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Reactivity of PPh_3 toward $Ru_2Cl(\mu\text{-}O_2CAr)_4$: Isolation of Asymmetric, Trapped Mixed-Valence Diruthenium(III,II) Compounds with an $\{Ru_2(\mu\text{-}OH_2)(\mu\text{-}O_2CAr)_2^{3+}\}$ Core (Ar = Ph, C_6H_4-*p*-OMe)

The reaction between $Ru_2Cl(\mu\text{-}O_2CMe)_4$ and PPh_3 is known[1] to form the (μ-oxo)diruthenium(III) compound $Ru_2O(O_2CMe)_4(PPh_3)_2$. On reinvestigation[2] of this reaction using arenecarboxylato compounds, we have discovered an unusual reorganization of the $\{Ru_2(\mu\text{-}O_2CAr)_4^{+}\}$ moiety to an $\{Ru_2(\mu\text{-}OH_2)(\mu\text{-}O_2CAr)_2^{3+}\}$ core leading to the formation of an asymmetric, trapped mixed-valence diruthenium(III,II) compound, $Ru_2(OH_2)Cl(MeCN)(O_2CAr)_4(PPh_3)_2$ (**1**, Ar = C_6H_4-*p*-OMe; **2**, Ar = Ph), which is believed to be an intermediate species in the formation of the μ-oxo compound. The isolation of **1** and **2** with cores analogous to the diiron(III,II) active center in the hemerythrin class of biomolecules[3-5] is an important development in the chemistry of $M_2(\mu\text{-}O_2CR)_4^{n+}$ compounds containing M–M multiple bonds.[6-8] A similar reaction of PPh_3 with $Ru_2Cl(ArCONH)_4$ is known[7] to form a diruthenium(III) compound with a different core structure. Orthometalation of PPh_3 acting as a three-atom-bridging ligand is reported[8] for Rh(II) and Os(III) compounds. Herein we report the preliminary results on the synthesis, structure, and reactivity of **1**, which is characterized by X-ray studies and has properties similar to those of **2**.

The compounds were prepared by reacting $Ru_2Cl(\mu\text{-}O_2CAr)_4$[9] and PPh_3 in a 1:2 molar ratio in an $MeCN\text{-}H_2O$ mixture at 5 °C and were isolated[10] in ca. 30% yield as paramagnetic yellow solids displaying EPR spectra as shown in Figure 1. Compound **2** exhibits a rhombic spectrum in the polycrystalline state at 25 °C with g_1, g_2, and g_3 values of 3.128, 2.644, and 1.593, respectively. The electronic spectra of **1** in $CHCl_3$ display a band at 960 nm (10417 cm^{-1}) with a band width at half-height ($\Delta\bar{\nu}_{1/2}$) of 4820 cm^{-1}, which compares well with the predicted[11] value of

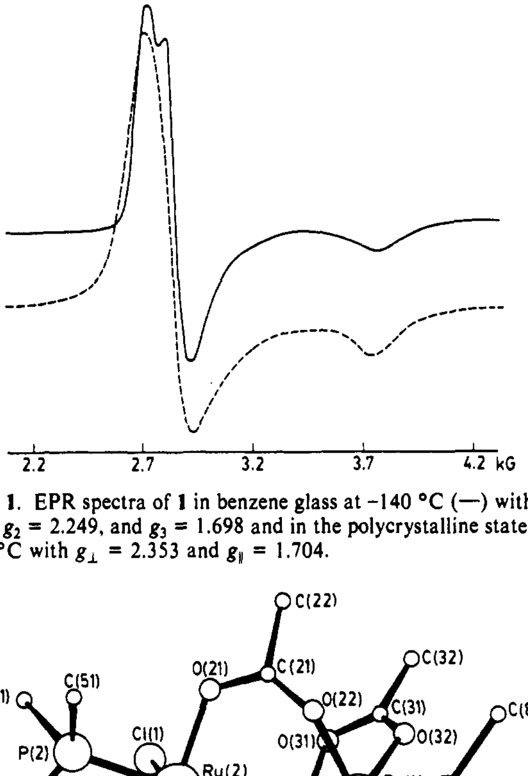

Figure 1. EPR spectra of **1** in benzene glass at −140 °C (—) with g_1 = 2.353, g_2 = 2.249, and g_3 = 1.698 and in the polycrystalline state (---) at 25 °C with $g_\perp$ = 2.353 and $g_\parallel$ = 1.704.

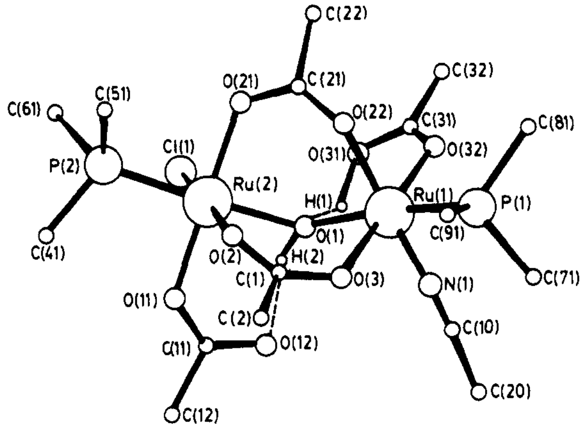

Figure 2. Perspective view of **1** along with atom-labeling scheme. Aryl groups are removed for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)–Ru(2), 3.605 (2); Ru(1)–O(1), 2.143 (12); Ru(2)–O(1), 2.107 (10); O(1)–H(1), 1.360 (13); O(1)–H(2), 1.077 (13); O(31)–H(1), 1.280 (19); O(12)–H(2), 1.740 (17); O(1)–O(12), 2.509 (22); O(1)–O(31), 2.504 (22); Ru(1)–N(1), 1.907 (18); Ru(1)–O(1)–Ru(2), 116.0 (6); H(1)–O(1)–H(2), 83.0 (9); O(1)–H(1)–O(31), 143.1 (9); O(1)–H(2)–O(12), 124.2 (9); Ru(1)–N(1)–C(10), 176.0 (16); O(1)–Ru(1)–P(1), 173.2 (4); O(1)–Ru(2)–P(2), 177.4 (5).

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(10) Compound **1**: Anal. Calcd for $C_{70}H_{63}NO_{13}P_2ClRu_2$: C, 58.91; H, 4.42; N, 0.98. Found: C, 58.14; H, 4.41; N, 0.77. Compound **2**: Anal. Calcd for $C_{66}H_{55}NO_9P_2ClRu_2$: C, 60.65; H, 4.21; N, 1.07. Found: C, 59.28; H, 4.22; N, 1.64.

(11) The calculation is done by using the relation $\Delta\bar{\nu}_{1/2} = [2310\bar{\nu}_{max}]^{1/2}$ cm^{-1}.[12a] The IT transition in **2** is observed at 880 nm in $CHCl_3$.

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4905 cm^{-1} for an intervalence charge-transfer (IT) transition.[12] Cyclic voltammetry of **1** in CH_2Cl_2–TBAP at 5 °C showed two oxidations and one reduction processes that are believed to be metal centered with the following $E_{1/2}$, V vs SCE (ΔE_p, mV) values: +0.615 (130), +0.230 (120), and −0.435 (150), respectively, at 20 mV s^{-1}. A peak at δ 16.98 in the ^1H NMR spectra of **1** in $CDCl_3$ is assignable to a μ-OH_2 group.

The X-ray structure of **1** is shown in Figure 2.[13] The molecule consists of a diruthenium(III,II) unit held by an aqua bridge and two bridging carboxylato ligands forming an $\{Ru_2(\mu\text{-}OH_2)(\mu\text{-}O_2CAr)_2{}^{3+}\}$ core. In this asymmetric molecule the metal centers are clearly distinguishable. The oxidation states of Ru(1) and Ru(2) are +2 and +3, respectively, since the Ru(1)–O(1) distance of 2.143 (12) Å is considerably longer than the Ru(2)–O(1) bond length of 2.107 (10) Å. Compound **1** thus exemplifies a trapped mixed-valence system.

The formal identification of a μ-OH_2 bridge in **1** is based on the location of two hydrogen atoms. The presence of strong hydrogen bonds is also inferred from the short O(1)···O(12) and O(1)···O(31) distances.[14] The considerably different O(1)–H(1) and O(1)–H(2) bond lengths could be due to the thermally unstable nature of **1**.

The unusual structural feature in **1** is the presence of three different types of ligands on the facial sites of each ruthenium. In the formation of **1**, the polymeric network of $[Ru_2Cl(\mu\text{-}O_2CAr)_4]_x$ is cleaved into discrete dimeric units along with a segregation of the oxidation states to $Ru^{III}Ru^{II}$ from the $Ru_2{}^{5+}$ core in the $\sigma^2\ \pi^4\ \delta^2\ (\delta^*\ \pi^*)^3$ ground electronic configuration of the starting compound. The Ru(1)–Ru(2) distance of 3.605 (2) Å in **1** is quite long for any direct Ru–Ru bond formation.

Compound **1** is unstable in the solution phase. In $CHCl_3$, it slowly forms a purple compound, $[\{Ru(PPh_3)(O_2CAr)\}_2(\mu\text{-}O)(\mu\text{-}O_2CAr)_2]$ (**3**), while in MeCN it converts to a blue species, $[\{Ru(PPh_3)(MeCN)_2\}_2(\mu\text{-}O)(\mu\text{-}O_2CAr)_2](ClO_4)_2$ (**4**), isolated as a perchlorate salt. Molecular structures of **3** and **4**, determined by X-ray studies,[15] show the presence of an $\{Ru_2(\mu\text{-}O)(\mu\text{-}O_2CAr)_2{}^{2+}\}$ met-analogue[4] core in these diamagnetic diruthenium(III) complexes. The facile formations of **3** and **4** are believed to be redox controlled, associated with ligand substitution.

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Supplementary Material Available: Tables I–IV, listing atomic coordinates, bond lengths, bond angles, and thermal parameters (13 pages); Table V, listing observed and calculated structure factors for **1** (23 pages). Ordering information is given on any current masthead page.

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(13) X-ray analysis of **1**: Triclinic, $P\bar{1}$, a = 13.538 (5) Å, b = 15.650 (4) Å, c = 18.287 (7) Å, α = 101.39 (3)°, β = 105.99 (4)°, γ = 97.94 (3)°, V = 3574 $Å^3$, Z = 2, d(calcd) = 1.32 g cm^{-3}, d(obsd) = 1.34 g cm^{-3}, μ(Mo Kα) = 4.55 cm^{-1}, $F(000)$ = 1446. A total number of 12 395 unique reflections were collected in the $4° \leqslant 2\theta \leqslant 50°$ range. R = 0.085 (unit weight) with 4092 reflections having $F_o > 10\sigma(F_o)$. Number of parameters = 474. Overall scale factor = 1.55. Largest shift/esd = 0.066. Highest peak in the final difference Fourier map = 1.12 e $Å^{-3}$ at 1.18 Å from Ru(2). One of the arene groups of the bridging carboxylato ligands was found to be disordered, and these atoms were refined with a site occupancy of 0.5. The higher R factor is due to the unstable nature of the crystal (decay ca. 40%) during data collection, and the molecule is found to be disordered.

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(15) Structural data on **3** with Ar = C_6H_4-*p*-OMe: Ru···Ru, Ru–(μ-O), and Ru–(μ-O)–Ru are 3.199 (3) Å, 1.860 (4) Å, and 118.7 (2)°, respectively. R = 0.065. Data for **4** with Ar = Ph: Ru···Ru, Ru–(μ-O), and Ru–(μ-O)–Ru are 3.240 (3) Å, 1.873 (4) Å, and 119.7 (2)°, respectively. R = 0.079. A detailed report on **3** and **4** will be made elsewhere.

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Polyoxoanions as Soluble Metal Oxide Analogues. 5.[1] Synthesis and Characterization of Polyoxoanion-Supported, Atomically Dispersed Iridium(I), $(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}{}^{8-}$

Polyoxoanions[1,2] are soluble oxides that resemble discrete fragments of solid metal oxides.[2c] As such, they are of considerable interest as catalyst support[3,4] materials, for both fundamental and practical reasons. However, a prototype catalyst precursor that leads to a polyoxoanion-*supported*[3] catalyst has not been previously described,[5] despite numerous reports over the last nine years of polyoxoanion-supported organometallics.[1,6] Herein we report the synthesis and characterization of $(Bu_4N)_5Na_3[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]$ (**1**) (Figure 3), which serves as an excellent precursor to an active and long-lived hydrogenation catalyst.[4] We also report key considerations and decision points that led to the successful combination of polyoxoanion (the second generation system,[1d] $P_2W_{15}Nb_3O_{62}{}^{9-}$), metal (Ir), coordinated ligand (1,5-COD), and counterions $[(Bu_4N)_5Na_3]$ in **1**, the *best* catalyst precursor from a series that we have prepared and examined.[7,8]

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(5) (a) While reports have appeared[5b–e] of catalysis by mixtures containing certain types of polyoxoanions and organotransition-metal complexes, in each case the active catalyst, although quite interesting, is not a tightly supported transition-metal–polyoxoanion complex, either by design or due to the use of polyoxoanions with negligible or insufficient[5c] surface-oxygen charge density. (b) Urabe, K.; Tanaka, Y.; Izumi, Y. *Chem. Lett.* **1985**, 1595. (c) Che, T. M. U.S. Patent 4,590,298 assigned to Celanese Corp., May 20, 1986. (d) Siedle, A. R.; Markell, C. G.; Lyon, P. A.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1987**, *26*, 219. (e) Siedle, A. R.; Newmark, R. A.; Gleason, W. B.; Skarjune, R. P.; Hodgson, K. O.; Roe, A. L.; Day, V. W. *Solid State Ionics* **1988**, *26*, 109.

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