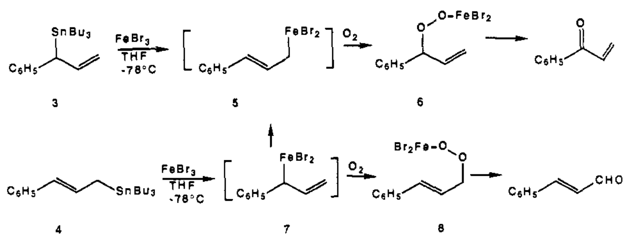

3-Phenylprop-2-enyltributyltin (**4**) was synthesized in 81% yield by the reaction of phenylpropenyllithium[3] with tri-*n*-butyltin triflate[4] in tetrahydrofuran (THF) at −78 °C initially and then at −78 °C to 23 °C over 10 min. Although **3** undergoes isomerization to **4** upon heating to 80 °C in benzene,[2] no interconversion of **3** and **4** occurred under the conditions of any of the experiments described herein.

Both **3** and **4** are stable against reaction with O_2 (1 atm) in various solvents for prolonged periods at room temperature. However, slow addition of a cold (−78 °C) solution of **3** in THF to a stirred solution of 1.2 equiv of anhydrous $FeBr_3$ in THF saturated with O_2 (1 atm) at −78 °C resulted in a very rapid reaction which produced in less than 1 min phenyl vinyl ketone as the only volatile product in 70% yield.[5] In contrast, under the same conditions **4** was converted mainly to cinnamaldehyde (60%) with phenyl vinyl ketone as a minor product (10% yield).[6] Both cinnamaldehyde and phenyl vinyl ketone are stable under both reaction and isolation conditions. This result immediately renders a free-radical mechanism improbable as a major pathway since **3** and **4** clearly should give the same product(s) via the common allyl radical.[7] In fact, when the phenylallyl radical is generated in THF at −78 °C under 1 atm of O_2 by the reaction of 3-phenylprop-2-enylmercuric bromide[3] with tri-*n*-butyltin hydride approximately equal amounts of primary and secondary benzylic oxygenation products (cinnamaldehyde, cinnamyl alcohol, and phenyl vinyl ketone) are formed.

The most reasonable nonradical mechanism for formation of the above described oxidation products from **3** or **4** involves electrophilic S_E2' attack by $FeBr_3(\cdot 2THF)$ on the allylic tin compound to generate a σ-organoiron intermediate which is then trapped by O_2.[8] The nature of the products suggests that the metalloene reaction with O_2 via a six-membered cyclic transition state is somewhat faster than σ-insertion of O_2 (four-membered transition state) at −78 °C in this particular system. Thus **3** would be converted to the organoiron intermediate **5** which would be transformed into phenyl vinyl ketone via **6**. Similarly S_E2' reaction of $FeBr_3$ with **4** would give **7**, which by metalloene reaction with O_2 would form **8**, the precursor of the major product cinnamaldehyde. The pathway from **4** to the minor product phenyl vinyl ketone appears to involve a 1,3-iron rearrangement which converts **7** to the more stable primary organoiron compound **5** at a rate that is roughly one-sixth that for oxygenation of **7**. Support for this possibility was obtained from an experiment in which **4** and $FeBr_3$ were allowed to react in THF at −78 °C with 2 equiv of O_2 as a 20:1 mixture of Ar–O_2 at 1 atm. Under these conditions phenyl vinyl ketone predominated over cinnamaldehyde by a factor of 3. This experimental result clearly argues against the formation of *both* cinnamaldehyde and phenyl vinyl ketone from **7** by competing metalloene and σ-O_2 insertion processes since the balance between these would be independent of O_2 concentration.

Interestingly, slow addition of either **3** or **4** to a solution of $FeBr_3$ in THF at 0 °C under an atmosphere of O_2 afforded essentially the *same* mixture of products: cinnamaldehyde (60% yield) and phenyl vinyl ketone (10% yield). It seems likely that under these conditions the products formed from **3** and **4** derive from the same organoiron intermediate. A free-radical-mediated process again seems unlikely since the product ratio is far from the expected 1:1. Whether the organoiron intermediate is the primary σ compound **5** or a π-allyl organoiron structure cannot be decided at present. Nonetheless it is clear that this organoiron system is one of delicate balance either between σ- and π-organoiron structures or metalloene and σ-bond–O_2 insertion pathways, with major perturbations possible with changing temperature or metal ligands.

The iron-mediated oxygenation reaction described above shows that the reaction of allylic organoiron intermediates with O_2 is a very facile process, fully able to compete with homolytic cleavage of the carbon–iron bond. Although it was not possible to demonstrate direct insertion of O_2 into the carbon–iron bond in the reactions of **3** or **4** with $FeBr_3$ and O_2, such insertions are known for other σ-carbon–transition-metal compounds.[9] Obviously, in the case of enzymatic lipoxygenation of unsaturated acids the balance between the reaction paths available to an organoiron intermediate will differ from the simple chemical system described herein, since major metal ligand and protein-binding effects can be expected. Further research is in progress to extend this study to other allylic systems and Fe(III) reagents.[10]

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(2) Jephcote, V. J.; Thomas, E. J. *Tetrahedron Lett.* **1985**, *26*, 5327–5330.

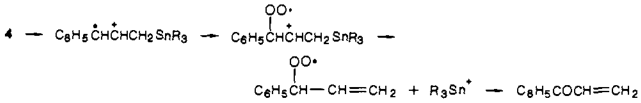
(3) A deep red solution of this lithium reagent in THF was prepared by reaction of 3-phenyl-1-propene with *n*-butyllithium at −20 °C for 1 h, see: Herbrandson, H. F.; Mooney, D. S. *J. Am. Chem. Soc.* **1957**, *79*, 5809–5814. Reaction of the lithium reagent with trimethylchlorosilane gave exclusively the primary trimethylsilyl derivative. Similarly, reaction with mercuric acetate at −20 °C followed by workup with aqueous sodium bromide gave the primary bromomercuric derivative as a crystalline solid.

(4) Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* **1984**, *25*, 2415–2418.

(5) Capillary gas chromatographic analysis using a DB-1 silicone column at 40 °C (5 min), rising to 100 °C over 5 min, and maintained at 100 °C. Cinnamaldehyde and phenyl vinyl ketone had retention times of 11.2 and 9.4 min, respectively.

(6) 5-Phenyl-(2*Z*)-pentenyltri-*n*-butyltin, the analogue of **4** with 2-phenylethyl in place of phenyl, underwent reaction with $FeBr_3$ and O_2 (1 atm) in THF solution at −78 °C to form 69% of 5-phenyl-(2*Z*)-pentenal and 11% of 5-phenyl-1-penten-3-one, an almost identical result with that reported above for **4**. In addition, the dependence of product ratio on O_2 pressure at −78 °C in THF was essentially the same for **4** and the (2-phenylethyl) analogue.

(7) (a) It is conceivable that the phenylallyl radical could result from **3** and **4** by electron transfer to $FeBr_3$ which would also produce $FeBr_2$ and Bu_3SnBr. (b) A radical–cation mechanism is also implausible for the observed iron-mediated oxidation of **3** or **4**, since it leads to incorrect prediction of products: for example, from **4** the formation of phenyl vinyl ketone is predicted (contrary to the experimental results) via the sequence



$$4 \rightarrow C_6H_5\dot{C}H\overset{+}{C}HCH_2SnR_3 \rightarrow C_6H_5\overset{\overset{OO\cdot}{|}}{C}H\overset{+}{C}HCH_2SnR_3 \rightarrow C_6H_5\overset{\overset{OO\cdot}{|}}{C}H{-}CH{=}CH_2 + R_3Sn^+ \rightarrow C_6H_5COCH{=}CH_2$$

(8) The strong preference for S_E2' over S_E2 attack by electrophiles on allylstannanes and allylsilanes is heavily documented in the literature.

(9) See, for example: Duong, K. N. V.; Fontaine, C.; Gianotti, C.; Goudemer, A. *Tetrahedron Lett.* **1971**, 1187–1189.

(10) This work was assisted financially by grants from the National Science Foundation and the National Institutes of Health.

Carbon–Hydrogen Bond Activation by Electrophilic Transition-Metal Compounds. Palladium(II)-Mediated Oxidation of Arenes and Alkanes Including Methane

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Received June 17, 1987

The activation of carbon–hydrogen bonds by transition metals that leads to the *selective functionalization* of hydrocarbons, especially alkanes, is one of the most challenging problems in organometallic chemistry.[2] Herein, we report our results on the

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(1) Alfred P. Sloan Research Fellow, 1984–1988.

(2) Reviews: (a) Halpern, J. In *Fundamental Research in Homogeneous Catalysis*; Shilov, A. E., Ed.; Gordon and Breach: New York, 1986; Vol. 1, p 393. (b) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition-Metal Complexes*; D. Reidel: Dordrecht, 1984. (c) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (d) Bergman, R. G. *Science* (*Washington, D.C.*) **1984**, *223*, 902.

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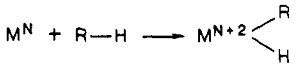
palladium(II)-mediated oxidation of arenes and alkanes through a *nonradical, electrophilic* C–H activation pathway.

The two common modes for the nonradical activation of C–H bonds are oxidative addition (eq 1) and electrophilic displacement (eq 2) pathways. Although the reaction depicted in eq 1 has been demonstrated even for alkanes,[3] this reaction usually requires the generation of high-energy, coordinatively unsaturated metal species (usually photochemically). Unfortunately, the presence of such highly reactive metal species generally precludes the simultaneous presence of most reagents capable of functionalizing the bound hydrocarbyl group in the oxidative addition product. Thus, it is difficult to construct a "one-pot" procedure for the functionalization of arenes and alkanes, based on eq *1*.[4]



$$M^N + R{-}H \longrightarrow M^{N+2}\langle^{R}_{H} \quad (1)$$

$$M^N + R{-}H \longrightarrow M^N{-}R^- + H^+ \quad (2)$$

(R = hydrocarbyl)

The electrophilic displacement (heterolytic cleavage) pathway (eq 2) is generally more favorable than the corresponding oxidative addition reaction for two reasons.[2a,5] First, the low reactivity of alkanes vis-a-vis most metal compounds is due, at least in part, to the absence of low-lying unoccupied orbitals. Hence, reactions involving such molecules often require the promotion of electrons into antibonding orbitals. Accordingly, the reactivity of alkanes is expected to be highest toward species having low-lying unoccupied orbitals, i.e., electrophiles. Second, the driving force for processes such as eq 2 can be favorably influenced by the stabilization of the leaving group, H^+.

In principle, it is possible to design a metal-mediated procedure for the oxidation of arenes and alkanes that is based on eq 2. The oxidant could be the metal itself, and the Pd(II) ion is a particularly attractive choice for two reasons. First, Pd(II) is both a strong electrophile[6] and a good $2e^-$ oxidant[7] (thus avoiding the formation of radicals). Second, Pd metal is readily oxidized back to Pd(II) by using several different cooxidants and this forms the basis of several Pd(II)-catalyzed oxidation processes (e.g., the Wacker process).[8]

Equation 3 summarizes our method for the functionalization of arenes and alkanes by using the Pd(II) ion both as an electrophile and an oxidant. The steps involved in eq 3 are not totally unprecedented since Shilov et al. have postulated a similar mechanistic pathway for the oxidation of hydrocarbons by a combination of Pt(II) and Pt(IV) reagents.[9] In addition, the alkylation of arenes by electrophilic palladium(II)–benzyl complexes that we have reported earlier[10] presumably proceeds through an analogous mechanism.

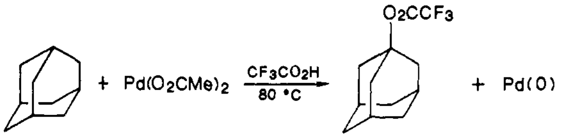
$$\begin{array}{c} Pd^{2+} + R{-}H \rightleftharpoons Pd{-}R^+ + H^+ \\ \downarrow {:}Nu^- \\ Pd(0) + R{-}Nu \end{array} \quad (3)$$

(:Nu^- = nucleophile)

The initial problem involved the proper choice of solvent, and CF_3CO_2H was selected for several reasons. The $CF_3CO_2^-$ ion is a relatively poor base and $M{-}O_2CCF_3$ bonds are known to be quite labile.[11] Thus, the Pd(II) species present in this system is expected to be highly electrophilic. Also, CF_3CO_2H lacks C–H bonds and is a good solvent for a wide range of organic substrates.

Heating equimolar amounts of adamantane and $Pd(O_2CMe)_2$ in CF_3CO_2H (i.e., effectively $Pd(O_2CCF_3)_2$[12]) at 80 °C resulted in the precipitation of Pd metal and the formation of 1-adamantyl trifluoroacetate in >50% yield in 1 h[13] (eq 4).

Perhaps more significantly, CH_4 (at 800 psi) was oxidized to CF_3CO_2Me in >60% yield (relative to Pd(II)), under the same conditions[13] (eq 5). We note that the only previous report of transition-metal-mediated oxidation of CH_4 was a low yield reaction.[9] Since the ester can be hydrolyzed to the corresponding alcohol, the overall reaction can be written as follows (eq 6).



(4)

$$CH_4 + Pd(O_2CMe)_2 \xrightarrow[80\ ^\circ C]{CF_3CO_2H} CF_3CO_2CH_3 + Pd(0) \quad (5)$$

$$R\text{-}H + Pd^{2+} + H_2O \rightarrow R\text{-}OH + Pd(0) + 2H^+$$

$$(R = 1\text{-adamantyl}, CH_3) \quad (6)$$

If the electrophilic displacement step in eq 3 is reversible, the incorporation of deuterium into the starting alkane may be expected in the presence of CF_3CO_2D. However, no deuterium incorporation into admantane was observed during its oxidation thus indicating that the subsequent nucleophilic attack was fast.

Further information concerning the mechanism of the Pd(II) oxidation of hydrocarbons was obtained through the study of arene oxidations which were also performed at 80 °C with use of $Pd(O_2CMe)_2$ in CF_3CO_2H.[13] Under these conditions, the monotrifluoroacetoxylation of 1 equiv of *p*-dimethoxybenzene proceeded to completion in 1 h.[14] Under identical conditions, monotrifluoroacetate esters of *p*-xylene were obtained in 35% yield. Furthermore, competition experiments indicated the following relative oxidation rates: *p*-dimethoxybenzene (1), *p*-xylene (0.1), toluene (0.02), benzene (0).[15] For *p*-xylene and toluene, attack on the ring rather than the benzylic position accounted for >97% and >90%, respectively, of the monotrifluoroacetate esters obtained (eq 7). This result is in sharp contrast to that reported for the $PtCl_4^{2-}$-mediated H–D exchange reaction where para-disubstituted benzenes do not exchange ring hydrogens at all.[9] For example, only the benzylic positions undergo H–D exchange in *p*-xylene. The two conclusions that can be drawn from our own observations on Pd(II) oxidations are that (a) radical pathways are *not* involved since the weak benzylic C–H bonds were not attacked to any

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(3) Leading references: (a) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (b) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726. (c) Jones, W. D.; Maguire, J. A. *Organometallics* **1987**, *6*, 1301. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814. (e) Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1987**, *6*, 696. (f) Felkin, H.; Fillebeen-Khan, T.; Gault, Y.; Holmes-Smith, R.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, 1279. (g) Nemeth, S.; Jenson, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442. (h) Chetcuti, P. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1987**, *109*, 942.

(4) An obvious exception is the metal-mediated dehydrogenation of alkanes, see: ref 3c,e,f. For other examples of functionalization of arenes and alkanes that proceed through an oxidative addition step, see: (a) Jones, W. D.; Foster, G. P.; Putinas, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5047. (b) Jones W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640. (c) Fisher, B. J.; Eisenberg, R. *Organometallics* **1983**, *2*, 764. (d) Gustavson, W. A.; Epstein, P. S.; Curtis, M. D. *Organometallics* **1982**, *1*, 884.

(5) Leading references for related "four-center" electrophilic activation of hydrocarbons by early transition-metal lanthanide and actinide complexes: (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santasiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (c) Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805.

(6) Specific examples: (a) Lai, T.-W.; Sen, A. *Inorg. Chem.* **1984**, *23*, 3257. (b) Sen, A.; Lai, T.-W. *Organometallics* **1983**, *2*, 1059. (c) Sen, A.; Lai, T.-W. *Organometallics* **1982**, *1*, 415. (d) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627.

(7) Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; D. Reidel: Dordrecht, 1980.

(8) Reference 7, Chapter II.

(9) Reference 2b, Chapter V.

(10) Gretz, E.; Sen, A. *J. Am. Chem. Soc.* **1986**, *108*, 6038.

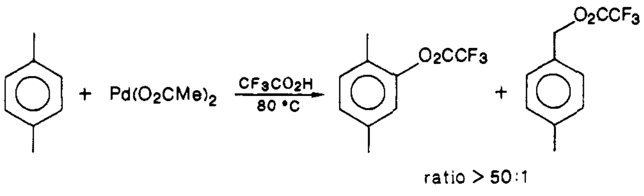
(11) Review: Garner, C. D.; Hughes, B. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 1.

(12) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

(13) No effort was made to exclude oxygen from this or other reactions described. Good yields of the products were obtained only by using *fresh* $Pd(O_2CMe)_2$. This was particularly critical for CH_4 oxidation. For example, depending on the sample of $Pd(O_2CMe)_2$ used, reaction times of several hours to several days were required to obtain a high yield of CF_3CO_2Me and Pd(0).

(14) Pd(II)-mediated ring acetoxylation of arenes, although known, remains poorly understood, see: ref 7, Chapter VI.

(15) Significant quantities of biaryls, formed by a mechanistically unknown pathway (ref 7, Chapter VI), were also observed for toluene and benzene.



(7)

significant extent and (b) the enhanced rate of oxidation with electron-rich arenes is consistent with an electrophilic displacement pathway as shown in eq 2 and 3.

By using toluene-d_0 and toluene-d_8, a primary isotope effect (k_H/k_D) of 5.0 (5) was observed for the oxidation reaction. The magnitude of the isotope effect clearly indicates that the rate-determining step involves C–H bond breaking rather than a simple π-coordination of the arene or the formation of a Wheland intermediate.[16] The formation of the latter species has been proposed as the slow step in the electrophilic metalation of arenes by Pt(IV).[17]

Finally, preliminary results indicate that the Pd(II)-mediated monotrifluoroacetoxylation of *p*-dimethoxybenzene can be made catalytic in Pd(II) by using $K_2S_2O_8$ as the cooxidant. For example, quantitative conversion of *p*-dimethoxybenzene was observed in 1 h at 80 °C in CF_3CO_2H, starting with the following concentrations: *p*-dimethoxybenzene (0.43 M), $Pd(O_2CMe)_2$ (0.09 M), and $K_2S_2O_8$ (1.1 M).

Acknowledgment. This research was funded by a grant from the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-84ER13295). We also thank Johnson Matthey, Inc. for a generous loan of palladium.

Registry No. $Pd(O_2CMe)_2$, 301-04-2; CH_4, 74-82-8; CF_3CO_2Me, 431-47-0; adamantane, 281-23-2; 1-adamantyl trifluoroacetate, 58652-54-3; *p*-dimethoxybenzene, 150-78-7; *p*-xylene, 106-42-3.

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(16) Reviews on isotope effects in aromatic electrophilic substitutions: (a) Zollinger, H. *Adv. Phys. Org. Chem.* **1964**, *2*, 163. (b) Berliner, E. *Prog. Phys. Org. Chem.* **1964**, *2*, 253.

(17) Shul'pin, G. B.; Nizova, G. V.; Nikitaev, A. T. *J. Organomet. Chem.* **1984**, *276*, 115. However, the mercuration of arenes is usually accompanied by large isotope effects: Lau, W.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 6720.

Synthesis and Structure of $Os_4(CO)_{16}$, a Metal Carbonyl Analogue of Cyclobutane

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We have recently described the synthesis of $Os_4(CO)_{15}$ (from $Os_3(CO)_{10}(C_8H_{14})_2$ and $Os(CO)_5$) along with the determination of its structure.[1] This was believed to be the first report of a tetranuclear binary carbonyl of osmium. At that time we remarked that, given the stability of $Os_3(CO)_{12}$, one might expect $Os_4(CO)_{16}$ would be stable. We now find that this intriguing cluster can be readily prepared from $Os_4(CO)_{15}$ but that, contrary to arguments based on simple bonding theory, the cluster is not particularly stable.

Treatment of $Os_4(CO)_{15}$[1] in CH_2Cl_2 at 0 °C with an atmosphere of CO caused essentially quantitative conversion to $Os_4(CO)_{16}$ (**1**) after 4 h; the compound was isolated (86% yield) as air-stable, yellow-orange crystals.[2] The structure of **1**[3] (Figure 1) shows a puckered Os_4 framework (the dihedral angle between the planes Os(1)–Os(2)–Os(3) and Os(1)–Os(3)–Os(4) is 158.9°), i.e., the compound is a metal carbonyl analogue of cyclobutane. The puckered configuration allows shorter, potentially bonding interactions between diagonally related osmium atoms and relieves the steric interactions between carbonyls syn to each other.[4] Unlike **1**, the syn carbonyls in $Os_3(CO)_{12}$ are eclipsed, an observation that has been taken to indicate that electronic considerations are more important than steric factors in determining the conformation of $Os_3(CO)_{12}$.[5]

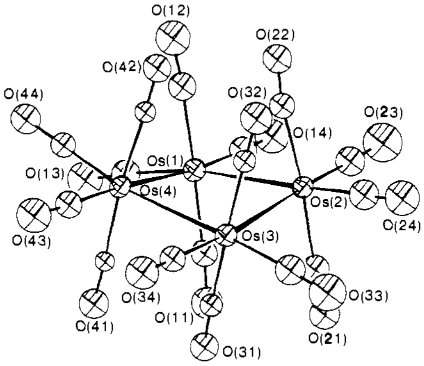

Figure 1. Molecular structure of $Os_4(CO)_{16}$ (**1**). Selected bond distances (Å) and angles (deg) not mentioned in the text: Os–C_{eq} range 1.84 (3)–1.91 (3), Os–C_{ax} range 1.92 (2)–1.97 (2), Os–Os–Os range 88.73 (3)–89.27 (3).

The metal–metal bonds in **1** are remarkably long for Os–Os single bonds: Os(1)–Os(2) = 2.997 (1) Å, Os(1)–Os(4) = 2.985 (1) Å, Os(2)–Os(3) = 2.979 (1) Å, Os(3)–Os(4) = 3.000 (1) Å. In $Os_3(CO)_{12}$, the average Os–Os bond length is 2.877 (3) Å. This indicates the metal–metal bonds in **1** are weak. In agreement with this view, **1** decomposes when stirred in hexane solution (under N_2) to give mainly $Os_3(CO)_{12}$[7] plus traces of $Os_4(CO)_{15}$[8] after 30 h, i.e., *$Os_4(CO)_{16}$ is thermodynamically unstable with respect to $Os_3(CO)_{12}$.* The metal–metal bonds in $Os_3(CO)_{12}$ are often regarded as two-center–two-electron bonds.[9] If this were the case then it might be expected that, even allowing for the increase in the steric interactions of the equatorial carbonyls, **1** would be more stable than $Os_3(CO)_{12}$. This is because in the former cluster the angles about the osmium atoms more closely approach the 90° required for octahedral coordination. That **1** is less stable than $Os_3(CO)_{12}$ suggests that the most important component of the metal–metal bonding in $Os_3(CO)_{12}$ is the occupancy of a molecular orbital that can be considered the result of the overlap of an atomic

---

(1) Johnston, V. J.; Einstein, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.* **1987**, *109*, 7220–7222.

(2) Anal. Calcd for $C_{16}O_{16}Os_4$: C, 15.90; H, 0.0. Found: C, 15.89; H, 0.0. Ir ν(CO) (hexane) 2075.5 (vs), 2054 (m), 2036.5 (s), 2018.5 (w), 2000 (w), 1993 (sh) cm^{-1}; ^{13}C NMR (CH_2Cl_2/CD_2Cl_2, 5/1, ambient temperature) δ 168.8 and 176.6. A satisfactory mass spectrum (EI, FAB) could not be obtained; peaks due to $[Os_3(CO)_{12}]^+$, $[Os_6(CO)_{18}]^+$, etc. observed in EI spectrum.

(3) X-ray diffraction data for $Os_4(CO)_{16}$: $M_r = 1208$; triclinic; space group $P\bar{1}$; $a = 9.436$ (1) Å, $b = 9.482$ (1) Å, $c = 14.082$ (2) Å, $\alpha = 87.67$ (1)°, $\beta = 79.09$ (1)°, $\gamma = 69.69$ (1)°; $V = 1159.93$ Å^3; $D_c = 3.462$ g cm^{-3} (an empirical absorption correction was applied); diffractometer, Enraf-Nonius CAD4F; radiation, Mo Kα, graphite monochromator ($\lambda(K\alpha_1)$ 0.709 30 Å); scan range = $0° \leq 2\theta \leq 50°$; reflections = 3019 with $I_o \geq 2.5\sigma(I_o)$; (no. of variables = 166) $R_f = 0.0448$, $R_w = 0.0538$.

(4) Torsion angles around Os–Os bonds are similar for opposite bond pairs: C(11)–Os(1)–Os(2)–C(21) = 6.4 (9)°, C(31)–Os(3)–Os(4)–C(41) = 8.4 (10)°; C(11)–Os(1)–Os(4)–C(41) = 25.6 (9)°, C(21)–Os(2)–Os(3)–C(31) = 25.4 (9)°.

(5) Lauher, J. W. *J. Am. Chem. Soc.* **1986**, *108*, 1521.

(6) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(7) It is most probable that **1** is the unidentified intermediate observed in the decomposition of $Os_2(CO)_9$ in heptane: Moss, J. R.; Graham, W. A. G. *J. Chem. Soc., Dalton Trans.* **1977**, 95.

(8) That the cluster $Os_4(CO)_{15}$ is stable in hexane solution at room temperature indicates **1** decomposes by different pathways to give $Os_3(CO)_{12}$ and $Os_4(CO)_{15}$.

(9) For example: (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 1083. (b) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: Chicester, England, 1980; p 211.

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