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# π-Bonded Acyl Complexes of Ruthenium

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*Summary* Reaction of aliphatic aldehydes with phosphine complexes of ruthenium(II) yields the first examples of π-bonded acyl groups, a new class of organo-transition-metal compounds.

THE decarbonylation of organic molecules by transition metals has received attention in several laboratories recently.[1] During the course of our investigation of the reaction between $Ru(Ph_3P)_3Cl_2$ and aldehydes, we have isolated as a minor product what we believe to be the first example of a π-bonded acyl group.

TABLE

| | $^1$H n.m.r.[a] chemical shift | | | Coupling constant $J$ (Hz) | | I.r.[b] | |
|---|---|---|---|---|---|---|---|
| Complex | Aromatic hydrogen | $CH_2$ | $CH_3$ | | | $\nu_{M-CO}$ | $\nu_{R-C=O}$ |
| (I) | $-2{\cdot}14$ (30)<br>(multiplet) | $+4{\cdot}45$ (2)<br>(quartet) | $+5{\cdot}27$ (3)<br>(triplet) | 7·5 | 7·5 | 1945 $cm^{-1}$<br>(vs) | 1510 $cm^{-1}$<br>(m) |
| (II) | $-2{\cdot}08$ (30)<br>(multiplet) | — | $+4{\cdot}83$ (3)<br>(singlet) | — | — | 1945 $cm^{-1}$<br>(vs) | 1505 $cm^{-1}$<br>(m) |

[a] In p.p.m. relative to $CH_2Cl_2$; relative intensities in parentheses; recorded on Varian HA-100.

[b] Recorded as KBr disc on Perkin-Elmer model 257; no significant variation in spectra noted in either Nujol mull or benzene solution.

Complexes (I) and (II) can be prepared in virtually quantitative yields from reaction of either $Ru(Ph_3P)_3HCl$ or $Ru(Ph_3P)_3(CO)HCl$ with propionaldehyde and acetaldehyde, respectively (equations 1—3).

$$Ru(Ph_3P)HCl + 4EtCHO \rightarrow (I) + C_2H_4 + 2Pr^nOH \quad (1)$$

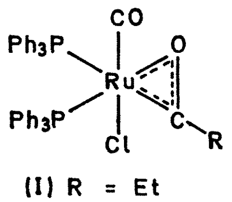
$$Ru(Ph_3P)_3HCl + 3MeCHO \rightarrow (II) + CH_4 + EtOH \quad (2)$$

$$Ru(Ph_3P)_3(CO)HCl + 2RCHO \rightarrow (I) \text{ or } (II) + RCH_2OH \quad (3)$$

Our tentative assignment of the unusual π-bonded acyl structure for these complexes is based upon the following arguments.

(i) The complexes are diamagnetic and in solution are monomeric, suggesting low-spin $d^6$ ruthenium(II).

(ii) The $^1$H n.m.r. spectrum (Table) of (I) in methylene chloride exhibits, in addition to the phenyl hydrogen multiplet, a quartet and a triplet at high field in the proper intensity ratios for an ethyl group. There is no evidence of further coupling of the $CH_2$ quartet or the $CH_3$ triplet with other nuclei, and spin-decoupling conclusively demonstrates the two multiplets are coupled with one another. The lack of additional coupling eliminates the possibility of an ethyl group directly bonded to the ruthenium, since coupling to phosphorus would be expected. The absence of additional resonances tends to eliminate the possibility of either a ruthenium hydride or a hydrogen on the carbon atom



(I) R = Et
(II) R = Me

bearing the ethyl group. (The lack of further coupling also indicates absence of the latter).

The n.m.r. spectrum of (II) shows only a high-field singlet in addition to the phenyl multiplet.

(iii) The mass spectra of (I) and (II) clearly show the presence of EtCO and MeCO moieties, respectively.

(iv) The i.r. spectra of (I) and (II) (Table) exhibit a single absorption in the 1800—2200 $cm^{-1}$ region, assigned as the metal carbonyl stretching frequency. The Raman spectra show no additional scattering in this region. Thus, there can be only one metal carbonyl group and the presence of a ruthenium hydride is unlikely. A broad medium intensity absorption at 1510 $cm^{-1}$ is observed. This absorption—absent in the spectra of all other complexes related to this work—is assigned as the carbon-oxygen stretching frequency of the RCO group. This would be a very low stretching frequency for a $\sigma$-bonded acyl group. The acyl C–O stretching frequency even in the anionic complexes[2] $[Mn(COMe)I(CO)_4]^-$ and $[OsBr_2(CO)_2(CO)_2(COMe)_2]^{2-}$ where extensive delocalization on to the acyl group would be expected, is only lowered to 1566 and 1552 $cm^{-1}$, respectively. Both the decrease in stretching frequency and intensity of the absorption suggest a $\pi$-bonded acyl group. Such a structure is in accord with the high chemical shifts observed for the alkyl groups in their n.m.r. spectra.

(v) The chemical properties of the complexes are also in agreement with the suggested structure. If the acyl group were $\sigma$-bonded, the complexes would be five-co-ordinate and would have a vacant co-ordination site. Compounds (I) and (II) are indefinitely stable in solution toward oxygen—behaviour not to be expected of a complex with both a vacant co-ordination site and a metal–carbon bond. A co-ordinately unsaturated compound would also be expected to take up carbon monoxide readily. Compound (II) reacts with carbon monoxide only very slowly. After three days in solution under 4500 $lb/in^2$ of carbon monoxide, only about a third of the complex has reacted. The product is $Ru(Ph_3P)_3(CO)_2Cl(\sigma\text{-}COMe)$. The latter complex exhibits peaks at 2050 and 1990 $cm^{-1}$ assigned as *cis* metal carbonyls and a peak at 1600 $cm^{-1}$ assigned to the $\sigma$-bonded acyl group.

Crystals of (I) and (II) suitable for *X*-ray crystallographic study have been obtained and the structure determination undertaken.

Reaction of $Ru(Ph_3P)_3(CO)HCl$ with anhydrides also yields (I) and (II) (equation 4). The possible utility of the reaction in the synthesis of other acyl complexes is currently under study.

$$Ru(Ph_3P)_3(CO)HCl + (RCO)_2O \rightarrow Ru(Ph_3P)_2(CO)\text{-}Cl(\pi\text{-}COR) + RCO_2H + Ph_3P \qquad (4)$$

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