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The formation of octahedral metal–carbon σ-bonded complexes by addition of hydrogen halide to mono-olefin chelate complexes of iron(0) and ruthenium(0)

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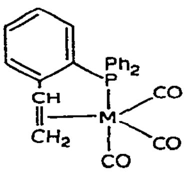
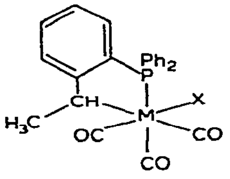
The addition of hydrogen chloride to iron tricarbonyl complexes of conjugated acyclic diolefins gives π-allylic complexes of general formula (π-allyl)$Fe(CO)_3Cl$ [1]. In contrast, mono-olefin complexes of the type (olefin)$Fe(CO)_4$ are readily decomposed by HCl or HBr (possibly via an iron(II)–alkyl intermediate) to the alkane and Fe^{2+} [2]. We find that treatment of the mono-olefin chelate complexes $[M(CO)_3(sp)]$ [3] (I, M = Fe or Ru; sp = *o*-styryldiphenylphosphine, *o*-CH_2=$CHC_6H_4PPh_2$), with HCl or HBr in n-hexane gives octahedral Fe^{II} – and Ru^{II}–carbon σ-bonded chelate complexes (IIa–IId). The properties of these derivatives are summarised in Table 1. The structural assignment is based on the single-crystal X-ray analysis of the HBr adduct of $[Ru(CO)_3(sp)]$. X-Ray powder diffraction patterns indicate that all four complexes IIa–IId are isomorphous, and probably isostructural.

The iron(II) compounds (IIa and IIb) appear to be the first characterised octahedral σ-bonded alkyl derivatives of the divalent element. They are stable in the solid phase under dry nitrogen, but decompose rapidly in benzene or chloroform solutions even in the absence of air. The Ru^{II} analogues are air-stable in the solid state, but they lose CO in solution. Molecular weight measurements in benzene and chloroform suggest that halogen-bridged dimers may be formed, but concurrent decomposition has prevented



(I)



(IIa, M = Fe, X = Cl;
IIb, M = Fe, X = Br;
IIc, M = Ru, X = Cl;
IId, M = Ru, X = Br)

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TABLE 1

PROPERTIES OF $[o\text{-}CH_3\overline{CHC_6H_4PPh_2M}(CO)_3X]$ COMPLEXES

M	X		ν(CO) (cm^{-1})[a]	^{1}H NMR[b]	
				CH	CH_3
Fe	Cl	Yellow crystals	2090, 2038, 2000	4.24 (broad) 4.54 (broad)	1.79 (doublet, $J \sim 4$Hz) (A)[c] 1.98 (doublet, $J \sim 4$Hz) (B)[c]
Fe	Br	Orange-brown crystals	2090, 2040, 2000	4.17 (broad)	2.07 (doublet, $J \sim 5$Hz)
Ru	Cl	Yellow crystals	2110, 2052, 2018	4.14 (1/3/3/1 quartet) ~4.3 (broad)	1.77 (doublet. $J = 7$Hz) (A)[d] 1.97 (doublet, $J = 7$Hz) (B)[d]
Ru	Br	Orange-yellow crystals	2106, 2054, 2022	3.9 (1/3/3/1 quartet) [e]	2.03 (doublet, $J = 7.5$Hz) (A)[f] 1.76 (doublet, $J = 7.5$Hz) (B)[f]

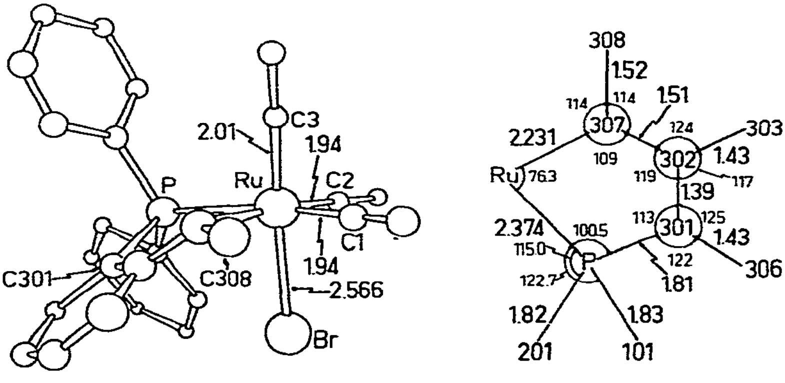
[a] Measured in Nujol mulls. [b] ppm downfield of TMS; measured in $CDCl_3$. [c] Relative intensity of (A)/(B) = 1.5, but decreases with time; spectrum broadened by paramagnetic decomposition product. [d] Relative intensity of (A)/(B) ~3.5. [e] Could not be located. [f] Relative intensity of (A)/(B) ~5, but decreases with time.

their identification. The ^{1}H NMR spectra of IIa, IIc, and IId show a number of resonances attributable to $CHCH_3$ groups in different environments, which probably results from isomerisation and/or dimerisation in solution (Table 1). There are no signals attributable to $-CH_2-CH_2-$, indicating that the HX addition to the coordinated double bond follows Markownikoff's rule.

Crystals of IId are monoclinic in the non-standard centrosymmetric space group $B2_1/c$, $a = 28.69$, $b = 8.62$, $c = 17.94$ Å, $\beta = 90.93°$, $Z = 8$. The eight general positions for $B2_1/c$ are: (x,y,z); (x+½,y,z+½); (−x,−y,−z); (½−x,−y,½−z); (x,½−y,½+z); (½+x,½−y,z); (−x,½+y,½−z); (½−x,½+y,−z). The 2664 unique reflexions, with $F_o^2/\sigma(F_o^2) \geqslant 3.0$, were measured on a Picker FACS-I automatic diffractometer, using crystal monochromated Cu-Kα radiation. With only the Ru, Br, and P atoms anisotropic the block-diagonal least-squares analysis has converged to the present conventional R-factor of 0.073. Data have yet to be corrected for absorption and extinction effects. ESD's of bond lengths in Fig. 1(a) and 1(b) are: Ru—Br, 0.002; Ru—P, 0.003; Ru—C, 0.015, C—C, 0.02 Å.

The central ruthenium atom is octahedrally coordinated by three *fac*-carbonyl groups, a bromine atom, and the phosphorus and 1'-carbon atom of the σ-$CH_3CHC_6H_4PPh_2$ group [Fig. 1(a)]. The Ru—C(307) distance (2.23 ± 0.015 Å) is 0.07 Å longer than the Ru—C σ-bond distance [2.16(1)Å] found in the σ-bonded naphthyl complex $[RuH(\sigma{-}C_{10}H_7)(Me_2PCH_2CH_2PMe_2)_2]$[4]. This bond lengthening must result, in part, from the differing σ-orbital radius of tetrahedrally and trigonally hybridised carbon atoms ($\Delta_r \sim 0.03$ Å). The Ru^{II} covalent radius derived from the Ru—C(307) distance is 1.46 Å, *cf.*, 1.43 Å from the σ-naphthyl data.

Individual Ru—C(carbonyl) distances in the present complex do not differ significantly from the mean [1.96(2)Å], and are comparable with those found in $[Ru(CO)_3Br_2]_2$ [av., 1.92(3)Å] [5], and $[Ru_3(CO)_{12}]$ [av., 1.91(2)Å]. The Ru—Br and Ru—P distances [2.566(2) and 2.374(3)Å, respectively], are longer than the corresponding bond lengths found in $[Ru(CO)_3Br_2]_2$ [terminal Ru—Br, 2.543(4)Å] [5], and the σ-naphthyl derivative [Ru—P, av. 2.305(3)Å] [4]. However, both the Ru—Br and Ru—P



(a) (b)

Fig.1. (a) The overall stereochemistry of the molecule; (b) The detailed geometry of the Ru—P chelate ring. Bond distances are in Å, and angles are in degrees.

distances are significantly shorter than the values calculated from covalent radii sums for simple σ-bonds [*viz.*, Ru–Br, 2.61; Ru–P, 2.56 Å].

Within the chelate ring [defined by Ru,P,C(301), C(302), C(307)], the P–C, C–C, and C(307)–C(308) distances are within experimental error of their expected values, although the angular deformations at Ru, P, and C(301) [see Fig. 1(b)], suggest that there is some steric strain within this chelate ring system.

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