

Preliminary communication

OXIDATIVE ADDITION REACTIONS OF $\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})\text{Me}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$). ISOLATION OF INTERMEDIATES DURING ALKYL—METAL ELECTROPHILIC CLEAVAGE REACTIONS

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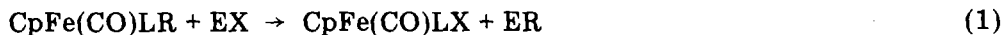
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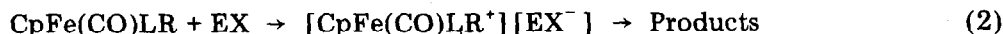
Summary

The compound $\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})\text{Me}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) (II) reacts with bromine and mercury(II) bromide to give $\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})\text{Br}$ (III) and either methyl bromide or methylmercuric bromide, respectively. The compounds $[\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{Me})\text{Br}]\text{Br}$ (IV) and $[\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{Me})(\text{HgBr})]\text{Br}$ (V), both formally complexes of osmium(IV), are isolable intermediates in the electrophilic cleavage reactions.

The mechanisms of electrophilic cleavage of transition metal—carbon σ bonds have been the subject of intense scrutiny in recent years, alkyliron compounds of the general formula $\text{CpFe}(\text{CO})\text{LR}$ (L = CO, tertiary phosphine; R = alkyl) being the metal system studied most extensively [1–6]. In general, cleavage reactions with electrophilic reagents EX (E = H, X, HgX, X = Cl, Br, I) proceed as in eq. 1.



Although earlier workers [1] believed that such reactions involved bimolecular $\text{S}_{\text{E}}2$ processes, we [2] and others [3–6] have presented evidence that attack occurs not at the metal—carbon bond, but rather directly at the metal. The reactions involve one- or two-electron transfer processes to give intermediates containing iron in the formal oxidation states +3 or +4, as in eq. 2 or 3, respectively.



Unfortunately, firm evidence for the oxidized intermediates postulated in

eq. 2 and 3 has been difficult to obtain, as any intermediates formed in eq. 1, 2 or 3 are very short-lived under normal reaction conditions. We [2c] and Giering et al. [6] have utilized rapid scan cyclic voltammetry at low temperatures to detect unstable species which have been characterized chemically and spectroscopically as oxidized species [6,7]. However, no iron(III) or iron(IV) complexes have been isolated, although rather similar ruthenium [8,9a] and osmium [9] compounds have been reported. We recently noted that compounds of higher oxidation states of ruthenium might be expected to be generally more stable than those of iron, but a chemical and electrochemical study of compounds of the type $\text{CpRu}(\text{CO})\text{LR}$ showed that our hopes were misplaced [10]. We have therefore initiated an investigation in the chemistry of analogous osmium compounds, in particular compounds containing a pentamethylcyclopentadienyl (Cp^*) group and at least one tertiary phosphine. In this way it was anticipated that it would be possible to obtain compounds more electron rich than those previously studied, and hence more easily oxidized. It also seemed likely that osmium intermediates would exhibit higher bond dissociation energies than do the iron and ruthenium analogues [11], and would therefore be more stable.

The compound $\text{Cp}^*\text{Os}(\text{CO})_2\text{Me}$ (I) ($\nu(\text{CO}) = 1994, 1934 \text{ cm}^{-1}$) was synthesized by treatment of $\text{Cp}^*\text{Os}(\text{CO})_2\text{Br}$ with CuMe [12], and was found to react with Br_2 (instantaneously) and HgBr_2 (4 h) to give $\text{Cp}^*\text{Os}(\text{CO})_2\text{Br}$ and MeBr or MeHgBr , respectively. Interestingly, although I exhibits an oxidation potential [13] comparable with that of $\text{CpFe}(\text{CO})_2\text{Me}$ [2c,6,7], suggesting that intermediates of higher oxidation states may not be stable, such an intermediate in the reaction with HgBr_2 was suggested by the presence of weak bands in the IR spectrum at 2114 and 2040 cm^{-1} . In an attempt, therefore, to isolate an oxidized intermediate, the more electron-rich compound $\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})\text{Me}$ (II) was synthesized by photolysis of I in the presence of PMe_2Ph [14]. The IR spectrum of compound II exhibits $\nu(\text{CO})$ at 1870 cm^{-1} (CH_2Cl_2), the $^{31}\text{P}\{^1\text{H}\}$ spectrum a singlet at $\delta -20.3$ ppm. The ^1H NMR spectrum (CD_2Cl_2) exhibits methyl resonances at δ 0.13 (d, $J(\text{H}-\text{P})$ 6.0 Hz, $\text{Os}-\text{Me}$), 1.62 (d, $J(\text{H}-\text{P})$ 8.9 Hz, $\text{P}-\text{Me}$), 1.66 (d, $J(\text{H}-\text{P})$ 1.1 Hz, Cp^*) and 1.73 (d, $J(\text{H}-\text{P})$ 9.2 Hz, $\text{P}-\text{Me}$), and phenyl resonances at δ 7.5 (m), while the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_2Cl_2) exhibits resonances at $\delta -37.0$ (d, $J(\text{C}-\text{P})$ 7 Hz, $\text{Os}-\text{Me}$), 9.4 and 92.1 (both s, Cp^* Me and C, respectively), 12.6 (d, $J(\text{C}-\text{P})$ 33 Hz, $\text{P}-\text{Me}$), 19.1 (d, $J(\text{C}-\text{P})$ 39 Hz, $\text{P}-\text{Me}$), 127–140 (m, Ph) and 191.6 (d, $J(\text{C}-\text{P})$ 12 Hz, CO). Thus the ^1H and ^{13}C NMR data confirm the chiral nature of II.

Compound II is much more electron-rich than is I [13], exhibiting a one electron (comparison with ferrocene [15]), irreversible oxidation at +0.74 V vs. $\text{Ag}/\text{AgCl}/\text{saturated KCl}$. Treatment of a methylene chloride solution of II with an equimolar amount of bromine produced a pale yellow solution, and inspection of the IR spectrum revealed that the $\nu(\text{CO})$ of I at 1870 cm^{-1} had been replaced by a new band at 2042 cm^{-1} . A well resolved ^1H NMR spectrum revealed a new osmium-methyl resonance at δ 1.26 (d, $J(\text{H}-\text{P})$ 9.6 Hz), while the $^{31}\text{P}\{^1\text{H}\}$ spectrum exhibited only a single new resonance at $\delta -37.2$. The new species was not isolated, as it converted cleanly over

about 2 h to $\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})\text{Br}$ (III) [16] and methyl bromide. However, the very significant increase in $\nu(\text{CO})$ coupled with the observed deshielding of the osmium-methyl resonance on treatment of II with bromine shows clearly that the intermediate contains an oxidized osmium atom. Furthermore, as the ^1H NMR spectrum of the reaction mixture remained well-resolved during the reaction, it would seem that the intermediate is diamagnetic and therefore is the osmium(IV) complex $[\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{Me})\text{Br}]\text{Br}$ (IV).

Reaction of II with HgBr_2 under the same conditions occurred immediately and yielded a yellow solution exhibiting both a new $\nu(\text{CO})$ at 2002 cm^{-1} in the IR spectrum and, in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, a single new resonance at $\delta -45.7$ with spin-spin coupling (720 Hz) to ^{199}Hg . The ^1H and ^{13}C NMR spectra both exhibited new osmium-methyl resonances at $\delta 0.86$ (d, $J(\text{H}-\text{P})$ 9.1 Hz) and $\delta -17.2$ (d, $J(\text{C}-\text{P})$ 11 Hz), respectively. Although all the evidence points to the new compound as being best formulated as $[\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{Me})\text{HgBr}]\text{Br}$ (V), it converts slowly (24–48 h) to III and MeHgBr and was not obtained pure. In an attempt to isolate the intermediate, therefore, equimolar amounts of II and HgBr_2 were allowed to react in methanol and then treated immediately with a solution of NaPF_6 . A pale yellow precipitate of $[\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{Me})\text{HgBr}][\text{PF}_6]$ (Va) [17] formed and was collected. In addition to the above-mentioned spectral information, pertinent spectroscopic data aiding in the formulation of Va are new osmium-methyl resonances in the ^1H and ^{13}C NMR spectra at $\delta 0.94$ (d with ^{199}Hg satellites, $J(\text{H}-\text{P})$ 9.3 Hz, $J(\text{H}-\text{Hg})$ 35.4 Hz) and $\delta -17.7$ (d, $J(\text{C}-\text{P})$ 11 Hz), respectively. The observations of spin-spin couplings of various resonances to the mercury would appear to confirm the presence of a direct mercury-osmium bond [18].

In summary, we have found that $\text{Cp}^*\text{Os}(\text{CO})_2\text{Me}$ (I) resembles its iron analogue in being oxidized electrochemically only at relatively high positive potentials. The osmium-methyl bond can be cleaved rapidly by bromine but only slowly by mercuric bromide, and oxidized intermediates are rather unstable. In contrast, the more electron-rich phosphine-substituted compound $\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})\text{Me}$ (II) exhibits a much lower oxidation potential, and undergoes more facile oxidative addition reactions with bromine and mercuric bromide to give the cationic complexes $[\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{Me})\text{Br}]\text{Br}$ (IV) and $[\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{Me})(\text{HgBr})]\text{Br}$ (V), respectively, both formally complexes of osmium(IV). The latter two complexes are of the type postulated in eq. 3, and in fact both convert cleanly and smoothly to $\text{Cp}^*\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})\text{Br}$ (III) and methyl bromide or methylmercuric bromide, respectively. Preliminary kinetic studies suggest that the conversion of IV to III, at least, is intermolecular, probably involving nucleophilic attack by bromide ion on cationic substrate [2c] rather than intramolecular and involving reductive elimination steps.

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References

- 1 D. Dodd and M.D. Johnson, *J. Chem. Soc. B*, (1971) 662.
- 2 (a) D.A. Slack and M.C. Baird, *J. Am. Chem. Soc.*, **98** (1976) 5539; (b) W.N. Rogers and M.C. Baird, *J. Organomet. Chem.*, **182** (1979) C65; (c) W.N. Rogers, J.A. Page and M.C. Baird, *Inorg. Chem.*, **20** (1981) 3521.
- 3 (a) L.J. Dizikes and A. Wojcicki, *J. Am. Chem. Soc.*, **99** (1977) 5295; (b) T.G. Attig, R.G. Teller, S.-M. Wu, R. Bau and A. Wojcicki, *J. Am. Chem. Soc.*, **101** (1979) 619; (c) N. De Luca and A. Wojcicki, *J. Organomet. Chem.*, **193** (1980) 359.
- 4 H. Brunner and G. Wallner, *Chem. Ber.*, **109** (1976) 1053.
- 5 T.C. Flood and D.L. Miles, *J. Organomet. Chem.*, **127** (1977) 33.
- 6 R.H. Magnuson, S. Zulu, W.-M. T'sai and W.P. Giering, *J. Am. Chem. Soc.*, **102** (1980) 6887.
- 7 (a) R.H. Magnuson, R. Meirowitz, S. Zulu and W.P. Giering, *J. Am. Chem. Soc.*, **104** (1982) 5790; (b) R.H. Magnuson, R. Meirowitz, S.J. Zulu and W.P. Giering, *Organometallics*, **2** (1982) 460.
- 8 (a) I.W. Nowell, K. Tabatabaian and C. White, *J. Chem. Soc., Chem. Commun.*, (1979) 547; (b) H. Nagashima, K. Mukai and K. Itoh, *Organometallics*, **3** (1984) 1314; (c) G.J. Baird, S.G. Davies, S.D. Moon, S.J. Simpson and R.H. Jones, *J. Chem. Soc., Dalton Trans.*, (1985) 1479; (d) T.D. Tilley, R.H. Grubbs and J.E. Bercaw, *Organometallics*, **3** (1984) 274.
- 9 (a) M.I. Bruce, I.B. Tomkins, F.S. Wong, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1982) 687; (b) J.K. Hoyano and W.A.G. Graham, *J. Am. Chem. Soc.*, **104** (1982) 3722; (c) D.B. Pourreau and G.L. Geoffroy, *Abstr. XIIth Intern. Conf. Organometal. Chem.*, Vienna, 1985, No. 237; (d) J.K. Hoyano, L.G. Sturgeooff and W.A.G. Graham, *ibid.*, No. 243.
- 10 M.F. Joseph, J.A. Page and M.C. Baird, *Organometallics*, **3** (1984) 1749.
- 11 J.A. Connor, *Topics Curr. Chem.*, **71** (1977) 71.
- 12 W.A.G. Graham and L.A.G. Sturgeooff, private communication.
- 13 C.V. experiments were carried out in CH_2Cl_2 with solutions 0.005 M in I, 0.1 M in Bu_4NBF_4 ; glassy carbon working electrode, Pt counter electrode, Ag/AgCl/saturated KCl reference electrode; scan rates 100–200 mV/sec. Under these conditions, I began to oxidize at +1.3 V.
- 14 A solution of I and a slight molar excess of PMe_2Ph in petroleum ether (b.p. 40–60°C) was photolyzed (Hanovia lamp) for 12–24 h. The product, II, was purified by eluting from an alumina column with 2/1 petroleum ether/methylene chloride, and was obtained as cream-coloured solid. Anal. Found: C, 47.37; H, 5.73. $\text{C}_{20}\text{H}_{19}\text{OOSp}$ calcd.: C, 47.42; H, 5.77%.
- 15 R.R. Gagné, C.A. Koval and G.C. Lisensky, *Inorg. Chem.*, **19** (1980) 2854.
- 16 The bromo compound can also be synthesized by treating $\text{Cp}^*\text{Os}(\text{CO})_2\text{Br}$ with the phosphine, either photochemically or in the presence of Me_3NO . Anal. Found: C, 39.78; H, 4.50. $\text{C}_{19}\text{H}_{26}\text{BrOOSp}$ calcd.: C, 39.93; H, 4.59%. The compound has been characterized by IR ($\nu(\text{CO})$ 1909 cm^{-1}), ^1H , ^{13}C and ^{31}P NMR spectroscopy.
- 17 The compound could be recrystallized from methylene chloride-methanol. Anal. Found: C, 25.43; H, 3.14. $\text{C}_{20}\text{H}_{19}\text{BrF}_6\text{HgOOSp}_2$ calcd.: C, 25.77; H, 3.14%.
- 18 The anion of compound V is probably bromide rather than, for instance, HgBr_3^- ; an NMR study of the reaction of II with slight deficiency of HgBr_2 showed that the conversion of II to V proceeded cleanly and essentially quantitatively.