, $[(p\text{-}FC_6H_4NC)_8Rh^I_2]Cl_2{\cdot}H_2O$,[5] and $[(p\text{-}O_2NC_6H_4NC)_8Rh^I_2]Cl_2$[5] but trimeric $[(i\text{-PrNC})_{12}Rh^I_3]Cl_3{\cdot}4.5H_2O$.

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Notes and references

† *Crystal data.* Yellow needles of $[(C_6H_{11}NC)_4Rh^I](BPh_4)$, M_w = 858.79, triclinic, space group $P\bar{1}$, a = 11.9948(7), b = 13.9469(8), c = 15.4951(9) Å, α = 72.1180(10), β = 86.7140(10), γ = 66.9070(10)°, V = 2263.4(2) Å^3 at 90(2) K, μ(Mo-Kα) = 0.416 mm^{-1}, Z = 2. Refinement of 9217 reflections, 571 parameters, and 18 restraints yielded w$R2$ = 0.114 for all data and a conventional R_1 = 0.054 based on 6911 reflections with $I > 2\sigma(I)$. Yellow blocks of $[(i\text{-}C_3H_7NC)_4Rh^I](BPh_4)$, M_w = 698.54, tetragonal, space group $I4_1/a$, a = 14.2642(6), b = 14.2642(6), c = 18.6642(16) Å, V = 3797.6(4) Å^3 at

90(2) K, μ(Mo-Kα) = 0.416 mm^{-1}, Z = 4. Refinement of 2913 reflections, 117 parameters, and no restraints yielded w$R2$ = 0.062 for all data and a conventional R_1 = 0.024 based on 2630 reflections with $I > 2\sigma(I)$. Red plates of $[(C_6H_{11}NC)_8Rh^I{}_2]Cl_2\cdot 0.5C_6H_6\cdot 2H_2O$, M_w = 1223.13, monoclinic, space group $P2_1/c$, a = 13.5495(4), b = 23.1451(7), c = 20.2848(6) Å, β = 105.449(3)°, V = 6131.6(3) Å^3 at 90(2) K, μ(Mo-Kα) = 0.672 mm^{-1}, Z = 4. Refinement of 14059 reflections, 650 parameters, and no restraints yielded w$R2$ = 0.068 for all data and a conventional R_1 = 0.026 based on 12657 reflections with $I > 2\sigma(I)$. Deep green blocks of $[(i\text{-PrNC})_{12}\text{-}Rh^I{}_3]Cl_3\cdot 4.5H_2O$, M_w = 1323.41, orthorhombic, space group $Pnnm$, a = 21.5193(6), b = 22.7979(6), c = 14.0456(4) Å, V = 6890.7(3) Å^3 at 180(2) K, μ(Mo-Kα) = 0.870 mm^{-1}, Z = 4. Refinement of 6591 reflections, 369 parameters, and 57 restraints yielded w$R2$ = 0.115 for all data and a conventional R_1 = 0.042 based on 5126 reflections with $I > 2\sigma(I)$. CCDC 285148–285151. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513700d

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