ORGANOMETALLICS

Volume 16, Number 3, February 4, 1997

Communications

Dehydrohalogenation of Iodoarenes To Give Ruthenium Clusters Containing μ_4-Naphthyne and μ_4-Phenanthryne Ligands

Antony J. Deeming[*,†] and Despo M. Speel[‡]

Department of Chemistry, University College London, 20 Gordon Street,
London WC1H 0AJ, U.K.

Received October 17, 1996[⊗]

Summary: Iodobenzene and 4-iodotoluene react with [Ru$_3$(CO)$_{12}$] to give the oxidative addition products [Ru$_3$(μ-I)(μ,η^1:η^6-C$_6$H$_4$R)(CO)$_8$] (R = H, 4-Me), whereas 1-iodonaphthalene and 9-iodophenanthrene give the aryne clusters [Ru$_4$(μ_4,η^2-L)(CO)$_{12}$] (L = 1,2-naphthyne, 9,10-phenanthryne).

Oxidative addition of alkyl and aryl halides is an extremely important route to alkyl and aryl transition-metal complexes and is involved in many catalytic processes. Whereas oxidative addition reactions of transition-metal carbonyl clusters have been used widely to form organometallic clusters, surprisingly little work has been reported on oxidative additions with carbon−halogen bond cleavage. We have been searching for straightforward and site-selective routes into arene ligands that are simultaneously σ- and π-coordinated in ruthenium and osmium clusters, as alternatives to known methods from hydrocarbons,[1,2] aryl phosphines,[1,3] aryl sulfides,[4] *etc.* Following reports that diphenyl sulfide reacts with [Ru$_3$(CO)$_{12}$] to give the structurally characterized product [Ru$_3$(μ-SPh)(μ,η^1:η^6-Ph)(CO)$_8$] (**1**) (Chart 1) by C−S cleavage,[4a] that 2-bromobenzothiophene reacts with [Os$_3$(CO)$_{10}$(MeCN)$_2$] to give [Os$_3$(μ-Br)(μ-benzothien-2-yl)(CO)$_{10}$] by C−Br cleavage, and that other halocarbons react similarly,[5] we have examined some simple iodoarenes as precursors to aryl− and aryne−ruthenium carbonyl clusters. Previously aryl and aryne ligands in clusters have been formed by P−C[6] or S−C[4] cleavage.

Iodobenzene and 4-iodotoluene react with [Ru$_3$(CO)$_{12}$] in refluxing octane (but not at lower temperatures) to give much dark barely soluble material, but TLC of the product mixture gave one soluble and tractable product in each case. These products are directly analogous: [Ru$_3$(μ-I)(μ,η^1:η^6-C$_6$H$_4$R)(CO)$_8$] (**2**) (R = H) as a yellow-orange oil (15%) and **3** (R = 4-Me) as orange crystals (14%).[7] Both **2** and **3** were characterized by MS, IR, and ^{1}H NMR spectroscopy,[8] and additionally the single-crystal X-ray structure of **3** was determined (Figure 1).[9] The ^{1}H NMR spectrum of **2** showed five separate signals at chemical shifts consistent with η^6-coordination of the Ph group, and the crystal structure of **3** established that it contains a μ,η^1:η^6-aryl ligand. The structure is closely related to that of [Ru$_3$(μ-SPh)(μ,η^1:η^6-Ph)(CO)$_8$] (**1**).[4] In addition to the μ,η^1:η^6-mode of Ph bridging, the μ,η^1:η^2

[†] E-mail: a.j.deeming@ucl.ac.uk. WWW: http://www.ucl.ac.uk/chem/people/deeming/index.html.

[‡] D.M.S. has previously published under her maiden name Despo M. Michaelidou.

[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1996.

(1) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

(2) Johnson, B. F. G.; Nairn, J. G. M.; Brown, D. B.; Lewis, J.; Gallop, M.; Parker, D. G. *Chem. Eur. J.* **1995**, *1*, 252 and references therein.

(3) Deeming, A. J.; Martin, C. M. *Chem. Commun.* **1996**, 53.

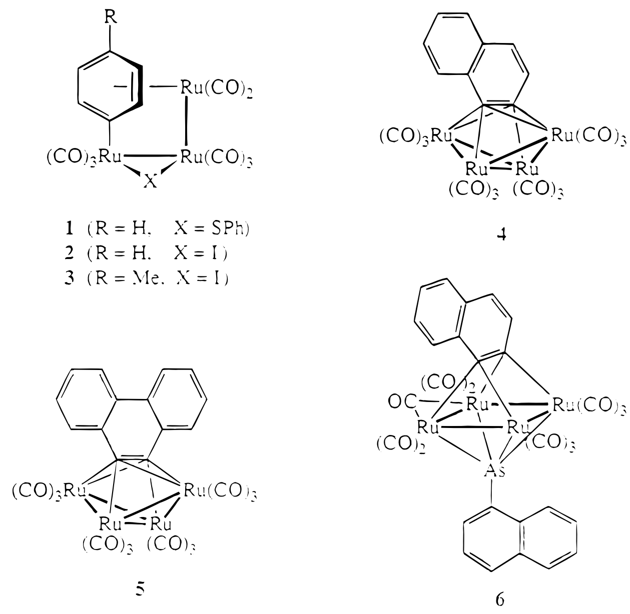
(4) (a) Cullen, W. R.; Rettig, S. J.; Zheng, T. C. *Polyhedron* **1995**, *14*, 2653. (b) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* **1982**, *1*, 235.

(5) Adams, R. D.; Qu, X. *Organometallics* **1995**, *14*, 2238. Adams, R. D.; Qu, X. *Organometallics* **1995**, *14*, 4167.

(6) (a) Cabeza, J. A.; Franco, R. J.; Llamazares, A.; Riera, V.; Pérez-Carreno, E.; Van der Maelen, J. F. *Organometallics* **1994**, *13*, 55. (b) Deeming, A. J.; Smith, M. B. *J. Chem. Soc., Dalton Trans.* **1993**, 3383.

S0276-7333(96)00878-3 CCC: $14.00 © 1997 American Chemical Society

Chart 1



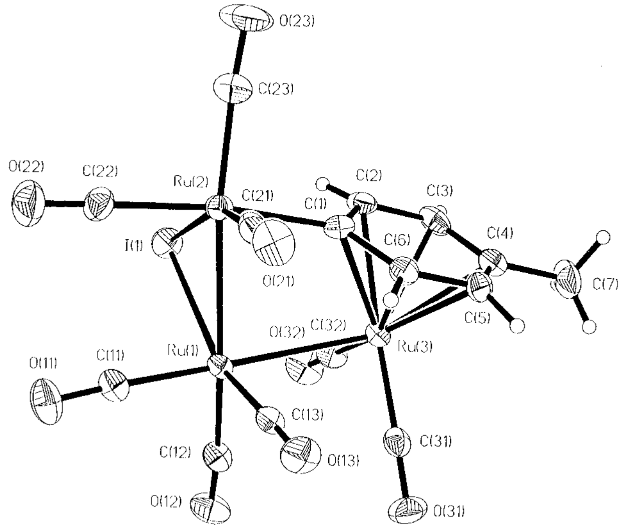


Figure 1. Structure of $[Ru_3(\mu\text{-I})(\mu,\eta^1{:}\eta^6\text{-}C_6H_4Me)(CO)_8]$ (**3**) with thermal ellipsoids at the 30% probability level. Bond lengths (Å): Ru(1)–Ru(2) 2.786(1), Ru(1)–Ru(3) 2.887(1), Ru(2)···Ru(3) 3.929(1), Ru(1)–I(1) 2.716(1), Ru(2)–I(1) 2.732(1), Ru(2)–C(1) 2.103(6), Ru(3)–C(1) 2.321(8), Ru(3)–C(2) 2.270(8), Ru(3)–C(3) 2.284(7), Ru(3)–C(4) 2.320(7), Ru(3)–C(5) 2.307(7), Ru(3)–C(6) 2.278(8).

and $\mu,\eta^1{:}\eta^1$ modes of Ph are also known,[6a,10] and there may be intermediates with these types of aryl coordination in the formation of **2**. We are now modifying the reaction conditions to try to improve yields of **2** and **3** so that the reactivities of these compounds may be easily explored.

Attempting to prepare analogues of **2** and **3** with naphthyl and phenanthryl bridges, we carried out similar reactions with 1-iodonaphthalene and 9-iodophenanthrene, but we were unable to isolate or even observe spectroscopically any clusters related to clusters **2** and **3**. In spite of substantial decomposition to a black material which did not elute on TLC (SiO_2) workup, we obtained small quantities of a red product in each case which were shown to be the iodo-free clusters $[Ru_4(\mu_4,\eta^2\text{-}C_{10}H_6)(CO)_{12}]$ (**4**) (12%) and $[Ru_4(\mu_4,\eta^2\text{-}C_{14}H_8)(CO)_{12}]$ (**5**) (15%). Cluster **5** was separated with difficulty by TLC from phenanthrene which was formed as a byproduct. The formation of phenanthrene might indicate a free-radical mechanism for the reaction. The fate of the iodine atoms is unknown; no ruthenium iodocarbonyl complexes were identified.

Compounds **4** and **5** have closely similar IR spectra around 2000 cm^{-1} and give parent molecular ions in the FAB mass spectra. Compound **4** gave six and compound **5** four (two of which overlap) ^1H NMR signals as expected for clusters containing a 1,2-naphthyne or a symmetrical 9,10-phenanthryne ligand. Single-crystal X-ray structures of **4** and **5** are closely similar so only that of **5** is reported here (Figure 2).[11] There is approximate molecular C_{2v} symmetry. The plane of the phenanthryne ligand is vertical with the σ-bonds Ru(3)–C(100) [2.167(4) Å) and Ru(4)–C(113) (2.151(5) Å] in the vertical plane. There are π-interactions between C(100)–C(113) and Ru(1) and Ru(2) in the range 2.238(4)–2.257(4) Å. The metal-bonded carbon atoms C(100) and C(113) are associated with longer C–C bonds [1.464(6)–1.476(6) Å] compared with the C–C distances in the noncoordinated C_6 rings which average 1.382 Å. This is the first aryne cluster of the type $[Ru_4(\text{aryne})(CO)_{12}]$ based on an Ru_4C_2 octahedral core, although there are alkyne compounds of this type

---

(7) Typical experimental procedures are as follows. $[Ru_3(\mu\text{-I})(\mu,\eta^1{:}\eta^6\text{-}C_6H_4CH_3)(CO)_8]$ (**2**): A mixture of 4-iodotoluene (0.074 g, 0.34 mmol) and $[Ru_3(CO)_{12}]$ (0.217 g, 0.34 mmol) in *n*-octane (15 mL) was refluxed for 4 h to give a brown suspension. The solvent was removed and the residue separated by preparative TLC on silica (eluent: 1:1 CH_2Cl_2–hexane) to give a yellow band identified as $[Ru_3(CO)_{12}]$ and a very weak uncharacterized orange band, followed by a third, yellow band from which **2** was isolated as orange crystals (14%), suitable for single-crystal X-ray diffraction, by crystallization from a dichloromethane–heptane mixture. Anal. Calcd for $C_{15}H_7IO_8Ru_3$: C, 26.57; H, 0.93. Found: C, 25.99; H, 1.06. Cluster **1** was prepared similarly but could not be crystallized. $[Ru_4(\mu_4,\eta^2\text{-}C_{14}H_8)(CO)_{12}]$ (**4**): A mixture of $Ru_3(CO)_{12}$ (0.263 g, 0.413 mmol) in *n*-octane (15 mL) and 9-iodophenanthrene (0.125 g, 0.411 mmol) was refluxed for 6 h, and the solvent was removed to give a dark powder. Preparative TLC (1:1 CH_2Cl_2–hexane) gave a yellow band yielding $[Ru_3(CO)_{12}]$, followed by a red band from which **4** was isolated as red crystals (15%) by recrystallization from a dichloromethane–heptane mixture. Anal. Calcd for $C_{26}H_8O_{12}Ru_4$: C, 33.97; H, 1.08. Found: C, 33.92; H, 0.99.

(8) Selected spectroscopic data (IR for cyclohexane solutions; ^1H NMR at 400 MHz for $CDCl_3$ solutions, *J* in Hz) are as follows: Data for **2**: IR $\nu(CO)/cm^{-1}$ 2080 s, 2050 vs, 2019 s, 2009 s, 1992 s, 1983 s, 1974 w, 1963 w; ^1H NMR δ 6.63 (tt, 1H, *J* 6.1, 1.2), 6.12 (td, 1H, *J* 1.3, 6.8), 5.96 (dt, 1H, *J* 1.2, 6.3), 5.39 (dt, 1H, *J* 1.3, 6.4), 4.78 (td, 1H, *J* 1.2, 6.6). Data for **3**: IR $\nu(CO)/cm^{-1}$ 2079 m, 2049 vs, 2017 s, 2008 s, 1991 s, 1981 s, 1971 w, 1961 w; ^1H NMR δ 6.08 (dd, 1H, *J* 6.8, 1.3), 5.99 (dd, 1H, *J* 6.5, 1.7), 5.43 (dd, 1H, *J* 6.7, 1.8), 4.68 (dd, *J* 6.6, 1.3), 2.52 (s, 3H). Data for **4**: IR $\nu(CO)/cm^{-1}$ 2093 w, 2068 vs, 2044 vs, 2035 vs, 2011 s, 1985 w, 1975 m; ^1H NMR δ 7.85 (d, 1H, *J* 9.0), 7.62 (dd, 1H, *J* 7.7, 1.0), 7.52 (dt, 1H, *J* 7.5, 1.3), 7.44 (dt, 1H, *J* 7.4, 1.3), 7.40 (dm, 1H, *J* 7.9), 6.70 (d, 1H, *J* 8.8). Data for **5**: IR $\nu(CO)/cm^{-1}$ 2093 w, 2068 vs, 2044 vs, 2038 vs, 2012 s, 1986 w, 1974 m; ^1H NMR δ 8.40 (m, 2H), 7.52 (m, 4H), 7.34 (m, 2H).

(9) Crystal data for **3**: $C_{15}H_7IO_8Ru_3$, monoclinic, $P2_1/c$, $a = 9.540(2)$ Å, $b = 13.940(2)$ Å, $c = 15.415(2)$ Å, $\beta = 107.48(1)°$, $V = 1955(1)$ Å^3, $Z = 4$, $M = 745.33$, $D_c = 2.04$ g cm^{-3}, μ(Mo Kα) = 38.47 cm^{-1}, $\lambda = 0.710\ 73$ Å. Intensity data were collected on a crystal of dimensions 0.30 × 0.38 × 0.40 mm on a Nicolet R3v/m diffractometer with graphite monochromator. A total of 4030 reflections were used with $I > 3\sigma(I)$. Solution was by direct methods with full-matrix least-squares refinement of 244 parameters. $R = 0.044$, and $R_w = 0.060$.

(10) Hoferkamp, L. A.; Rheinwald, G.; Stoeckli-Evans, H.; Süss-Fink, G. *Organometallics* **1996**, *15*, 704. (b) Arce, A. J.; Arrojo, P.; Deeming, A. J.; De Sanctis, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 1491.

(11) Crystal data for **5**: $C_{26}H_8O_{12}Ru_4$, monoclinic, $C2/c$, $a = 16.878(2)$ Å, $b = 9.444(2)$ Å, $c = 34.547(5)$ Å, $\beta = 90.57(1)°$, $V = 5504(1)$ Å^3, $Z = 8$, $T = 293(1)$ K, $M = 916.62$, $D_c = 2.21$ g cm^{-3}, μ(Mo Kα) = 21.75 cm^{-1}, $\lambda = 0.710\ 73$ Å. Intensity data were collected on a crystal of dimensions 0.65 × 0.40 × 0.30 mm on a Nicolet R3v/m diffractometer with graphite monochromator. A total of 5259 reflections were used with $I > 3\sigma(I)$. Solution was by direct methods with full-matrix least-squares refinement of 379 parameters. $R = 0.036$, and $R_w = 0.044$.

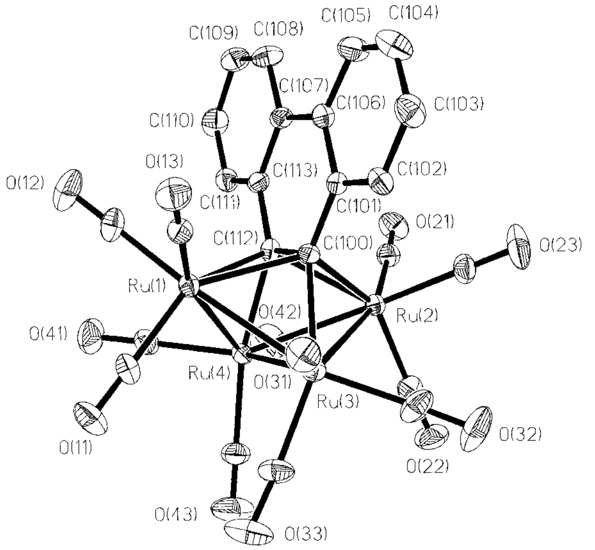


Figure 2. Structure of $[Ru_4(\mu_4,\eta^2\text{-}C_{14}H_8)(CO)_{12}]$ (**5**) with thermal ellipsoids at the 30% probability level. Bond lengths (Å): Ru(1)−Ru(3) 2.706(1), Ru(1)−Ru(4) 2.751(1), Ru(2)−Ru(3) 2.734(1), Ru(2)−Ru(4) 2.719(1), Ru(3)−Ru(4) 2.865(1), Ru(3)−C(100) 2.167(4), Ru(4)−C(113) 2.151(5), Ru(1)−C(100) 2.244(4), Ru(1)−C(113) 2.249(4), Ru(2)−C(100) 2.238(4), Ru(2)−C(113) 2.257(4), C(100)−C(101) 1.476(6), C(100)−C(113) 1.464(6), C(113)−C(112) 1.468(6).

known for Ru.[12] The other known example of a 1,2-naphthyne Ru_4 cluster is geometrically very different from **4**. Reaction of tris(1-naphthyl)arsine with $[Ru_3(CO)_{12}]$ gives, among other products, the 1,2-naphthyne cluster $[Ru_4(\mu_4,\eta^2\text{-}C_{10}H_6)(AsC_{10}H_7)(CO)_{11}]$ (**6**).[13] A square Ru_4 arrangement is adopted for the 62-electron cluster **6**, whereas clusters **4** and **5** are 60-electron clusters with butterfly geometries. Whereas the naphthyne plane is vertical in **4**, it lies 75.3° to the metal plane in **6** and benzyne ligands in the closely related clusters $[Ru_4(\mu_4,\eta^2\text{-}C_6H_4)(PR)(CO)_{11}]$ (R = Ph, Fc, CH_2NPh_2) are ataround 51° to the metal plane and are considered to be 6-electron-donating $\eta^1{:}\eta^1{:}\eta^4$ ligands.[14]

The reason that two types of products are formed from iodobenzene, 4-iodotoluene, 1-iodonaphthalene, and 9-iodophenanthrene is not clear to us. Possibly the latter two compounds form clusters like **2** and **3** initially before further reaction with more $[Ru_3(CO)_{12}]$ to give clusters **4** and **5**, respectively. Cluster **2** was reacted with $[Ru_3(CO)_{12}]$ in an attempt to form the benzyne compound $[Ru_4(\mu_4,\eta^2\text{-}C_6H_4)(CO)_{12}]$, but there was no evidence for this compound from this reaction. However, our results do point to the potential of iodoarenes as precursors to aryl and aryne ligands in ruthenium clusters and we are examining other examples to develop this chemistry.

Acknowledgment. We thank the EPSRC for financial support.

Supporting Information Available: Text giving synthetic experimental details and tables giving crystal data and a structure determination summary, atomic coordinates, bond distances and angles, thermal parameters, and hydrogen atoms positions for clusters **3** and **5** (14 pages). Ordering information is given on any current masthead page. Observed and calculated structure factors are available from the authors on request.

OM960878S

---

[12] (a) Johnson, B. F. G.; Lewis, J.; Reichert, B. E. Schorpp, K. T.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1417. (b) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Will, G. J.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Chem. Commun.* **1980**, 1190.

[13] Cullen, W. R.; Rettig, S. T.; Zheng, T. C. *Organometallics* **1995**, *14*, 1466.

[14] Knox, S. A. R.; Lloyd, B. R.; Morton, D. A. V.; Nicholls, S. M.; Orpen, A. G.; Viñas, J. M.; Weber, M.; Williams, G. K. *J. Organomet. Chem.* **1990**, *394*, 385. Zheng, T. C.; Cullen, W. R.; Rettig, S. J. *Organometallics* **1994**, *13*, 3594.