Journal of Organometallic Chemistry, 171 (1979) C21—C26

Preliminary communication

Reactions of Small Molecules with Transition Metal Cluster Hydrides. The Reaction of $H_2Os_3(CO)_{10}$ with Aryl-isocyanates and -isothiocyanates

By Richard D. Adams and Nancy M. Golembeski

Department of Chemistry,
Yale University, New Haven CT 06520 (U.S.A.)

(Received January 24th, 1979)

Summary

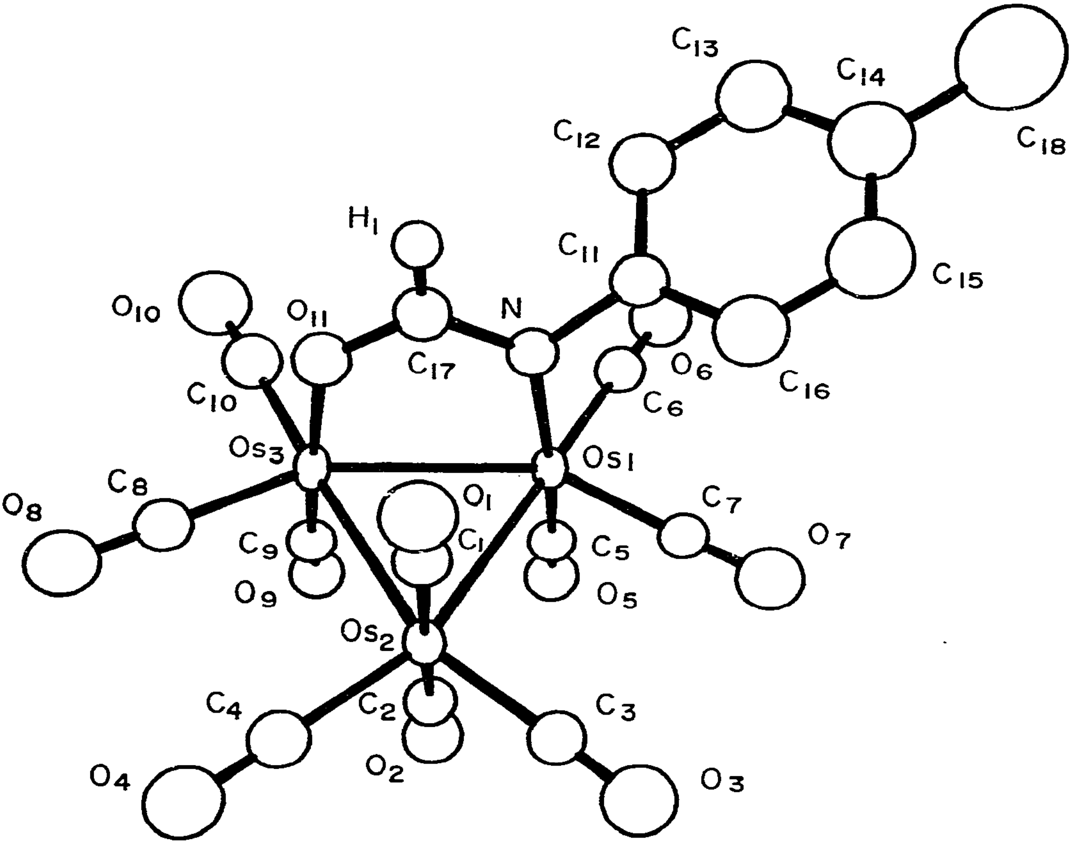
The transition metal cluster hydride complex $H_2Os_3(CO)_{10}$ reacts with aryl isocyanates and isothiocyanates to yield products containing N-aryl-formamido and -thioformamido ligands. The compound $(\mu\text{-}p\text{-}CH_3C_6H_4NC(H)O)(\mu\text{-}H)Os_3(CO)_{10}$ has been analyzed by x-ray crystallographic methods and is shown to contain a formamido ligand bridging the edge of the triosmium cluster.

The activation of small molecules by transition metal cluster compounds is presently an area of intense study [1-3]. A particularly important interest is their potential use as catalysts for new and unusual types of chemical reactions [4-6]. As part of a project focusing on the overall hydrogenation of the X=C=Y molecules with cluster-hydride catalysts, we wish to report that we have found that the complex $H_2Os_3(CO)_{10}$ readily reacts with aryl isocyanides and isothiocyanates to incorporate one molecule into the coordination sphere of the cluster, transfer one hydrogen atom to the carbon atom of the isocyanate, and produce an N-aryl-formamido or -thioformamido ligand which bridges the edge of a triosmium cluster.

In a typical reaction a solution of 0.1 g of $H_2Os_3(CO)_{10}$ and 0.6 ml of p-$CH_3C_6H_4NCO$ in 25 ml of hexanes solvent was refluxed 3 hrs. The solution turned yellow and the solvent was removed in vacuo. The residue was chromatographed over $Al_2O_3\cdot6\%H_2O$ with 1/1; hexanes/benzene solvent. The yellow product was crystallized from hexanes solution by cooling to -20°. Yield: 0.066g, 62%; m.p. 128-130°; IR (hexanes); 2110m, 2075s, 2060s, 2040w,sh, 2030s, 2010s, 2005s,sh, 1987m, 1980mcm^{-1}. The ^1H nmr spectrum showed resonances at δ = -11.35(1), (μ-H); 7.65(1), (C-H); 7.01(4), C_6H_4; 2.34(3), (CH_3)ppm. We have isolated each of the compounds (μ-RNC(H)X)(μ-H)$Os_3(CO)_{10}$; I, R = C_6H_5, X = O, II, R = p-$CH_3C_6H_4$, X = O, and III, R = C_6H_5, X = S. Low field resonance shifts at δ = 7.74, 7.65, and 8.12 ppm for I, II, and III, respectively, lie in the region known to be characteristic of the hydrogen atom of thioformamido ligands [7].

Compound II has also been characterized by x-ray crystallographic methods. The compound crystallizes in the triclinic space group $P\bar{1}$, a = 7.925(2), b = 11.705(3), c = 13.928(4)Å, α = 66.71(2), β = 80.17(2), γ = 79.18(2)°, Z = 2. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer. The data were corrected for absorption. The structure was solved by a combination of Patterson, difference Fourier, and least squares refinement techniques using the Enraf-Nonius SDP program library on a Digital PDP 11/45 computer. The final R value was 0.052 for 3902 reflections having $Fo^2 \geq 3\sigma(Fo^2)$ obtained in the range 2θ = 0-54°.

The molecular structure of II is shown in the figure. Pertinent bond distances and angles are listed in Tables I and II. The hydrogen atoms were not observed crystallographically, and the atom H(1) shown in the figure was placed in an idealized position. Ten linear carbonyl ligands are bonded to three osmium atoms which are arranged in a triangle. The most interesting feature is a formamido ligand which bridges the Os(1)-Os(3) bond. The nitrogen atom is bonded solely to Os(1), Os(1)-N = 2.156(6)Å, while the oxygen atom is bonded solely to Os(3), Os(3)-O(11) = 2.145(6)Å. The carbon-nitrogen and carbon-oxygen distances are short, C(17)-N = 1.33(1)Å and C(17)-O(11) = 1.27(1)Å and indicative of partial multiple bonding across



An ORTEP diagram of $(\mu\text{-}p\text{-}CH_3C_6H_4NC(H)O)(\mu\text{-}H)Os_3(CO)_{10}$ showing 50% probability ellipsoids. The hydrogen atom H(1) is shown in an idealized position.

the ligand. The O(11)-C(17)-N angle is 124.8(8)°. The plane of the ligand is nearly perpendicular to the plane of the osmium triangle. The dihedral angle is 74°.

While the molecules, CO_2, RNCS, and CS_2, are well-known to react with mononuclear transition metal hydrides to form chelating formato [8], thioformamido [7], and dithioformato [9] ligands, studies of similar reactions employing transition metal cluster hydrides are exceedingly rare. We believe that hydrogen transfer and the formation of bridging chelates may be a characteristic feature of the reaction of this class of molecule with poly-

Table I

Bond Distances with Errors for $(\mu\text{-}p\text{-}CH_3C_6H_4NC(H)O)(\mu\text{-}H)Os_3(CO)_{10}$

Atoms	Distances (Å)	Atoms	Distances (Å)
Os(1)-Os(2)	2.903(1)	C(11)-C(12)	1.40(1)
Os(1)-Os(3)	2.909(1)	C(12)-C(13)	1.39(1)
Os(2)-Os(3)	2.888(1)	C(13)-C(14)	1.36(2)
Os(1)-C(5)	1.912(9)	C(14)-C(15)	1.39(2)
Os(1)-C(6)	1.898(9)	C(15)-C(16)	1.41(1)
Os(1)-C(7)	1.910(8)	C(16)-C(11)	1.39(1)
Os(1)-N	2.156(6)	C(14)-C(18)	1.56(2)
Os(2)-C(1)	1.963(8)	C(1)-O(1)	1.13(1)
Os(2)-C(2)	1.948(9)	C(2)-O(2)	1.15(1)
Os(2)-C(3)	1.901(8)	C(3)-O(3)	1.15(1)
Os(2)-C(4)	1.924(10)	C(4)-O(4)	1.17(1)
Os(3)-C(8)	1.902(10)	C(5)-O(5)	1.13(1)
Os(3)-C(9)	1.889(9)	C(6)-O(6)	1.17(1)
Os(3)-C(10)	1.903(11)	C(7)-O(7)	1.14(1)
Os(3)-O(11)	2.145(6)	C(8)-O(8)	1.18(1)
C(17)-O(11)	1.27(1)	C(9)-O(9)	1.16(1)
C(17)-N	1.33(1)	C(10)-O(10)	1.16(1)
N-C(11)	1.45(1)		

nuclear metal-hydride groupings. Indeed this reaction may have mechanistic implications in some aspects of surface catalysis. It has been proposed that the catalytic hydrogenation of CO_2 on metal surfaces proceeds through CO[10], $H_2C(OH)_2$[11], and $C(OH)_2$[12] intermediates[13]. Our results would tend to support the formation of intermediate species having carbon-bound hydrogen atoms and metal bound oxygen atoms.

Table II

Selected Bond Angles with Errors for $(\mu\text{-}p\text{-}CH_3C_6H_4NC(H)O)(\mu\text{-}H)Os_3(CO)_{10}$

Atoms	Angle (deg)	Atoms	Angle (deg)
Os(1)-Os(2)-Os(3)	60.31(1)	C(13)-C(14)-C(15)	118.8(12)
Os(2)-Os(1)-Os(3)	59.60(1)	C(14)-C(15)-C(16)	121.5(12)
Os(1)-Os(3)-Os(2)	60.09(1)	C(15)-C(16)-C(11)	118.9(10)
Os(2)-Os(1)-N	92.8(2)	C(13)-C(14)-C(18)	119.7(13)
Os(2)-Os(3)-O(11)	89.8(1)	C(15)-C(14)-C(18)	121.4(13)
Os(1)-Os(3)-O(11)	81.7(2)	Os(1)-C(5)-O(5)	178.6(8)
Os(3)-Os(1)-N	82.0(2)	Os(1)-C(6)-O(6)	175.9(8)
Os(1)-N-C(11)	119.0(5)	Os(1)-C(7)-O(7)	177.1(8)
Os(1)-N-C(17)	124.2(5)	Os(2)-C(1)-O(1)	172.8(7)
Os(3)-O(11)-C(17)	126.1(6)	Os(2)-C(2)-O(2)	175.5(8)
O(11)-C(17)-N	124.8(8)	Os(2)-C(3)-O(3)	176.8(8)
C(17)-N-C(11)	115.2(7)	Os(2)-C(4)-O(4)	177.8(8)
N-C(11)-C(12)	121.8(8)	Os(3)-C(8)-O(8)	177.3(8)
N-C(11)-C(16)	118.8(8)	Os(3)-C(9)-O(9)	173.8(8)
C(16)-C(11)-C(12)	119.3(9)	Os(3)-C(10)-O(10)	177.5(9)
C(11)-C(12)-C(13)	120.1(9)		
C(12)-C(13)-C(14)	120.9(11)		

Acknowledgement

Support of this research under Contract No. ER-78-S-02-4900 from the Office of Basic Energy Sciences, U.S. Department of Energy is gratefully acknowledged.

References

1. E. L. Muetterties, Science, 196 (1977) 839.
2. E. L. Muetterties, Bull. Soc. Chim. Belg., 84 (1975) 959.

3. J. Lewis, and B. F. G. Johnson, Pure Appl. Chem., 44 (1975) 43.
4. M. G. Thomas, B. F. Beier, and E. L. Muetterties, J. Amer. Chem. Soc., 98 (1976) 1296.
5. E. Band, W. R. Pretzer, M. G. Thomas, and E. L. Muetterties, 99 (1977) 7380.
6. M. A. Andrews, and H. D. Kaesz, J. Amer. Chem. Soc., 99 (1977) 6763.
7. S. D. Robinson and A. Sahajpal, Inorg. Chem., 16 (1977) 2722.
8. M. E. Volpin, and I. S. Kolomnikov, Organomet. React., 5 (1975) 313.
9. I. S. Butler and A. E. Fenster, J. Organometal. Chem., 66 (1974) 161.
10. H.A. Bahr, Ges. Abhandl. Kenntnis Kohle, 8 (1929) 219.
11. S. Medsforth, J. Chem. Soc., 123 (1923) 1452.
12. H. Pichler, Brennst. Chem., 24 (1943) 39.
13. V.M. Vlasenko and G.E. Yuzefovich, Russ. Chem. Rev., 38 (1969) 728.

SUPPLEMENTARY MATERIAL

The following supplementary material has been deposited:

Table III. Positional and Thermal Parameters with Estimated Standard Deviations for $(\mu\text{-}p\text{-}CH_3C_6H_4NC(H)O)(\mu\text{-}H)\text{-}Os_3(CO)_{10}$

Table IV. F_{obs} & F_{calc} x 10 in Electrons for H(Form amido)-$Os_3(CO)_{10}$

Deposition was made as NAPS Document No. 03419 (30 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting \$ 3.00 for photocopies or \$ 7.50 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.