Reactions of Cyclopentadiene with Carbonyl-ruthenium and -osmium Complexes: Formation of Carbonyl-metal Hydrides

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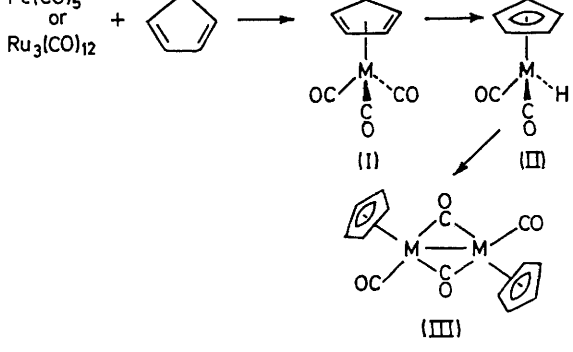
Summary The reaction of cyclopentadiene with $Ru_3(CO)_{12}$ yields $Ru(\pi\text{-}C_5H_5)(CO)_2(H)$ quantitatively, *via* intermediate formation of $Ru(2\text{–}5\text{-}\eta\text{-cyclopentadiene})(CO)_3$; hydrides $M(\pi\text{-}C_5H_5)(CO)_2(H)$ (M = Ru, Os) are similarly formed from $H_4Ru_4(CO)_{12}$ and $H_2Os_3(CO)_{10}$.

The reaction of cyclopentadiene with pentacarbonyliron has been suggested[1,2] to proceed as shown in the Scheme (M = Fe), *via* two intermediate complexes, to the observed (III; M = Fe). The complex (I; M = Fe) has been obtained by treating cyclopentadiene with $Fe_2(CO)_9$ and shown[3] to decompose at 140° to (III; M = Fe). Intermediate formation of the thermally very unstable (II; M = Fe)[4] is not firmly established by this observation, although it is known that (II; M = Fe) does decompose to (III; M = Fe). We report here related reactions with ruthenium and osmium carbonyls which show that metal hydrides, formed *via* (I), are indeed intermediates in such syntheses, and which provide the first convenient high yield routes to (II; M = Ru) and (III; M = Ru).

In the absence of oxygen, treatment of $Ru_3(CO)_{12}$ with cyclopentadiene in refluxing heptane, rapidly (*ca.* 1 h) and quantitatively yields (II; M = Ru), previously prepared[5] by borohydride reduction of the corresponding iodide. When a solution of the hydride in heptane is heated for 24 h



at reflux in the absence of air, only traces of (III; M = Ru) can be detected. However, refluxing a heptane solution of $Ru_3(CO)_{12}$ and cyclopentadiene in air for 24 h gives (III; M = Ru) (60—70%).

I.r. spectroscopy indicated the existence of (I; M = Ru) as a precursor of (II; M = Ru). Compound (I) was apparent in larger quantities in a solution of $Ru_3(CO)_{12}$ and cyclopentadiene in hexane at reflux, although quantitative conversion into (II; M = Ru) occurred after 20 h. The previously unreported (I; M = Ru) was isolated as a pale yellow liquid ν_{CO} 2062s, 1998s, and 1986s cm^{-1}; τ 4·25m (2H), 6·96m (2H), 7·20m (1H), and 7·82m (1H); *m/e* 252 (M^+), 234 $(M - CO)^+$, 196 $(M - 2CO)^+$, 168/167 $(M - 3CO)^+/(M - 3CO - H)^+$. Heating a pure sample of (I; M = Ru) in heptane yielded (II; M = Ru) exclusively after 1·5 h, establishing the intermediacy of the former. It seems probable that this conversion occurs through a novel intramolecular hydrogen transfer with oxidative-elimination of carbon monoxide.

Under conditions similar to those employed with $Ru_3(CO)_{12}$, cyclopentadiene quantitatively generates (II; M = Ru) on reaction with $H_4Ru_4(CO)_{12}$.[6–8] That the terminal hydride ligand in (II; M = Ru) did not originate as a bridging hydride of $H_4Ru_4(CO)_{12}$ was determined by treating $(^2H)_4Ru_4(CO)_{12}$[9] with cyclopentadiene, when 100% of $Ru(\pi\text{-}C_5H_5)(CO)_2(^1H)$ was formed, established by ^1H n.m.r. study of its air-stable monotriphenylphosphine derivative.

From $Os_3(CO)_{12}$ and cyclopentadiene a complex mixture of products was obtained. The diene did not react with $H_4Os_4(CO)_{12}$[9] on heating in octane at reflux, but the new osmium hydride $Os(\pi\text{-}C_5H_5)(CO)_2(H)$ has been isolated as a minor product of the reaction with $H_2Os_3(CO)_{10}$.[10] This is a pale yellow, air- and thermally-stable liquid ν_{CO} 2024s and 1962s cm^{-1}; τ 4·61 (5H, C_5H_5) 24·93 (1H, OsH); *m/e* 314 (M^+), 286/285 $(M - CO)^+/(M - CO - H)^+$, 258/257 $(M - 2CO)^+/(M - 2CO - H)^+$.

(*Received*, 19*th March* 1973; *Com.* 397.)

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