CHEMISTRY LETTERS, pp. 2041-2044, 1989.

Synthesis and Structural Characterization of a Polyoxoanion Supported 1,5-Cyclooctadieneiridium(I) Complex, $[(\eta\text{-}C_8H_{12})Ir(\kappa^3\underline{O}\text{-}C_5Me_5TiW_5O_{18})]^{2-}$

Walter G. KLEMPERER* and Atsushi YAGASAKI
Department of Chemistry, University of Illinois,
Urbana, Illinois 61801, U.S.A.

Reaction of the pentamethylcyclopentadienyltitaniumtungstate salt $[(\underline{n}\text{-}C_4H_9)_4N]_3(C_5Me_5TiW_5O_{18})$ with $[(\eta\text{-}C_8H_{12})Ir(CH_3CN)_2]PF_6$ in tetrahydrofuran yields $[(\eta\text{-}C_8H_{12})Ir(\kappa^3\underline{O}\text{-}C_5Me_5TiW_5O_{18})]^{2-}$ as a tetra-n-butylammonium salt. In the product anion, both of the C=C bonds in the 1,5-cyclooctadiene ligand plus three contiguous doubly-bridging OW_2 oxygen atoms in the $C_5Me_5TiW_5O_{18}{}^{3-}$ ligand are coordinated to the iridium(I) center to generate an eighteen-electron, distorted square pyramidal complex.

Although polyoxoanion supported organometallic complexes have been known for over a decade,[1)] investigations of their reaction chemistry have only recently been reported.[2,3)] Cyclooctadieneiridium(I) complexes have attracted particular attention due to their reactivity under both reducing and oxidizing conditions. In order to elucidate the structural basis for this reactivity, we have begun to isolate and structurally characterize a variety of polyoxoanion supported cyclooctadieneiridium(I) complexes and describe here the first structurally characterized species of this type.

Reaction of $[(\underline{n}\text{-}C_4H_9)_4N]_3(C_5Me_5TiW_5O_{18})$[4)] (0.96 g, 0.45 mmol) with $[(C_8H_{12})\text{-}Ir(CH_3CN)_2]PF_6$ [7)] (0.26 g, 0.49 mmol) in 20 mL tetrahydrofuran under dry nitrogen for ca. 1.5 h followed by addition of 20 mL of diethylether produced an orange precipitate after stirring for 5-10 min. This material was collected by filtration, washed with 2x2 mL of diethylether, and dried under vacuum for 12 h to yield 0.72 g of $[(\underline{n}\text{-}C_4H_9)_4N]_2[(C_8H_{12})Ir(C_5Me_5TiW_5O_{18})]$ (0.33 mmol, 73% yield based on W).[8)]

X-Ray structural analysis of crystalline $[(\underline{n}\text{-}C_4H_9)_4N]_2[(C_8H_{12})Ir(C_5Me_5TiW_5O_{18})]\cdot 2[(C_2H_5)_2O]$,$^{9)}$ obtained by diffusion of diethylether into a tetrahydrofuran solution, revealed the presence of $(\underline{n}\text{-}C_4H_9)_4N^+$ cations, $(C_2H_5)_2O$

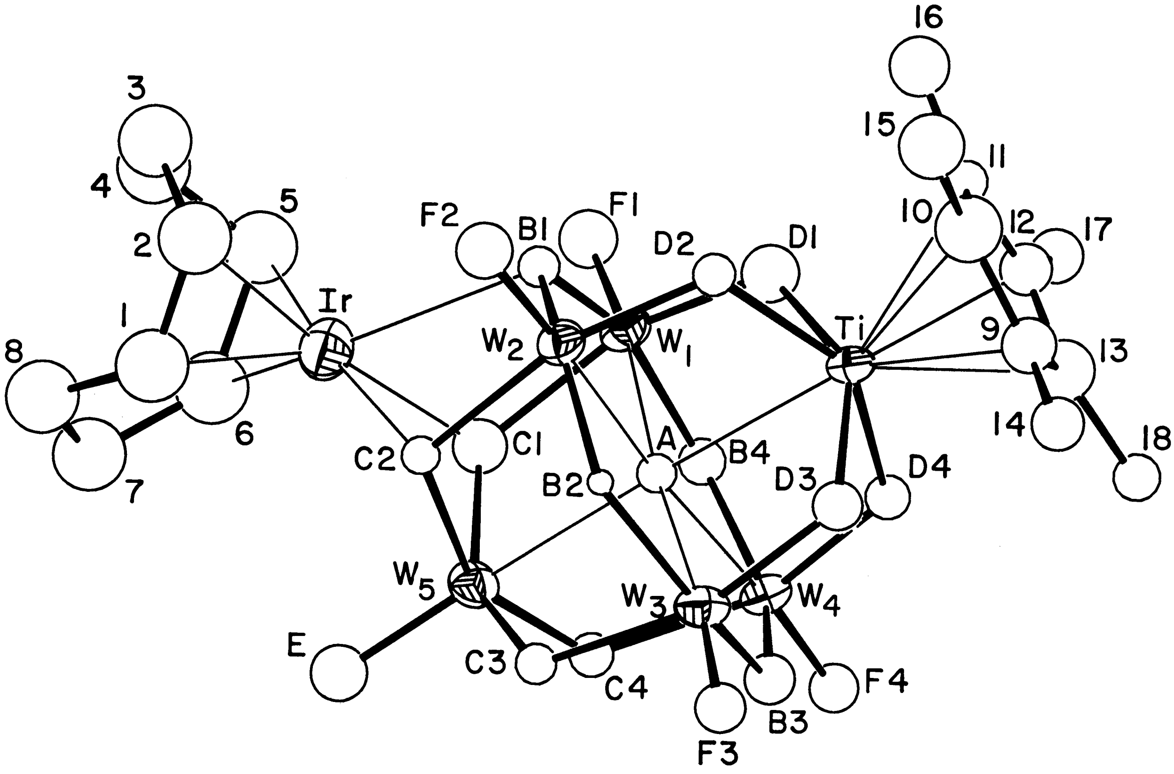

Fig. 1. ORTEP drawing of the non-hydrogen atoms in the solid state structure of the $[(C_8H_{12})Ir(C_5Me_5TiW_5O_{18})]^{2-}$ anion in $[(\underline{n}\text{-}C_4H_9)_4N]_2[(C_8H_{12})Ir(C_5Me_5TiW_5O_{18})]\cdot 2[(C_2H_5)_2O]$. Metal atoms were refined anisotropically and are represented by thermal vibration ellipsoids drawn to encompass 35% of the electron density. Oxygen and carbon atoms were refined isotropically and are represented by spheres drawn to encompass 35% of the electron density. Metal atoms are labeled with their elemental symbols plus, in the case of tungsten, a numerical subscript. Oxygen and carbon atoms are labeled with their subscripts: capital letters and numbers for oxygens and numbers only for carbons.

molecules of crystallization, and discrete $[(C_8H_{12})Ir(C_5Me_5TiW_5O_{18})]^{2-}$ anions having the structure shown in Fig. 1. Here, the iridium center achieves an eighteen-electron configuration through distorted square pyramidal coordination by two olefinic cyclooctadiene C=C bonds and three doubly-bridging OW_2 oxygens of the $C_5Me_5TiW_5O_{18}{}^{3-}$ ligand. The midpoints of the two C=C bonds and the two basally coordinated oxygen atoms O_{C1} and O_{C2} are coplanar to within 0.06 Å, and the iridium atom is displaced from this plane by 0.28 Å. Average bond lengths within the basal plane are $\underline{d}$(Ir-C) = 2.18(0.06, 0.07, 0.11, 4) Å and $\underline{d}$(Ir-O) = 2.20(0.03, 0.00, 0.00, 2) Å.$^{10)}$ The apical oxygen atom O_{B1} is weakly bonded to the iridium center [$\underline{d}$(Ir-O_{B1}) = 2.52(3) Å] and markedly displaced from its idealized position above the center of the basal plane.

This research was supported by the National Science Foundation. We thank Dr. Scott Wilson of the University of Illinois X-ray Crystallographic Laboratory for carrying out the X-ray crystal structure determination.

References

1) V. W. Day and W. G. Klemperer, Science (Washington, D.C.), 228, 533 (1985).

2) R. G. Finke, D. J. Edlund, and D. K. Lyon, Abstracts of Papers, 3rd Chemical Congress of North America, Toronto, Ontario, Canada; American Chemical Society: Washington, D.C., 1988; INOR426.

3) V. W. Day, W. G. Klemperer, S. P. Lockledge, and D. J. Main, Abstracts of Papers, 197th National Meeting of the American Chemical Society, Dallas, Texas; American Chemical Society: Washington, DC, 1989; INOR268.

4) $[(\underline{n}-C_4H_9)_4N]_3[(C_5Me_5TiW_5O_{18})]$ was prepared in 76% (based on W) yield by mixing $C_5Me_5TiCl_3$ $^{5)}$ solution (0.40 g, 1.4 mmol, in 8 mL CH_3CN) with a solution of $[(\underline{n}-C_4H_9)_4N]_2(WO_4)$ $^{6)}$ (5.0 g, 6.8 mmol) and CCl_3COOH (0.90 g, 5.5 mmol) in 8 mL CH_3CN for 3 h under dry nitrogen, reducing the volume to ca. 1/3 under vacuum, adding 200 mL of diethylether, drying the resulting sticky solid under vacuum for ca. 40 min, washing the solid with 20 mL of H_2O, and then drying it in a desiccator over P_2O_5 overnight.

5) J. Blenkers, H. J. DeLiefde Meijer, and J. H. Teuben, J. Organomet. Chem., 218, 383 (1981).

6) T. M. Che, V. W. Day, L. C. Francesconi, M. F. Fredrich, W. G. Klemperer, and W. Shum, Inorg. Chem., 24, 4055 (1985).

7) A. C. Sievert and E. L. Muetterties, Inorg. Chem., **20**, 489 (1981). $AgPF_6$ was used instead of $AgBF_4$.

8) Anal. Calcd for $C_{50}H_{99}IrN_2O_{18}TiW_5$: C, 27.60; H, 4.59; Ir, 8.83; N, 1.29; Ti, 2.20; W, 42.25%. Found: C, 27.62; H, 4.53; Ir, 8.91; N, 1.30; Ti, 2.09; W, 42.07%. IR (Nujol, 1000 - 600 cm^{-1}): 975 (w), 949 (s), 875 (sh), 826 (s), 804 (sh), 765 (sh), 652 (w). ^1H NMR ($CDCl_3$, 360 MHz): δ 4.35 (s, 4H), 3.30 (m, 16H), 2.19 (s, 4H), 2.04 (s, 15H), 1.67 (m, 16H), 1.52 (m, 16H), 1.29 (m, 4H), 1.02 (3, 24H).

9) Single crystals of $[(\underline{n}\text{-}C_4H_9)_4N]_2[(C_8H_{12})Ir(C_5Me_5TiW_5O_{18})]\cdot 2(C_2H_5)_2O$ (formula weight 2323.95) are at -75°C monoclinic, space group $P2_1/\underline{c}$, with $\underline{a}$ = 12.782(4), $\underline{b}$ = 20.789(8), $\underline{c}$ = 27.932(11) A, β = 96.17(3)°, $\underline{V}$ = 7379(9) A^3, $\underline{Z}$ = 4, $\underline{d}_{calcd}$ = 2.09 g cm^{-3}. $\underline{R}$ = 0.067 and R_w = 0.066 for 3216 independent reflections.

10) The first number in parentheses following an average value of a bond length is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements that are included in the average value.

(Received August 5, 1989)