*Journal of Organometallic Chemistry*, 358 (1988) 405–409
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# Radical formation during an attempted photochemical substitution reaction of $\eta^5$-$C_5Me_5Os(CO)_2CH_2Ph$

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(Received March 22nd, 1988)

## Abstract

Photolysis of $\eta^5$-$C_5Me_5Os(CO)_2CH_2Ph$ in the presence of $PMe_2Ph$ does not result in simple CO substitution, but rather in the formation of the two isomeric phosphine-substituted compounds $(\eta^4$-$C_5Me_5CH_2Ph)Os(CO)_2(PMe_2Ph)$ (I) and $\eta^5$-$C_5Me_5Os(CO)(PMe_2Ph)(COCH_2Ph)$ (II). It is suggested that the very unusual formation of I involves homolysis of the osmium–benzyl bond of $\eta^5$-$Cp^{\star}Os(CO)_2CH_2Ph$, followed by addition of the resulting benzyl radical to a ring carbon atom.

We have recently initiated a study of the oxidative addition reactions and the mechanisms of electrophilic cleavage reactions of osmium complexes of the type $Cp^{\star}Os(CO)LR$ ($Cp^{\star} = \eta^5$-$C_5Me_5$; L = CO, $PMe_2Ph$; R = alkyl) [1]. While we have explored a variety of synthetic routes to the required phosphine-substituted compounds, photochemical procedures have been generally of great utility for the syntheses of analogous compounds of iron and ruthenium [2]. Thus an obvious route to the desired compounds would involve photolysis of solutions containing the dicarbonyl alkyl compound and the tertiary phosphine is as shown in eq. 1.

$$Cp^{\star}Os(CO)_2R + L \xrightarrow{h\nu} Cp^{\star}Os(CO)LR + CO \qquad (1)$$

While a photochemical approach as in eq. 1 (three-fold excess of $PMe_2Ph$ in hexane) results in good yields of the substituted methyl compound [1], the procedure does not work for the ethyl and isopropyl dicarbonyl compounds, which are inert to substitution reactions under these conditions [1], or for the benzyl compound, $Cp^{\star}Os(CO)_2CH_2Ph$, which appears to undergo Os-$CH_2Ph$ homolysis. We now report on the nature of the unexpected products obtained from the photolysis of $Cp^{\star}Os(CO)_2CH_2Ph$ in the presence of $PMe_2Ph$.

## Experimental

*Instrumentation.* Infrared spectra were recorded on a Bruker IFS-85 FTIR spectrometer, $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra on a Bruker AM-400 NMR spectrometer. Elemental analyses were carried out by Canadian Microanalytical Service, Ltd., New Westminster, B.C.

*Photochemical procedure.* Photochemical reactions were carried out by irradiating a stirred solution through a watercooled quartz finger with a Hanovia lamp. In a typical experiment, a solution of Cp$^*$Os(CO)$_2$CH$_2$Ph [1b] (0.25 g, 0.53 mmol) and PMe$_2$Ph (0.1 ml, 1.79 mmol) in 200 ml hexane was photolyzed for 90 min. Monitoring of the reaction solution by IR spectroscopy showed that, as the $\nu$(CO) of the starting material (1985, 1920 cm$^{-1}$) disappeared, new bands of comparable intensity at about 1965, 1909 and 1890 cm$^{-1}$ grew in. The solvent was then removed in vacuo, and the residue was dissolved in 4/1 hexane/methylene chloride and eluted through an alumina column. A compound, I, exhibiting two strong $\nu$(CO) bands, was eluted first, as an oil contaminated with a small amount of the starting compound. The yield was 35–45%. Subsequent elution of the remaining material from the column with methylene chloride gave a compound, II, exhibiting a single $\nu$(CO) band; again, yields were 35–45%. IR and NMR data for compounds I and II are presented in Table 1.

## Results and discussion

Compound II was identified as Cp$^*$Os(CO)(PMe$_2$Ph)(COCH$_2$Ph) by elemental analyses (Found: C, 53.26; H, 5.51. C$_{27}$H$_{33}$O$_2$OsP calc.: C, 53.10; H, 5.45%.) and by its spectroscopic properties, listed in Table 1. The IR spectrum exhibits a single $\nu$(CO) band at 1890 cm$^{-1}$, somewhat higher than is observed ($\approx$ 1870 cm$^{-1}$) for compounds of the type Cp$^*$Os(CO)(PMe$_2$Ph)R (R = alkyl) [1], and an acyl stretch-

Table 1

IR and NMR data for I and II (CH$_2$Cl$_2$ or CD$_2$Cl$_2$)

| Compound | $\nu$(CO) (cm$^{-1}$) | $^1$H, $^{13}$C{$^1$H}, $^{31}$P{$^1$H} NMR |
|---|---|---|
| I | 1965, 1909 | $\delta$($^1$H): 7.5–6.8 (m, 10H, Ph), 2.36 (s, 2H, CH$_2$), 1.83 (d, *J* 8.7 Hz, 6H, PMe), 1.65 (d, *J* 2.0 Hz, 6H, CMe), 1.49 (s, 3H, CMe), 1.32 (d, *J* 1.4 Hz, 6H, CMe), $\delta$($^{13}$C): 192.4 (CO), 142–125 (Ph), 97.2, (s, *C*$_4$Me$_4$), 94.7 (s, *C*$_4$Me$_4$), 69.1 (s, *C*MeCH$_2$Ph), 49.5 (d, *J* 4.1 Hz, *C*H$_2$Ph), 29.1 (s, C*Me*CH$_2$Ph), 12.7 (s, C$_4$*Me*$_4$), 11.6 (s, C$_4$*Me*$_4$), $\delta$21.6 (d, *J* 35.1 Hz, PMe)<br>$\delta$($^{31}$P): −30.3 |
| II | 1890<br>$\nu$(C=O) 1558 | $\delta$($^1$H): 7.6–7.2 (m, 10H, Ph), $\delta$3.99 (d, *J* 13.1 Hz, 1H, CH$_2$), 3.81 (d, *J* 13.1 Hz, 1H, CH$_2$), 1.78 (d, *J* 9.9 Hz, 3H, PMe), 1.74 (d, *J* 9.5 Hz, 3H, PMe), 1.62 (d, *J* 1.1 Hz, 15H, Cp$^*$) $\delta$($^{13}$C): 234.9 (d, *J* 9 Hz, *C*OCH$_2$Ph), 190.5 (d, *J* 9 Hz, CO), 137.8–125.3 (Ph), $\delta$95.5 (Cp$^*$C), 75.3 (CH$_2$), 21.2 (d, *J* 40 Hz, PMe), $\delta$13.0 (d, *J* 37 Hz, PMe), $\delta$9.3 (Cp$^*$Me), $\delta$($^{31}$P): −16.9 |

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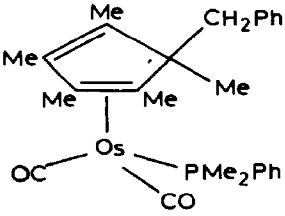
* Reference number with asterisk indicates a note in the list of references.

ing mode at 1558 $cm^{-1}$. The $^1H$ NMR spectrum exhibits separate resonances for the two diastereotopic methylene hydrogen atoms, consistent with the presence of a chiral centre in the molecule, but with no spin–spin coupling to $^{31}P$, suggesting that the benzylic group is not coordinated directly to the metal [3*]. In addition, the $^{13}C\{^1H\}$ NMR spectrum exhibits a doublet resonance at $\delta$ 234.9 ppm, which may be assigned to the acyl carbonyl resonance [5], while the $^{31}P\{^1H\}$ NMR spectrum exhibits a resonance at $\delta$ $-16.9$, similar to the $^{31}P\{^1H\}$ chemical shifts ($\delta$ $-20$ to $-25$) of several compounds of the type $Cp^*Os(CO)(PMe_2Ph)R$ (R = alkyl) [1]. The other NMR data listed in Table 1 are completely compatible with the structure suggested, and there would seem to be little room for doubt concerning its identity.

Compound I was obtained in comparable yields, but was rather more difficult to identify initially because it could be obtained only as an oil contaminated with a small amount of $Cp^*Os(CO)_2CH_2Ph$. However, it was eventually identified as the previously unreported 5-benzylpentamethylcyclopenta-1,3-diene complex, $(\eta^4$-$C_5Me_5CH_2Ph)Os(CO)_2(PMe_2Ph)$.



(I)

As elemental analyses could not be obtained, recourse was made to mass spectrometry in an attempt to characterize I. Consistent with the proposed formulation, a high resolution methane chemical ionization mass spectrum clearly showed an intense ion at $m/z$ 613.1901, corresponding closely to the $[MH]^+$ ion (613.1911, $^{192}Os$), and with the correct isotopic distribution for a compound of osmium.

The structure of I was deduced from its spectroscopic properties, listed in Table 1. Thus the IR spectrum contains two carbonyl groups, consistent with the proposed structure, while the $^1H$ NMR spectrum exhibits a singlet resonance for the benzyl methylene group, showing that the methylene hydrogen atoms are magnetically equivalent and are not coupled to $^{31}P$. The phosphine methyl resonances (in both the $^1H$ and the $^{13}C\{^1H\}$ spectra) are also equivalent, consistent with a lack of a chiral centre in the molecule. Interestingly, the $^1H$ and the $^{13}C\{^1H\}$ NMR spectra both exhibit three ring methyl resonances; in the $^1H$ spectrum, the relative intensities are 6/6/3, the first two exhibiting spin–spin coupling to $^{31}P$. There are also three ring carbon resonances at $\delta$ 69.1, 94.7 and 97.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum.

These data suggest that the ring is not $\eta^5$-coordinated, but rather is coordinated as illustrated above, a structure which contains three different ring carbon and three different ring methyl environments. It is also probably highly significant that the $^1H$ resonances of the methyl groups bonded to metal-coordinated carbon ring atoms exhibit spin–spin coupling to $^{31}P$, but that the $^1H$ resonances of the methylene and methyl groups on the tilted ring carbon atom do not.

We note that the $^1H$ and $^{13}C$ NMR spectroscopic data of I are very similar to the corresponding data of a rhodium compound containing the same *exo*-substituted diene ligand [6]. Thus for the compound $Cp^{\star}Rh(CH_2Ph)(\mu\text{-}CH_2)_2Rh(\eta^4\text{-}C_5Me_5CH_2Ph)$, the strucure of which has been established crystallographically, three methyl and three ring carbon environments are apparent, the chemical shifts being very similar to those of I [6]. As this rhodium compound was prepared via reaction of $[Cp^{\star}Rh(\mu\text{-}CH_2)Cl]_2$ with $PhCH_2MgCl$, its formation presumably involved nucleophilic attack of the carbanion on the metal-activated $Cp^{\star}$ ring, thus rationalizing the *exo*-orientation of the benzyl group. There have also been reports of ligand-induced migration of coordinated alkyl and aryl groups to cyclopentadienyl rings to give *endo*-cyclopentadienyl complexes [7]. These thermal reactions appear to involve concerted migrations of the alkyl or aryl groups from metal to ring.

The closest precedent for the photochemical process observed here, however, lies in the analogous chemistry of the iron compounds $(\eta^5\text{-}C_5R_5)Fe(CO)_2CH_2Ph$ ($R =$ H, Me), which undergo photo-induced homolysis to form the corresponding iron-centered radicals (eq. 2). The latter dimerize to $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]_2$ in the absence of added ligand L ($L = CO, PPh_3$) (eq. 2a), but react further in the presence of free ligands L to form the corresponding compounds $(exo\text{-}\eta^4\text{-}C_5R_5CH_2Ph)Fe(CO)_2L$ (eq. 2b), characterized by X-ray crystallography [8].

$$\begin{tikzcd} & \left[(\eta^5\text{-}C_5R_5)Fe(CO)_2\right]_2 \\ (\eta^5\text{-}C_5R_5)Fe(CO)_2CH_2Ph \arrow[r, "h\nu"] & \{(\eta^5\text{-}C_5R_5)Fe(CO)_2\cdot,\ \cdot CH_2Ph\} \arrow[u, "a"] \arrow[d, "b"', "L"] \\ & (exo\text{-}\eta^4\text{-}C_5R_5CH_2Ph)Fe(CO)_2L \end{tikzcd} \tag{2}$$

Interestingly, the osmium-methyl compound $\eta^5\text{-}Cp^{\star}Os(CO)_2Me$ does not undergo this type of chemistry, only photo-induced substitution being observed when $\eta^5\text{-}Cp^{\star}Os(CO)_2Me$ is irradiated in the presence of $PMe_2Ph$ [1b]. As the Os–Me bond energy is presumably significantly higher than the corresponding $Os\text{–}CH_2Ph$ bond energy [9], it is reasonable that the benzyl compound would more readily undergo homolytic cleavage, and that photolysis of $\eta^5\text{-}Cp^{\star}Os(CO)_2CH_2Ph$ would result in preferential homolysis while similar treatment of $\eta^5\text{-}Cp^{\star}Os(CO)_2Me$ might result in preferential CO dissociation. The observation that $\eta^5\text{-}Cp^{\star}Fe(CO)_2Me$ [8b] undergoes photo-induced conversion to $(exo\text{-}\eta^4\text{-}C_5R_5CH_3)Fe(CO)_3$ does not negate this argument, as an iron–carbon $\sigma$ bond is expected to be weaker than the corresponding osmium–carbon $\sigma$ bond [9], and thus $\eta^5\text{-}Cp^{\star}Fe(CO)_2Me$ and $\eta^5\text{-}Cp^{\star}Fe(CO)_2CH_2Ph$ may both be more photo-labile than is $\eta^5\text{-}Cp^{\star}Os(CO)_2Me$.

As the photochemical reactions of the iron compounds $\eta^5\text{-}Cp^{\star}Fe(CO)_2R$ ($R =$ Me, $CH_2Ph$) result in the *exo*-orientation for the alkyl groups on the five-membered rings [8], the same structure seems likely for I. Furthermore, while it might be anticipated that homolysis would result in dimerization of the resulting $\{\eta^5\text{-}Cp^{\star}Os(CO)_2\}$ radicals to form the known $[\eta^5\text{-}Cp^{\star}Os(CO)_2]_2$ [10], this osmium dimer has not been detected in the IR spectra of any reaction mixtures. This result is consistent with the behaviour of the iron system, where dimer formation is suppressed in the presence of both free carbon monoxide and free triphenylphosphine [8b], presumably because of the pronounced substitution lability of the seventeen-electron species [11].

We note, finally, that the acetyl compound $\eta^5\text{-}Cp^{\star}Os(CO)(PMe_2Ph)(COMe)$ is not observed during the photochemical substitution reaction of $\eta^5\text{-}Cp^{\star}Os(CO)_2Me$.

It thus seems possible that II is not formed via a conventional migratory insertion process, but rather via a process not available to the methyl system. It seems possible that benzyl radical coupling with a coordinated CO group may occur, although this type of reaction does not seem to occur in the iron system [8b].

However, it has been established that sufficient spin density resides on carbonyl groups of nineteen-electron complexes such as $[Fe(CO)_5]^-$ and $[Cr(CO)_6]^-$ that these species can abstract a hydrogen atom from $(n\text{-Bu})_3SnH$ to form the formyl complexes $[Fe(CO)_4CHO]^-$ and $[Cr(CO)_5CHO]^-$, respectively [12]. It seems possible, for the system under consideration here, that interaction of a molecule of $PMe_2Ph$ with the radical $\{(\eta^5\text{-}C_5Me_5)Os(CO)_2\}$ would lead to the formation of the nineteen-electron species $\{(\eta^5\text{-}C_5Me_5)Os(CO)_2(PMe_2Ph)\}$, with significant localization of the odd electron on the carbonyl groups. Coupling with a benzyl radical at a carbonyl group to give II might then be very facile.

In conclusion, the $(\eta^5\text{-}C_5Me_5)Os(CO)_2$ system studied here exhibits chemistry which appears to duplicate some of the chemistry of the much more extensively studied iron system, but which also differs distinctly in other ways. A full understanding of the osmium chemistry must await a more detailed IR study of the photo-generated intermediates.

## Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for scholarships to L.J.J. and for operating grants to M.C.B. We also thank Dr. R.W. Smith of the McMaster Regional Centre for Mass Spectrometry for obtaining mass spectral data on I, and Professor J.A. Stone for assisting in the interpretation of the data.

## References

1 (a) L.J. Sanderson and M.C. Baird, J. Organomet. Chem. 307 (1986) C1; (b) L.J. Sanderson and M.C. Baird, Organometallics, in press.
2 D.B. Pourreau and G.L. Geoffroy, Adv. Organomet. Chem., 24 (1985) 249.
3 The corresponding vicinal H–P couplings in iron and ruthenium compounds of the type $\eta^5$-$CpM(CO)L(CH_2Ph)$ are readily resolved [4].
4 (a) K. Stanley and M.C. Baird, J. Amer. Chem. Soc., 97 (1975) 4292; (b) M.F. Joseph, J.A. Page and M.C. Baird, Organometallics, 3 (1984) 1749.
5 B.E. Mann and B.F. Taylor, $^{31}$C NMR Data for Organometallic Compounds, Academic Press, London, 1981, p. 147.
6 N.J. Meanwell, A.J. Smith and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1986) 1419.
7 H.E. Bunting, M.L.H. Green and P.A. Newman, J. Chem. Soc., Dalton Trans., (1988) 557, and ref. therein.
8 (a) G.A. Sim, D.I. Woodhouse and G.R. Knox, J. Chem. Soc., Dalton Trans., (1979) 629; (b) J.P. Blaha and M.S. Wrighton, J. Am. Chem. Soc., 107 (1985) 2694.
9 J.A. Connor, Topics in Current Chemistry, 71 (1977) 71.
10 L. Weber and D. Bungardt, J. Organomet. Chem., 311 (1986) 269.
11 (a) B.D. Moore, M.B. Simpson, M. Poliakoff and J.J. Turner, J. Chem. Soc., Chem Commun., (1984) 972; (b) A.J. Dixon, M.A. Healy, M. Poliakoff and J.J. Turner, J. Chem. Soc., Chem Commun., (1986) 994; (c) A.J. Dixon, S.J. Gravelle, L.J. van de Burgt, M. Poliakoff, E. Weitz and J.J. Turner, ibid., (1987) 1023. (d) B.D. Moore, M. Poliakoff and J.J. Turner, J. Am. Chem. Soc., 108 (1986) 1819.
12 B.A. Narayanan, C. Amatore and J.K. Kochi, Organometallics, 5 (1986) 926.