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High-Nuclearity Ruthenium Carbonyl Cluster Chemistry. Synthesis and X-ray Structure of $[Ru_2(\mu\text{-}H)(\mu\text{-}NC_5H_4)_2(CO)_4(NC_5H_5)_2][Ru_{10}(\mu\text{-}H)(\mu_6\text{-}C)(CO)_{24}]$

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Summary: Pyrolysis of $Ru_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}$ in chlorobenzene results in the formation of $[Ru_2(\mu\text{-}H)(\mu\text{-}NC_5H_4)_2(CO)_4(NC_5H_5)_2][Ru_{10}(\mu\text{-}H)(\mu_6\text{-}C)(CO)_{24}]$ in high yield; an X-ray structural study suggests that the hydrido ligand in the anion, previously believed to occupy an interstitial tetrahedral site, possibly bridges a metal–metal bond external to the cluster core.

The development of high-nuclearity ruthenium carbonyl cluster chemistry has lagged behind that of its heavier congener osmium, primarily due to the lack of facile syntheses. High-nuclearity hydrido clusters in particular have been little explored; the largest hydridoruthenium cluster anions, $[HRu_{10}C(CO)_{24}]^-$,[1] $[H_2Ru_{10}(CO)_{25}]^{2-}$,[2] and $[HRu_{11}(CO)_{27}]^{3-}$,[3] have been obtained in reported yields of 15%, 20%, and 15%, respectively. The carbido hydrido cluster $[HRu_{10}C(CO)_{24}]^-$ is one of at least six products from the residues obtained from pyrolyzing $Ru_3(CO)_{12}$ in mesitylene for 3–5 days.[1] We herein report the facile high-yield synthesis of $[Ru_{10}(\mu\text{-}H)(\mu_6\text{-}C)(CO)_{24}]^-$ as its $[Ru_2(\mu\text{-}H)(\mu\text{-}NC_5H_4)_2(CO)_4(NC_5H_5)_2]^+$ salt, from thermolysis of a readilly available triruthenium precursor.

Thus, a solution of $Ru_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}$[4] (238 mg, 0.359 mmol) in chlorobenzene (25 mL) was heated at reflux temperature under an atmosphere of dry nitrogen for 60–90 min, at which stage no starting material was observed by IR. The resulting black solution was filtered and reduced to dryness *in vacuo*. Recrystallization from dichloromethane/hexane gave green-black crystalline $[Ru_2(\mu\text{-}H)(\mu\text{-}NC_5H_4)_2(CO)_4(NC_5H_5)_2][Ru_{10}(\mu\text{-}H)(\mu_6\text{-}C)(CO)_{24}]$ (1; 137 mg, 66%) (calculated yield based on $Ru_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}$), which is stable in air as a solid for up to several days. The spectral data[5] are consistent with the formulation above; the structure was confirmed by an X-ray diffraction study.[6]

The X-ray structural determination (Figure 1) confirms the bimetallic cation and decametallic anion. The cation has two bridging pyridyl groups in a head-to-tail arrangement, a bridging hydride (located in the structural determination), two σ-bound pyridines, and four terminal carbonyls; as such, it is related to $Ru_2(\mu\text{-}NC_5H_4)_2(CO)_6$, obtained as a mixture of head-to-head and head-to-tail isomers from pyrolysis of $Ru_3(CO)_{12}$ with pyridine.[8] The

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(5) IR (CH_2Cl_2; $\nu(CO)$): 2052 s, 2009 s, 1997 m, sh cm^{-1}. ^1H NMR (acetone-d_6, 25 °C, 300 MHz): δ 8.61 (dt, 4H, $^3J_{H-H} = 5.0$ Hz, $^4J_{H-H} = 1.5$ Hz, H2,2′,6,6′), 8.54 (dq, 2H, $^3J_{H-H} = 5.0$ Hz, $^4J_{H-H} = 1.0$ Hz, H06,06′), 8.05 (tt, 2H, $^3J_{H-H} = 7.5$ Hz, $^4J_{H-H} = 1.5$ Hz, H4,4′), 7.73 (dt, 2H, $^3J_{H-H} = 7.5$ Hz, $^4J_{H-H} = 1.0$ Hz, H03,03′), 7.57 (m, 4H, $^3J_{H-H} = 5.0, 7.5$ Hz, $^5J_{H-H} = 1.5$ Hz, H3,3′,5,5′), 7.52 (m, 2H, $^3J_{H-H} = 7.5$ Hz, $^4J_{H-H} = 1.5$ Hz, H04,04′), 7.09 (m, 2H, $^3J_{H-H} = 5.0, 7.5$ Hz, $^4J_{H-H} = 1.5$ Hz, H05,05′), −10.74 (s, 1H, Ru_2–H), −13.55 (s, 1H, Ru_{10}–H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 25 °C, 75 MHz): δ 363.4 (μ_6-C), 190.3 ($Ru_{10}CO$, other signals for $Ru_{10}CO$ not observed), 176.3 (CO2,O2′), 155.3 (CO6,O6′), 154.9 (C2,6,2′,6′), 140.9, 140.0 (CO3,O3′, C4,4′), 136.0 (CO4,O4′), 127.1 (C3,3′,5,5′), 122.4 (CO5,O5′). Satisfactory analyses could not be obtained due to sample decomposition over a period of days.

(6) **Structure Determination.** A unique room-temperature diffractometer data set ($T \approx 295$ K; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; $2\theta/\theta$ scan mode, $2\theta_{max} = 50°$) was measured, yielding 11 442 independent reflections, 4882 of these with $I > 3\sigma(I)$ being considered "observed" and used in the large-block least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ for the "organic" hydrogen atoms were included constrained at estimated values. Conventional residuals R and R_w on $|F|$ at convergence were 0.048 and 0.029, statistical weights applied being derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$. Neutral atom complex scattering factors were employed, computation using the XTAL 3.2 program system[7] implemented by S. R. Hall. Pertinent results are given in Figure 1 and the supplementary material. **Crystal Data:** $[Ru_2H(NC_5H_4)_2(CO)_4(NC_5H_5)_2][HCRu_{10}(CO)_{24}]\cdot CH_2Cl_2 \equiv C_{49}H_{20}N_4O_{28}Ru_{12}\cdot CH_2Cl_2$, $M_r = 2410.5$; monoclinic, space group $P2_1/c$ (C^5_{2h}, No. 14), $a = 18.163(8)$ Å, $b = 15.934(9)$ Å, $c = 23.75(1)$ Å, $\beta = 103.62(4)°$, $V = 6679$ Å^3; $D_c(Z = 4) = 2.40$ g cm^{-3}; $F(000) = 4544$; $\mu(Mo) = 27.9$ cm^{-1}; specimen 0.08 × 0.12 × 0.18 mm; $A^*_{min,max} = 1.23, 1.50$. **Abnormal Features/Procedural Variations.** (a) Difference map artifacts are suggestive of the presence of chlorinated solvent, three substantial peaks being observed in the same lattice void. The history of the sample was suggestive of dichloromethane rather than chloroform of solvation; refinement of site occupancies suggested a totality of one solvent molecule, and it was modeled constrained as such with three chlorine residues (with populations refined subject to the total constraint) disposed about a smaller residue refined as a single carbon atom. (b) Despite the limited data, seemingly a consequence of small crystal size and solvent exhibiting disorder coupled with high apparent thermal motion, cation and anion components were generally well-behaved and well-defined. Cation "organic" hydrogen atoms were located in difference maps and constrained; the hydride bridging the two Ru atoms was clearly evident and refined in (x, y, z). In this context, it is therefore surprising that no residues representing substantial hydride fractions were evident about the anion; particular examination was made of the region between Ru(7) and Ru(8), where the carbonyl groups are somewhat more splayed than elsewhere, but nothing substantial was found. Crystallographic evidence for anionic hydride, either overt or implied, must therefore be regarded as circumstantial (see discussion of structure). (c) Assignment of the Ru-bound pyridyl C, N atoms of the cation was made on the basis of refinement behavior and associated geometries. As refined, U_{eq} values (see supplementary material) are comparable and are comparable with U_{eq} values for their parent Ru atoms; nevertheless, Ru–C,N distances are not greatly different—less so than in other examples of undisordered pyridyl-*C,N* groups bridging Ru_2 moieties. This, together with the C,N ellipsoids being of less agreeable anisotropy and disposition than those of neighboring atoms, suggests that the possibility of some disorder cannot be ruled out.

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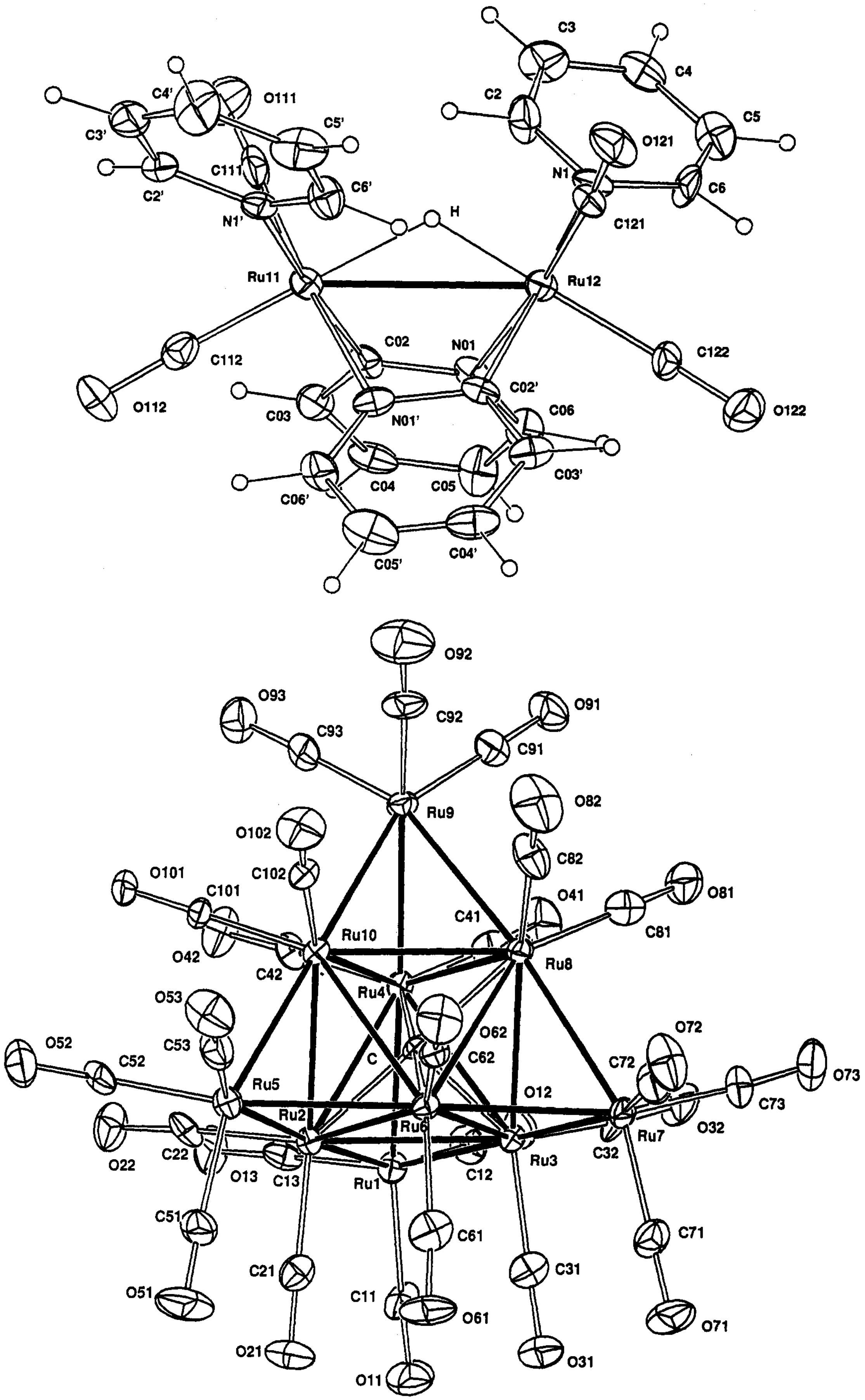

Figure 1. Projections of the cation (top) and anion (bottom), 20% thermal envelopes being shown for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å. Selected bond distances (Å) and angles (deg): (a) Ru(11)–Ru(12) = 2.963(2), Ru–CO(av) = 1.86, Ru–H(av) = 1.7; (b) Ru(7)–Ru(8) = 2.877(2), Ru(8)–Ru(9) = 2.823(2), Ru–Ru(octahedral core, av) = 2.86, other Ru–Ru(av) = 2.77, Ru–C(av) = 2.02, Ru–CO(av) = 1.86, Ru–Ru–CO = 79.4(6)–108.3(6).

anion has an interstitial carbide (shown to be derived from coordinated CO by ^{13}CO labeling of the precursor) and a hydrido ligand, possibly in an edge-bridging location. The position of the latter has been inferred from the structural data; thus, all Ru–Ru bonds external to the octahedral carbido cavity are in the range 2.748(2)–2.791(2) Å, except Ru(8)–Ru(9) (2.823(2) Å) and Ru(7)–Ru(8) (2.877(2) Å), and ∠CO–Ru(a)–Ru(b) + ∠Ru(a)–Ru(b)–CO sums for cisoid carbonyls are 187.7–197.1°, except ∠C(72)–Ru(7)–Ru(8) + ∠Ru(7)–Ru(8)–C(82) (211.6°) and ∠C(82)–Ru(8)–Ru(9) + ∠Ru(8)–Ru(9)–C(92) (184.2°). The hydrido ligand is therefore possibly located on Ru(7)–Ru(8) between C(72) and C(82), inducing a lengthening of the metal–metal bond, a "splaying back" of CO(72) and CO(82), and a concomitant "folding in" of CO(82) and CO(92); this "folding in" is probably responsible for the slight lengthening of Ru(8)–Ru(9).

Considering the change in nuclearity, the reaction is remarkably clean, with no evidence for other carbonyl-containing products. Mechanistic speculation as to the formation of 1 from $Ru_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}$ is not warranted at this stage; monitoring the reaction by IR and ^1H NMR failed to reveal evidence for any reaction intermediates.

The hydridodecametallic cluster anions have been suggested as model systems for the chemisorption of synthesis gas on the surface of bulk metals or colloidal particles,[9] due to the "close-packed" arrays of carbonyl ligands approximately perpendicular to the surface found in previous structural determinations; this is the first example from this system showing the marked displacement of carbonyl ligands normally found with edge-bridging hydrides in low-nuclearity clusters.

Ruthenium clusters with hydrido ligands in octahedral interstitial sites are well-known (e.g. $[Ru_6(\mu_6\text{-}H)(CO)_{18}]^-$,[10,11] $[Ru_8(\mu\text{-}H)(\mu_6\text{-}H)(CO)_{21}]^{2-}$ [12]). No structurally characterized example of a tetrahedral interstitial hydrido ligand has thus far been established. On the basis of spectroscopic data[13] and structural determinations of the $[AsPh_4]^+$ and $[PMePh_3]^+$ salts,[14] it was proposed some time ago that $[HOs_{10}C(CO)_{24}]^-$ contains a hydrido ligand in a tetrahedral site. However, a neutron diffraction study on the related cluster $[H_4Os_{10}(CO)_{24}]^{2-}$ revealed that the four hydrido ligands were external to the cluster core,[9] and recent spectroscopic studies have cast doubts on the interstitial location of the hydride in $[HOs_{10}C(CO)_{24}]^-$.[15] The present work casts further doubt on $[HM_{10}C(CO)_{24}]^-$ as candidates for clusters containing hydrido ligands in tetrahedral holes.

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Supplementary Material Available: Details of the structure determination (Table S1), fractional atomic coordinates (Table S2), hydrogen coordinates and thermal parameters (Table S3), anisotropic thermal parameters (Table S4), and bond distances and angles (Table S5) (21 pages). Ordering information is given on any current masthead page.

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