ORGANOMETALLICS

Syntheses of the highly charged cluster anions [Ru4(CO)11]6-, [Ru6(CO)17]4-, and [Ru6(CO)16]6-

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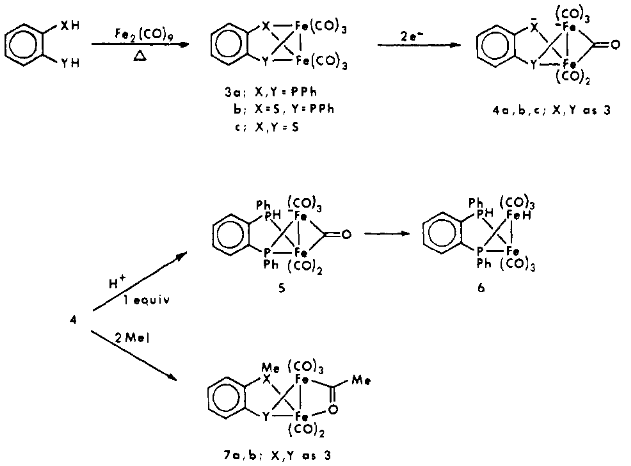
Scheme I



Not unexpectedly, the reduction of **3b** resulted in cleavage of the Fe–S bond in preference to the Fe–P bond to yield **4b**.[12] Subsequent methylation afforded the orange μ–acyl complex **7b**.[13-15]

We are continuing to examine the chemistry of these new complexes and, more generally, the chemical importance of linking phosphido bridges in polynuclear complexes.

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Registry No. 3a, 57139-08-9; **3b**, 86480-53-7; **3c**, 84577-31-1; **4a**, 86480-54-8; **4b**, 86480-55-9; **4c**, 86480-56-0; **5**, 86480-57-1; **6**, 86480-58-2; **7a**, 86480-59-3; **7b**, 86480-60-6; Fe, 7439-89-6; $Fe_2(CO)_9$, 15321-51-4.

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(11) The orange and magenta complexes **3b** and **3c** were prepared from the reactions of excess nonacarbonyldiiron with 1-thio-2-(phenylphosphino)benzene (73%) and dithiocatechol (69%), respectively. **3b**: mp 140–141 °C; MS, *m/e* 495.8570 (M^+) (calcd 495.8555). **3c**: mp 114–116 °C; MS, *m/e* 419.8156 (M^+) (calcd 419.8147). Their structures were established by X-ray crystallography (Hassett, K. L.; Davis, R. E.; unpublished results). We thank C. N. Clubb for a sample of 1-thio-2-(phenylphosphino)benzene, the preparation of which will be reported elsewhere.

(12) **4b**: IR (THF) 1962 (s), 1915 (vs), 1875 (s), 1700 (sh), 1665 (w) cm^{-1}; ^{31}P NMR (THF) δ 143.5 (s).

(13) **7b**: mp 127–129 °C; IR (C_2Cl_4) 2043 (s), 1988 (vs), 1973 (s), 1965 (s), 1930 (s), 1480 (w), 1435 (vw) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.0–7.5 (m, 9 H), 2.73 (s, 3 H), 1.93 (s, 3 H); ^{31}P NMR (THF) 190.1 (s); MS, *m/e* 525.9016 (M^+) (Calcd 525.9025).

(14) The reduction of **3c** in THF yielded a solution of **4c**, based on its IR spectrum: 1978 (s), 1922 (s), 1881 (s), 1695 (sh), 1660 (w) cm^{-1}. Exposure of the solution to air gave a solution with an IR spectrum identical with that of **3c**. Treatment of the dianion with methyl iodide yielded a species with an IR spectrum similar to that observed for **7a** and **7b**: (THF) 2045 (s), 1995 (vs), 1970 (s), 1932 (w) cm^{-1}.

(15) While this manuscript was in preparation, we were informed (personal communication) that Wojcicki and his co-workers have observed the generation of a monoanion analogous to **5**, but emanating from the unlinked system **1** by the use of $HBEt_3^-$ as the reducing agent: Yu, Y.-F.; Gallucci, J.; Wojcicki, A. submitted for publication.

Syntheses of the Highly Charged Cluster Anions $[Ru_4(CO)_{11}]^{6-}$, $[Ru_6(CO)_{17}]^{4-}$, and $[Ru_6(CO)_{16}]^{6-}$

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Summary: Syntheses of the highly charged cluster anions $[Ru_4(CO)_{11}]^{6-}$, $[Ru_6(CO)_{17}]^{4-}$, and $[Ru_6(CO)_{16}]^{6-}$ are described. The anion $[Ru_4(CO)_{11}]^{6-}$ was prepared by the reduction of $Ru_3(CO)_{12}$ and also $[Ru_4(CO)_{12}]^{4-}$ using stoichiometric amounts of $Na[(C_6H_5)_2CO]$. The hexanuclear anions $[Ru_6(CO)_{17}]^{4-}$ and $[Ru_6(CO)_{16}]^{6-}$ were prepared by reducing $[Ru_6(CO)_{18}]^{2-}$ with 2 and 4 equiv of $Na[(C_6H_5)_2CO]$, respectively. Electrical conductivities of tetraphenylphosphonium salts of these anions are consistent with the assigned charges.

Transition-metal carbonyl cluster anions with a charge of 4– or higher are rare.[1] Prior to this report $[Ru_4(CO)_{12}]^{4-}$ was the only ruthenium carbonyl cluster anion cited with a charge as large as 4–. It was prepared[2] through the reduction of $Ru_3(CO)_{12}$. The possibility of obtaining additional highly charged ruthenium carbonyl cluster anions that could be isolated as salts has been of interest to us. We present here the preparation of the new highly charged anions $[Ru_4(CO)_{11}]^{6-}$, $[Ru_6(CO)_{17}]^{4-}$, and $[Ru_6(CO)_{16}]^{6-}$.

The title anions were prepared according to the following reduction reactions ((1)–(3)) in which carefully measured stoichiometric ratios of reactants were employed. These reactions produced CO (analyzed mass spectrometrically) in yields of 98–100% of theory.

$$2Ru_3(CO)_{12} + 9Na[(C_6H_5)_2CO] \xrightarrow[60\ ^\circ C]{THF} 1.5Na_6[Ru_4(CO)_{11}] + 7.5CO + 9(C_6H_5)_2CO \quad (1)$$

$$Na_2[Ru_6(CO)_{18}] + 2Na[(C_6H_5)_2CO] \xrightarrow[60\ ^\circ C]{THF} Na_4[Ru_6(CO)_{17}] + CO + 2(C_6H_5)_2CO \quad (2)$$

$$Na_2[Ru_6(CO)_{18}] + 4Na[(C_6H_5)_2CO] \xrightarrow[60\ ^\circ C]{THF} Na_6[Ru_6(CO)_{16}] + 2CO + 4(C_6H_5)_2CO \quad (3)$$

The anion $[Ru_4(CO)_{11}]^{6-}$ was obtained according to reaction 1. It was also produced by reducing $[Ru_4(CO)_{12}]^{4-}$ with 2 equiv of $Na[(C_6H_5)_2CO]$. When $[Ru_6(CO)_{18}]^{2-}$ was reduced with 2 equiv of $Na[(C_6H_5)_2CO]$ (reaction 2) and 4 equiv of $Na[(C_6H_5)_2CO]$ (reaction 3), the anions $[Ru_6(CO)_{17}]^{4-}$ and $[Ru_6(CO)_{16}]^{6-}$ were prepared. Reduction of $[Ru_6(CO)_{17}]^{4-}$ with 2 equiv of $Na[(C_6H_5)_2CO]$ also gives $[Ru_6(CO)_{16}]^{6-}$.

The anions $[Ru_4(CO)_{11}]^{6-}$ and $[Ru_6(CO)_{16}]^{6-}$ appear to be the limiting anions that can be obtained under the conditions described here. When excess reducing agent was employed under the conditions cited above, no new species were obtained. More vigorous conditions might produce carbide systems.[3]

The new anions were isolated as the tetraphenylphosphonium salts $[P(C_6H_5)_4]_6[Ru_4(CO)_{11}]$, $[P(C_6H_5)_4]_4[Ru_6(CO)_{17}]$, and $[P(C_6H_5)_4]_6[Ru_6(CO)_{16}]$. Although highly air sensitive,[4] these salts are stable at room temperature under dry N_2. Conductivity measurements of these salts in CH_3CN at room temperature were performed in a controlled atmosphere box. Figure 1 shows conductivities as a function of (molarity)$^{1/2}$. The limiting molar conductivities Λ_0 = 764, 787, and 514 cm^2 Ω^{-1} mol^{-1} for $[P(C_6H_5)_4]_6[Ru_4(CO)_{11}]$, $[P(C_6H_5)_4]_6[Ru_6(CO)_{16}]$, and [P-

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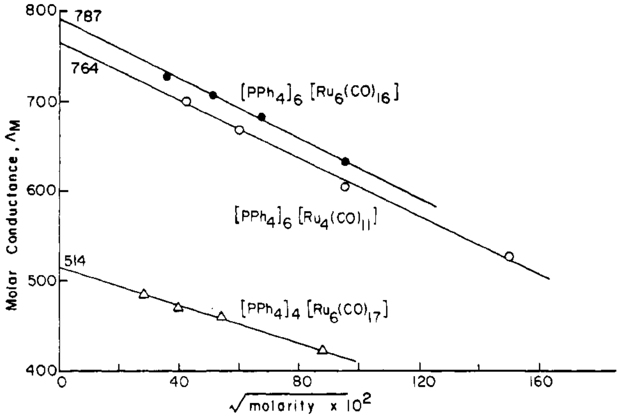

Figure 1. Molar conductivities in acetonitrile.

$(C_6H_5)_4]_4[Ru_6(CO)_{17}]$ are in accord with values for 6:1 and 4:1 electrolytes.[5]

In a typical preparation of the sodium salt of $[Ru_4(CO)_{11}]^{6-}$, a 0.532-mmol quantity (0.340 g) of $Ru_3(CO)_{12}$ was allowed to react with 2.402 mmol (0.495 g) of $Na[(C_6H_5)_2CO]$ in THF at 60 °C for 4 days. During this time 1.86 mmol of CO was produced (98% of theory based on reaction 1). The sodium salt that was isolated was heavily solvated with THF (ca. 6:1 THF/$Na_6[Ru_4(CCO)_{11}]$). It was extremely air sensitive, inflaming in air when in contact with tissue paper. From a metathesis reaction of $[P(C_6H_5)_4]Br$ in CH_3CN this salt was converted to $[P(C_6H_5)_4]_6[Ru_4(CO)_{11}]$ in 76% yield (based on initial amount of $Ru_3(CO)_{12}$). Anal. Calcd for $C_{155}H_{120}O_{11}P_6Ru_4$: C, 67.73; H, 4.60; P, 6.76; Ru, 14.71. Found: C, 66.36; H, 4.65; P, 6.47; Ru, 14.63.

Procedures for preparing the sodium and tetraphenylphosphonium salts of $[Ru_6(CO)_{17}]^{4-}$ and $[Ru_6(CO)_{16}]^{6-}$ were generally similar to those described above. The only significant difference involved choice of molar ratio of reactants consistant with the desired product (reactions 2 and 3). The salts $[P(C_6H_5)_4]_4[Ru_6(CO)_{17}]$ and $[P(C_6H_5)_4]_6[Ru_6(CO)_{16}]$ were isolated in 82% and 78% yields (based on initial amount of $Na_2[Ru_6(CO)_{18}]$. Anal. Calcd for $C_{113}H_{80}O_{17}P_4Ru_6$: C, 55.62; H, 3.30; P, 5.08; Ru, 24.85. Found: C, 55.49; H, 3.64; P, 4.98; Ru, 24.39. Anal. Calcd for $C_{160}H_{120}O_{16}P_6Ru_6$: C, 62.17; H, 3.91; P, 6.01; Ru, 19.62. Found: C, 61.86; H, 4.21% P, 6.03, Ru, 19.75.

Terminal and bridging carbonyl groups in all of the tetraphenylphosphonium salts are indicated by infrared spectra (in CH_3CN) in the carbonyl stretching region: $[P(C_6H_5)_4]_6[Ru_4(CO)_{11}]$, 1940 (s, sh), 1910 (s, br), 1710 (m, br) cm^{-1}; $[P(C_6H_5)_4]_4[Ru_6(CO)_{17}]$, 1970 (s), 1955 (m, sh), 1750 (w), 1660 (vw), 1590 (vw) cm^{-1}; $[P(C_6H_5)_4]_6[Ru_6(CO)_{16}]$, 1955 (w, sh), 1903 (s), 1830 (w, sh), 1720 (w, br) cm^{-1}.

Carbon-13 NMR spectra of a 50% ^{13}C-enriched sample of $Na_6[Ru_4(CO)_{11}]$ in THF-d_8 were recorded at 25 and −90 °C. A slow-exchange limit was not obtained. At room temperature a single sharp resonance was observed at 234 ppm. When this sample was cooled, three resonances at 228, 217, and 211 ppm were observed in the terminal CO region and peaks due to bridging carbonyls[6] in the region 279–295 ppm were beginning to rise from the base line. For $Na_4[Ru_6(CO)_{17}]$ ^{13}C NMR spectra were recorded at 25 and −50 °C. Low-temperature studies were limited due to precipitation of the salt. At room temperature a single resonance was observed at 228.7 ppm, indicating the complete equivalence of all carbonyl groups. When the sample was cooled to −50 °C, three resonances of 228.7, 218.6, and 212.0 ppm and a signal just emerging from the base line at 279 ppm were observed. Carbon-13 NMR spectra of $[PPh_4]_6[Ru_6(CO)_{16}]$ in CH_3CN exhibited one signal at 228.6 ppm at room temperature.

The sodium salts of the anions $[Ru_4(CO)_{11}]^{6-}$, $[Ru_6(CO)_{17}]^{4-}$, and $[Ru_6(CO)_{16}]^{6-}$ were protonated by using stoichiometric amounts of HCl in THF at −78 °C. Sodium chloride precipitated from the protonated solutions. At room temperature these solutions decomposed to give CO, H_2, and a mixture of nonvolatile products that are undergoing further study.

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Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Na_2[Ru_6(CO)_{18}]$, 85781-89-1; $Na[(C_6H_5)_2CO]$, 3463-17-0.

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Organolanthanide and Organoyttrium Hydride Chemistry. 4. Reaction of Isocyanides with $[(C_5H_4R)_2YH(THF)]_2$ To Form a Structurally Characterized *N*-Alkylformimidoyl Complex[1]

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Summary: The yttrium hydrides $[(C_5H_4R)_2YH(THF)]_2$ react with *tert*-butyl isocyanide to form $\{(C_5H_4R)_2Y[HC{=}NC(CH_3)_3]\}_2$, in which both C and N formimidoyl atoms coordinate to the yttrium.

The reaction of organometallic alkyls and hydrides with isocyanides has acquired significant interest in recent years due to the formal electronic analogy of isocyanides and carbon monoxide.[3-9] Reactivity ranging from simple ad-

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(1) Presented in part at the "184th National Meeting of the American Chemical Society", Kansas City, MO, Sept 1982; American Chemical Society: Washington DC, 1982; INOR 213.

(2) (a) Camille and Henry Dreyfus Teacher-Scholar. Alfred P. Sloan Research Fellow. To whom correspondence should be addressed at the University of California. (b) University of Chicago. (c) University of Alabama.

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