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Preparation and Characterization of 92-Electron Hexahydridohexaruthenium Carbonyl Cluster Complexes. Their Potential Significance in Homogeneous Catalytic Hydrogenation

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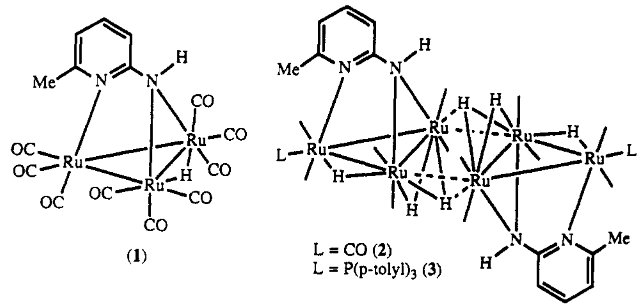
Summary: The 48-electron complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}ampy)(CO)_9]$ (1; ampy = 2-amino-6-methylpyridinate) reacts with molecular hydrogen (110 °C, 1 atm) to give the 92-electron hexanuclear hexahydrido derivative $[Ru_6(\mu\text{-}H)_6(\mu_3\text{-}\eta^2\text{-}ampy)_2(CO)_{14}]$ (2). This hexanuclear compound undergoes CO substitution instead of ligand addition when treated with P(p-tolyl)$_3$ to give the complex $[Ru_6(\mu\text{-}H)_6(\mu_3\text{-}\eta^2\text{-}ampy)_2\{P(p\text{-}tolyl)_3\}_2(CO)_{12}]$ (3), which has been characterized by X-ray diffraction methods. Compound 2 is an efficient catalyst precursor for the homogeneous hydrogenation of diphenylacetylene to cis-stilbene under mild conditions (50 °C, 1 atm).

In a previous paper,[2a] we reported that the carbonyl cluster complex $[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-ampy})(CO)_9]$[3] (1; ampy = 2-amino-6-methylpyridinate) is an efficient catalyst precursor for the homogeneous hydrogenation of alkynes to alkenes and of dienes to monoenes. This catalytic activity prompted us to study stoichiometric reactions that might be involved in the catalytic processes.

We now report that the reaction of complex 1 with hydrogen (110 °C, 1 atm) leads to the hexanuclear hexahydrido 92-electron derivative $[Ru_6(\mu\text{-H})_6(\mu_3\text{-}\eta^2\text{-ampy})_2(CO)_{14}]$[2b,4] (2; Chart 1), a compound which is remarkable for three reasons. (a) Its structure is unique, since it consists of two trinulear units connected to each other through two bridging hydride ligands, each interacting with at least three ruthenium atoms, and through two weak metal–metal bonds. (b) It regenerates complex 1 when exposed to a CO atmosphere; however, it undergoes CO substitution instead of ligand addition when treated with P(p-tolyl)$_3$ at room temperature to give $[Ru_6(\mu\text{-H})_6(\mu_3\text{-}\eta^2\text{-ampy})_2\{P(p\text{-tolyl})_3\}_2(CO)_{12}]$ (3).[4] (c) It is even more effective[5] than 1[2] as a catalyst precursor for the homogeneous hydrogenation of diphenylacetylene under very mild conditions.

Chart 1



The X-ray molecular structure of 3[6] (Figure 1) shows that it consists of two symmetry-related (inversion center) trinuclear fragments. The three Ru–Ru distances within each trinuclear unit are quite different (Ru(1)–Ru(2) = 2.724(2) Å, Ru(1)–Ru(3) = 2.991(2) Å, Ru(2)–Ru(3) = 2.799(2) Å), the shortest corresponding to the edge not bridged by hydride ligands. Although the presence of metal–metal bonds between both Ru_3 units cannot be completely ruled out, these interactions have to be weak, since the Ru(2)–Ru(3′), Ru(2)–Ru(2′), and Ru(3)–Ru(3′) distances (3.292(3), 4.266(3), and 4.376(5) Å, respectively) are much longer than what is normally expected for a Ru–Ru single bond;[7] therefore, each trinuclear unit can be considered as an unsaturated 46-electron fragment.[8]

NMR experiments (^{1}H, ^{13}C, ^{13}C{^{1}H}, ^{1}H NOE, and indirect ^{13}C–^{1}H correlations)[4] demonstrated that complex 2 is isostructural with complex 3. In particular, the

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[1] (a) Departamento de Química Organometálica. (b) Departamento de Química Física y Analítica.

[2] (a) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V. *J. Mol. Catal.* **1992**, *71*, L7. (b) In that work,[2a] compound 2 was formulated as $[Ru_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-ampy})(CO)_8]$.

[3] Andreu, P. L.; Cabeza, J. A.; Riera, V.; Jeannin, Y.; Miguel, D. *J. Chem. Soc., Dalton Trans.* **1990**, 2201.

[4] (a) Synthesis of complex 2: Hydrogen was bubbled through a toluene solution (50 mL) of complex 1 (100 mg, 0.150 mmol) at reflux temperature for 75 min. The solvent was removed under reduced pressure and the residue washed with a mixture of THF (2 mL) and hexane (20 mL) and then with pure hexane (2 × 10 mL) to give complex 2 as a red-brown solid (60 mg, 65%). Anal. Calcd (found) for $C_{26}H_{20}N_4O_{14}Ru_6$: C, 25.62 (25.38); H, 1.65 (1.77); N, 4.60 (4.79). Synthesis of complex 3: A THF solution (15 mL) of P(p-tolyl)$_3$ (15.3 mg, 0.050 mmol) and complex 2 (30 mg, 0.025 mmol) was stirred at room temperature for 3 h. The solution was evaporated to dryness under reduced pressure and the residue washed with hexane (2 × 6 mL) to give complex 3 as a red solid (23 mg, 53%). Anal. Calcd (found) for $C_{66}H_{62}N_4O_{12}P_2Ru_6$: C, 44.75 (44.84); H, 3.53 (3.99); N, 3.16 (3.48). The ^{1}H and ^{13}C NMR assignments given below (labeling as in Figure 1) are based on ^{1}H NOE and ^{13}C–^{1}H correlation experiments. (b) Selected spectroscopic data for 2: IR (THF) 2063 (s), 2039 (s), 2003 (vs), 1981 (sh), 1941 (w) cm^{-1}; ^{1}H NMR (THF-d_8) δ 7.46 (t, 7.8 Hz, H^{10}), 6.84 (d, 7.8 Hz, H^{11}), 6.80 (d, 7.8 Hz, H^9), 6.17 (s, H^4), 1.62 (s, H^{81-83}), −10.84 (m, H^2), −13.53 (m, H^1), −16.74 (m, H^3); ^{13}C ^{1}H NMR (THF-d_8, ^{13}CO-enriched sample) δ(CO) 205.1 (C^6), 200.4 (C^1 or C^3), 200.3 (C^1 or C^3), 200.1 (C^2), 199.1 (C^4 or C^5), 193.8 (C^4 or C^5), 188.6 (C^P) ppm. (c) Selected spectroscopic data for 3: IR (THF) 2027 (s), 2014 (vs), 1980 (m), 1973 (m), 1925 (w) cm^{-1}; ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 26.0 (s) ppm; ^{1}H NMR (CD_2Cl_2) δ 7.8–6.8 (m), 6.72 (d, 7.5 Hz, H^{11}), 6.24 (d, 7.5 Hz, H^9), 5.87 (s, H^4), 2.34, (s, $H^{171-173,241-243,311-313}$), 1.55 (s, H^{81-83}), −10.82 (s, br, H^2), −13.16 (d, 19.3 Hz, H^1), −16.21 (s, br, H^3); ^{13}C{^{1}H} NMR (THF-d_8, ^{13}CO-enriched sample) δ(CO) 207.0 (C^6), 206.5 (C^2), 205.2 (C^1), 201.1 (C^3), 200.9 (C^4), 195.8 (C^5) ppm.

[5] Catalytic conditions: reaction time 105 min, 1,2-dichloroethane, 50 °C, 1 atm of H_2, [2] = 8.2×10^{-4} M, [Ph_2C_2] = 0.112 M. Results: 83% conversion (TON = 1.1 min^{-1}) into *cis*-stilbene (78%) and *trans*-stilbene (22%). Further details are given in the supplementary material.

[6] Crystal data for $3\cdot 2CH_2Cl_2$: monoclinic, space group $P2_1/c$, a = 19.39(2) Å, b = 11.964(8) Å, c = 18.19(1) Å, β = 116.42(6)°, V = 3778(5) Å^3, Z = 2, μ(Mo K$_\alpha$) = 13.9 cm^{-1}, R = 0.049, R_w = 0.046, T = 200 K.

[7] The average Ru–Ru distance in $[Ru_3(CO)_{12}]$ is 2.855 Å: Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

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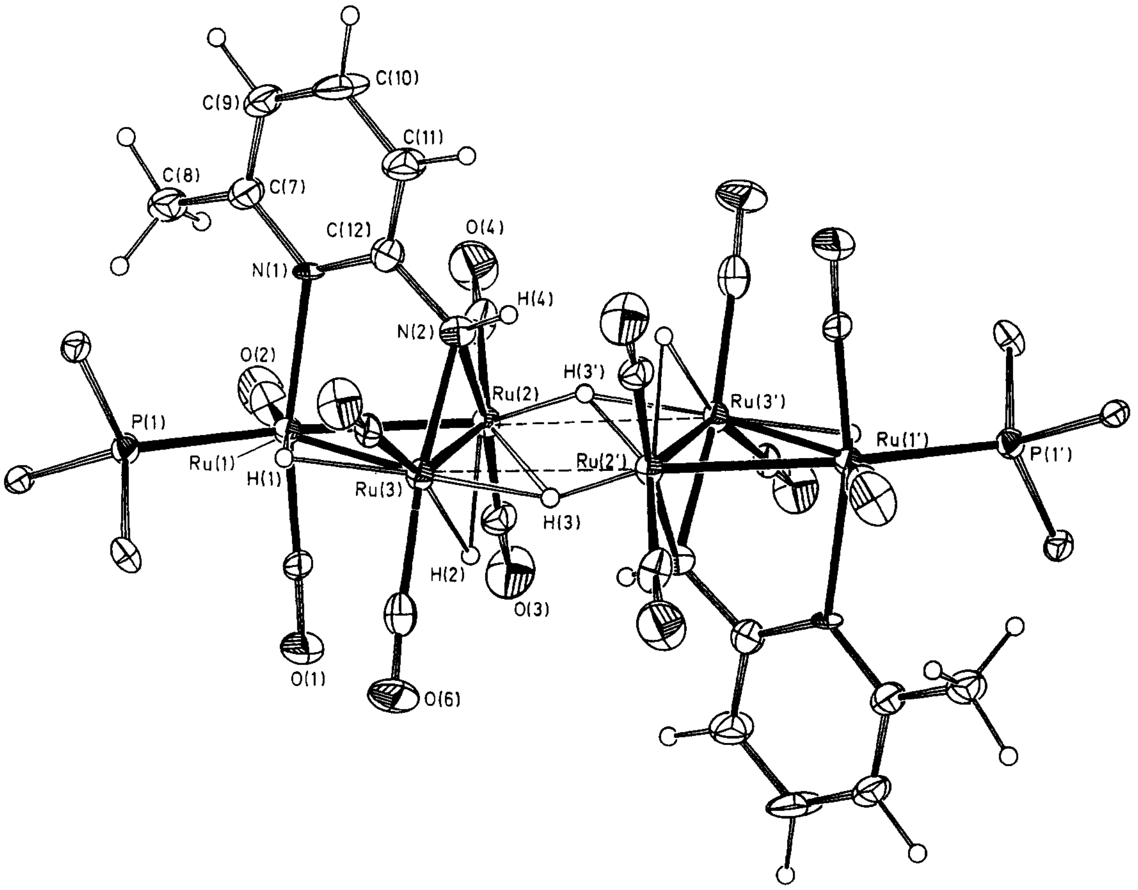

Figure 1. X-ray molecular structure of 3. The primed atoms are related to the unprimed ones by an inversion center. For clarity, only the C_{ipso} atoms of the *p*-tolyl groups are shown.

hexanuclear structure of 2 was clearly established by NOE difference experiments, since selective presaturation of the amidic H(4) proton affords positive NOE enhancements over the hydrides H(2) and H(3) (the unprimed atoms cannot be distinguished from the symmetry-related primed ones by NMR experiments; see numbering in Figure 1), whereas in the hypothesis that 3 was a trinuclear compound, presaturation of H(4) should result in a negative enhancement (because of transmission through three nuclei) or no enhancement at all over H(2) because H(3) would lie between H(4) and H(2).[9] Comparable conclusions were drawn from a NOESY spectrum of complex 3. Furthermore, low-temperature ^1H NMR experiments confirmed the absence of an equilibrium between hexanuclear and trinuclear species in solution.

As occurs with $[Os_3(CO)_{12}]$,[10] the hydrogenation of 1 implies the oxidative addition of hydrogen to a trinuclear carbonyl cluster complex and the elimination of two CO ligands to give an unsaturated 46-electron species (which stabilizes via dimerization to give 2, while in the case of the osmium complex the unsaturated derivative is stable: $[Os_3(\mu\text{-}H)_2(CO)_{10}]$). This type of reaction, which is novel in ruthenium chemistry, may have significance in homogeneous catalytic hydrogenation processes involving carbonyl cluster complexes. It is also interesting to note that 2 and 3, which essentially consist of two 46-electron fragments linked by hydride ligands, represent a unique type of compound in the chemistry of the transition metals and that unsaturated 46-electron cluster complexes of the iron triad are very rare; in fact, to date, only a few examples of such compounds have been isolated, namely $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$,[11] $[Os_3(\mu\text{-}H)_2(CO)_{10}]$,[10] and other osmium derivatives,[12a] and all present a rich derivative chemistry[10-13] and interesting catalytic activity.[14,15]

The reactivity of complexes 2 and 3 and their activity in other catalytic hydrogenation reactions are currently under investigation.

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(8) (a) The positions of the bridging hydrides of 3 were determined by difference Fourier syntheses. These positions could be well refined for H(1) and H(2), but the position of H(3) was quite sensitive to small changes in the refinement conditions; therefore, the coordinates given for H(3) may not be very accurate.[8b] Nevertheless, the obtained positions for the hydrides have to be close to the real ones because they agree with the NMR data. (b) Hardcastle, K. I.; Irving, M. *J. Cluster Sci.* **1993**, *4*, 77.

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(14) $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$ as catalyst precursor: Castiglioni, M.; Giordano, R.; Sappa, E. *J. Organomet. Chem.* **1989**, *362*, 399.

(15) $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ as catalyst precursor: Gladfelter, W. L.; Roesselet, K. J. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; Chapter 7, p 329, and references therein.

Supplementary Material Available: Text giving experimental details for the synthesis and characterization of **2** and **3** and for the catalytic hydrogenation of Ph_2C_2, crystallographic data for **3**·$2CH_2Cl_2$, including tables of positional parameters, bond distances and angles, and anisotropic thermal parameters, and figures showing the catalytic activity of **2** in the hydrogenation of Ph_2C_2, ^1H NOE difference NMR spectra for **2**, the ^1H NOESY spectrum for **3**, and the complete numbering scheme of **3** (18 pages). Ordering information is given on any current masthead page.

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