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Communications

Cluster Synthesis via Inorganic Diazo Compounds. The Synthesis and Crystal and Molecular Structure of $H_2IrOs_3(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_9PPh_3$

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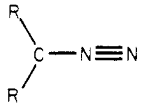
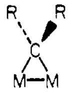
Summary: The reaction of $Ir(N_2)(PPh_3)_2Cl$ with $H_2Os_3(CO)_{10}$ has yielded the mixed metal cluster complex $H_2IrOs_3(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_9PPh_3$, I, in 15% yield. I has been characterized by IR, ^1H NMR, elemental, and single-crystal X-ray diffraction analyses.

Diazoalkanes A have recently attracted the attention of synthetic organometallic chemists and have been used for the synthesis of a variety of new organometallic complexes[1] including those containing the currently popular, bridging alkylidene ligand B.[2] Such reactions take advantage of



A



B

$M{-}N{\equiv}N$

C

D

the facile loss of N_2 from the diazoalkane. By analogy, it seems reasonable to expect that inorganic dinitrogen compounds C,[3] which could be viewed as inorganic analogues of diazoalkanes, might be useful reagents for the synthesis of polynuclear metal complexes D via loss of N_2 and formation of metal–metal bonds. This notion has been realized through the reaction of $Ir(N_2)(PPh_3)_2Cl$ with $H_2Os_3(CO)_{10}$.

When heated to reflux in benzene solvent for 6 h, $Ir(N_2)(PPh_3)_2Cl$ (40 mg, 0.05 mmol) reacted with $H_2Os_3(CO)_{10}$ (44 mg, 0.05 mmol) to yield the air-stable red product $H_2IrOs_3(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_9(PPh_3)$, I (10 mg, 0.0075 mmol, 15% yield, eq 1, which was isolated by TLC.[4] I was characterized by IR and ^1H NMR spectroscopies[6] and elemental[7] and X-ray crystallographic[8] analyses.

$$Ir(N_2)(PPh_3)_2Cl + H_2Os_3(CO)_{10} \xrightarrow[6\ h]{68\ ^\circ C} H_2IrOs_3(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_9PPh_3 + N_2 + PPh_3 \quad (1)$$

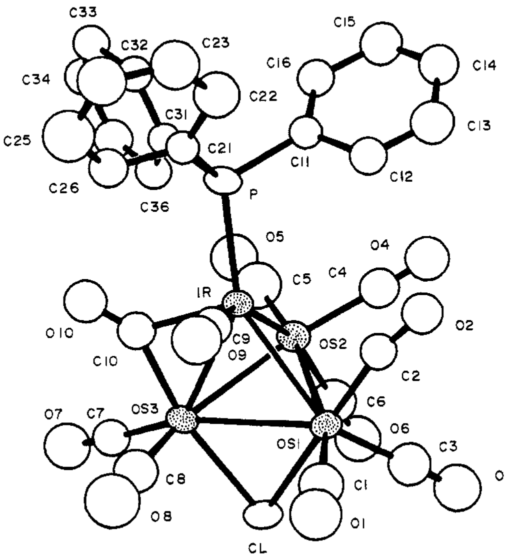


Figure 1. An ORTEP drawing of $H_2IrOs_3(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_9PPh_3$, I, showing 50% probability electron-density ellipsoids.

An ORTEP diagram of the molecular structure of I is shown in Figure 1.[10] The molecule consists of a tetrahedral cluster containing one iridium and three osmium atoms, as expected for a 60-electron tetranuclear cluster. A chloride ligand bridges the Os(1)–Os(3) metal–metal bond and apparently migrated to that site from the iridium atom. A terminal carbonyl ligand on the iridium atom must have originated on the Os_3 cluster. A similar transfer of a CO ligand from $H_2Os_3(CO)_{10}$ was observed in the synthesis of the mixed-metal cluster $H_2Os_3Pt(CO)_{10}[P(c\text{-}C_6H_{11})_3]$.[11] Overall, I contains 10 carbonyl ligands which include a symmetric bridge C(10)–O(10) across the Ir–Os(3) bond, a semibridge C(2)–O(2) across the Ir–Os(1) bond, and eight linear ligands arranged as shown in Figure 1. The molecular contains two hydride ligands (not observed crystallographically). One is believed to bridge the elongated Os(2)–Os(3) metal–metal bond of 3.005 (1) Å. The other hydride ligand is coupled magnetically to the phosphorus atom.[6] Thus, it probably bridges an Ir–Os bond, most likely Ir–Os(2) since the other Ir–Os bonds contain either bridging or semibridging CO ligands.

The importance of N_2 loss in the formation of I was demonstrated by the attempted synthesis of I from the

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(1) Lappert, M. F.; Poland, J. S. *Adv. Organomet. Chem.* **1970,** *9,* 397.

(2) (a) Herrmann, W. A. *Pure and Appl. Chem.* **1982,** *54,* 65. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978,** *17,* 800. (c) Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1980,** *102,* 7789. Clavert, R. B.; Shapley, J. R. *Ibid.* **1977,** *99,* 5225.

(3) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978,** *6,* 589.

(4) Significant amounts of $H_2Os_3(CO)_9PPh_3$ together with a few other uncharacterized products were also obtained. The $H_2Os_3(CO)_9PPh_3$ could have been formed in a secondary reaction of free PPh_3 with $H_2Os_3(CO)_{10}$.[5]

(5) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976,** *114,* 313.

(6) IR ν (CO) in hexane: 2087 (m), 2060 (vs), 2041 (vs), 2017 (m), 2010 (m, sh), 1996 (s), 1956 (w), 1828 (n). ^1H NMR in $CDCl_3$: 7.46 (m, 15 H), −13.79 (d, $J_{P\text{-}H}$ = 13 Hz, 1 H), −18.22 ppm (s, 1 H).

(7) Satisfactory elemental analyses have been obtained for C, H, and N.

(8) Crystal data: space group $P2_1/c$ at 25°; a = 11.564 (6) Å, b = 17.645 (4) Å c = 16.956 (2) Å, β = 108.11 (2)°; V = 3288 (3) Å^3; Z = 4, ρ_{calcd} = 2.71 g/cm^3. The structure was solved by the heavy-atom method.[9] Least-squares refinement on 2383 reflections ($F^2 \geq 3.0\sigma(R^2)$) produced the final residual R_F = 0.035 and R_{wF} = 0.032.

(9) Diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer. All structure solution and refinement calculations were done on a Digital PDP 11/45 computer by using the Enraf-Nonius SDP program library, Version 18.

(10) Selected bond distances (Å) and angles (deg) are as follows: Ir–Os(1) = 2.881 (1), Ir–Os(2) = 2.906 (1), Ir–Os(3) = 2.785 (1), Os(1)–Os(2) = 2.802 (1), Os(1)–Os(3) = 2.884 (1), Os(2)–Os(3) = 3.005 (1), Os(1)–Cl = 2.465 (4), Os(3)–Cl = 2.456 (4), Ir–C(10) = 2.11 (2), Os(3)–C(10) = 2.02 (2), Os(1)–C(2) = 1.89 (2), Ir···C(2) = 2.81 (2), Ir–Os(3)–C(10) = 49.1 (4), Os(3)–Ir–C(10) = 46.3(4), Ir–Os(1)–C(2) = 68.7 (5), Os(1)–C(2)–O(2) = 167(1), Os(1)–Cl–Os(3) = 71.8 (1).

(11) Farrugia, L. J.; Howard, J. A. K.; Mitrachachon, P.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981,** 155.

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reagents $Ir(CO)(PPh_3)_2Cl$ and $H_2Os_3(CO)_{10}$. Although some new products have been obtained,[12] we did not observe the formation of I in any thermal reaction up to and including reaction in refluxing octane solvent.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences of the U.S. Dept. of Energy under Contract No. DE-AC-2-78ER04900 and the Alfred P. Sloan Foundation through a fellowship to R.D.A. NMR studies were supported in part under Grant No. CHE-7916210 from the Chemistry Division of the National Science Foundation. We also thank Engelhard Industries for a load of osmium tetroxide.

Registry No. $Ir(N_2)(PPh_3)_2Cl$, 15695-36-0; $H_2Os_3(CO)_{10}$, 41766-80-7.

Supplementary Material Available: Tables of interatomic distances and angles, final positional and thermal parameters, and structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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[12] These are currently being characterized.

Cyclotantalation of 2,6-Di-*tert*-butylphenoxide[1]

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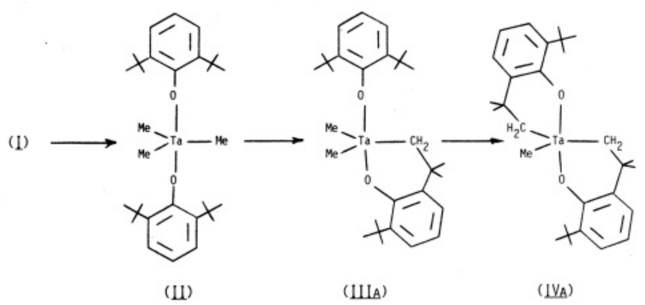
Summary: Alkylation of $Ta(OAr')_2Cl_3$ (OAr′ = 2,6-*tert*-butylphenoxide) followed by thermolysis leads to cyclometalation of the aryl oxide ligand in which one of the CH bonds of a *tert*-butyl group has been activated to cleavage.

Since the discovery of the first cyclometalation reaction by Kleinmann in 1963[2], a large number of such intramolecular, cyclic metalations have been reported.[3,4] Most known cyclometalation reactions are with ligands containing N of P-donor atoms reacting with low-valent group 7 or 8 metal systems to activate aromatic or benzylic type CH bonds, with a strong tendency to form five-membered chelate rings.[4] With trialkylphosphine ligands activation of purely aliphatic CH bonds has been seen, sometimes with the formation of four- or six-membered rings.[5] We wish to report here our characterization of a new type of cyclometalation reaction involving a high-valent, early transition-metal system in which the ligand contains an oxygen donor atom and involves the activation of an aliphatic CH bond to form a six-membered ring.[6]

Scheme I



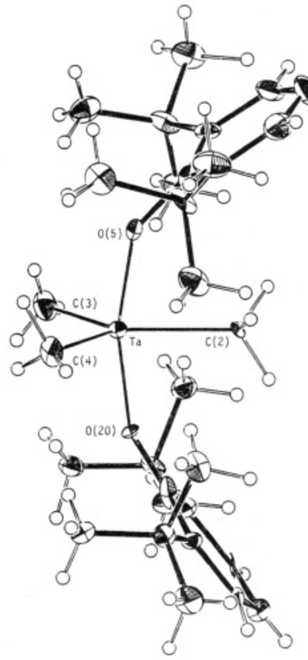


Figure 1. ORTEP view of II. Some pertinent bond distances (Å) and angles (deg) are Ta–O(5) = 1.930 (6), Ta–O(2) = 1.945 (6), Ta–C(2) = 2.248 (10), Ta–C(3) = 2.136 (10), Ta–C(4) = 2.138 (10), O(5)–Ta–O(20) = 164.1 (2), C(2) = 81.1 (3), –C(3) = 95.2 (3), C(4) = 95.2 (3), O(20)–Ta–C(2) = 83.0 (3), –C(3) = 95.0 (3), –C(4) = 94.1 (3), C(2)–Ta–C(3) = 127.0 (4), C(2)–Ta–C(4) = 128.3 (4), C(3)–Ta–C(4) = 104.7 (4).

Treatment of $TaCl_5$ with an excess of LiOAr′ (OAr′ = 2,6-di-*tert*-butylphenoxide) in benzene leads to the formation of $Ta(OAr')_2Cl_3$ (I) as an orange, hydrocarbon-soluble solid. Further substitution by LiOAr′ does not occur.[7] Alkylation of I with $LiCH_3$ at 25 °C in benzene leads to substitution of the chloride ligands and formation of $Ta(OAr')_2(Me)_3$ (II).[8] A single-crystal X-ray structure analyisis of this compound revealed an approximate tbp coordination geometry about the metal with equatorial methyl groups and axial aryl oxide ligands (vide infra). Thermolysis of II in toluene in a sealed tube (120 °C) leads to the generation of methane (2 equiv) and the formation of a new complex (IVa) in which each of the aryl oxide ligands has undergone attack on one of the CH bonds of

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[1] The Chemistry of Sterically Crowded Aryl-Oxide Ligands. 2. For part 1, see: Chamberlain. L; Huffman, J. C.; Keddington, L.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.*, in press.

[2] Kleinmann, J. P.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, *85*, 1544.

[3] De-hand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 326.

[4] Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.

[5] Goel, R. G.; Ogini, W. O. *Organometallics* **1982**, *1*, 654.

[6] The observed attack on the CH bonds of the $N(SiMe_3)_2$ ligand can be considered to be a cyclometalation reaction, in which a four-membered ring is formed: Bennett, C. R.; Bradley, D. C. *J. Chem. Soc., Chem. Commun.* **1974**, 29. Simpson, S. J.; Turner, H. W.; Anderson, R. A. *Inorg. Chem.* **1981**, *20*, 2991.

[7] Anal. Calcd for $TaCl_3O_2C_{28}H_{42}$ (I): C, 48.19; H, 6.07; Cl, 15.24. Found: C, 48.82; H, 6.13; Cl, 14.98%.

[8] Anal. Calcd for $TaO_2C_{31}H_{51}$ (II): C, 58.48; H, 8.07. Found: C, 57.90; H, 7.96. ^1H NMR (benzene-d_6; 35 °C): $\delta(C_6H_3)$ 6.7–7.2 (m), δ $(C_6H_3\text{-}t\text{-}Bu_2)$ 1.45 (s), δ $(TaCH_3)$ 1.19 (s).

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