Reaction of η-Tetracarbonyldicyclopentadienyldiruthenium with Phosphine and Phosphite Ligands

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Summary Reaction of $(cp)_2Ru_2(CO)_4$ (cp = η^5-C_5H_5) with $P(OR)_3$ (R = Me, Et, or Bu^n) proceeds by R–O bond cleavage to yield $(cp)Ru(CO)_2R$ derivatives; reaction with PPr_3 yields, in addition to $(cp)_2Ru_2(CO)_3(PPr_3)$, products also derived from cleavage of the Ru–Ru bond.

DURING our work on the fluxional nature of isonitrile complexes of the $(cp)_2M_2(CO)_4$ series (**1**, M = Fe; **2**, M = Ru; cp = η^5-C_5H_5),[1] we wished to prepare complexes of the types $(cp)_2Ru_2(CO)_3(PR_3)$ (**3**) and $(cp)_2Ru_2(CO)_3[P(OR)_3]$ (**4**) to enable a comparison with the well-documented iron complexes.[2] However, we have found that attempts at thermal substitution of (**2**) with PR_3 and $P(OR)_3$ ligands result instead in a novel series of bond cleavage reactions.

Thus, reaction of a slight excess of $P(OR)_3$ with (**2**) in xylene at 140 °C over a period of 24 h results in essentially quantitative conversion into the alkyl derivatives $(cp)Ru(CO)_2R$ [R = Me, Et, or Bu^n (**5a**—**c**)]. I.r. (**5b**; ν_{CO} = 2016 and 1958 cm^{-1}) and mass spectroscopic measurements (**5b**; M^+ = 252 based on ^{102}Ru) are identical with values observed for an authentic sample.[3] No trace of the simple substitution product (**4**; R = Et) was observed either on purification or during the reaction, although its intermediacy in the reaction cannot be discounted. Because of difficulty in separation of these rather volatile compounds from organic impurities and from the traces of $(cp)Ru(CO)[P(OR)_3]R$ also formed, we have isolated as pure crystalline compounds the PPh_3 substitution products $(cp)Ru(CO)(PPh_3)R$ (**6a**—**c**; R = Me, Et or Bu^n) by reaction of PPh_3 with the initially obtained impure (**5a**—**c**), followed by column chromatography. I.r. and n.m.r. data are shown in the Table, and, in the case of (**6b**), are identical with a specimen prepared by PPh_3 substitution of authentic (**5b**). It is of interest to note that in (**6b** and **c**), the α-CH_2 protons form an AB system (confirmed by decoupling) due to proximity to the chiral ruthenium centre. Computer simulated spectra for (**5b**) confirm the ABX_3P nature of the spectrum.

Reaction of (**2**) with an excess of PPr_3 in xylene at 140 °C over 48 h, followed by chromatography on alumina using CH_2Cl_2, yields the expected substitution product (**3**; R = Pr) (50%),† together with a product identified as

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† The fluxional properties of this molecule will be discussed elsewhere.

TABLE. Spectral data

Compound	ν_{C-O}/cm^{-1} [a]	δ/p.p.m.[b]	
		cp	Other
(cp)Ru(CO)(PPh_3)R			
(**6a**; R = Me)	1935	4·99[c]	2·08 (Me, J_{P-H} 0·5 Hz)[d]
(**6b**; R = Et)	1933	4·98[c]	2·4 (m, CH_2), 0·52 (t, Me)[d]
(**6c**; R = Bu^n)	1928	4·95[c]	2·35 (m,CH_2), 0·73—1·40 (m, Pr)[d]
(Cp)Ru(CO)(PPr_3)Cl (**7**)	1953	5·03[c]	1·22—1·98 (m, CH_2CH_2), 1·03 (t, Me)
(cp)Ru(CO)(PPr_3)Br (**8**)	1958	5·04[c]	1·33—2·01 (m, CH_2CH_2), 1·03 (t, Me)
$(cp)_2Ru_2(CO)_3(PPr_3)$ (**3**)	1943 (term.), 1762 (bridge)	5·22, 4·99	1·40 (m. CH_2CH_2), 0·98 (t, Me)

[a] Hexane solution. [b] $CDCl_3$ solution; Me_4Si as standard. [c] J_{P-H} 0·4 Hz. [d] PPh_3 multiplet at δ 7·40.

(cp)Ru(CO)(PPr_3)Cl (**7**) (50%). Use of CH_2Br_2 yields the analogous bromide (**8**). Thus, (**7**) is not an initial reaction product, and i.r. analysis of the reaction mixture before chromatography reveals a single absorption at 1930 cm^{-1} clearly assignable to a (cp)Ru(CO)(PPr_3)X derivative. Observation of a phosphorus-coupled doublet (J 32.7 Hz) at τ 22.2 in the ^{1}H n.m.r. spectrum of the crude product identifies this intermediate as the hydride (η^5-Cp)Ru(CO)(PPr_3)H. Other workers have recently shown that pyrolysis of $Os_3(CO)_{11}(PEt_3)$ yields products resulting from both carbon-to-metal hydrogen transfer and P–C bond cleavage,[4] and that pyrolysis of $Os_3(CO)_{11}[P(OMe)_3]$ yields products resulting from carbon-to-metal hydrogen transfer and C–O bond cleavage.[5] Surprisingly, $(cp)_2Os_2(CO)_4$ is unreactive to $P(OR)_3$ ligands and PPr_3 under the conditions used for reaction with (**2**).

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