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Preliminary communication

REACTIONS OF COPPER ACETYLIDES. STRUCTURE OF $(\pi\text{-}C_5H_5)Ru(PPh_3)_2(C{\equiv}CPh)CuCl$, AND NEW SYNTHESES OF TRANSITION METAL CLUSTER COMPOUNDS

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Summary

In contrast to a related iron—copper compound, the complex $(\pi\text{-}C_5H_5)Ru(PPh_3)_2(C_2Ph)CuCl$ is shown to be monomeric, and contains linear dicoordinate copper(I); the reactions of this and similar complexes with metal carbonyls are sources of new mixed-metal clusters, such as $(\pi\text{-}C_5H_5)Fe_2Ru(C_2Ph)(CO)_6(PPh_3)$.

The reactions of copper acetylides with certain transition metal halide complexes have recently afforded new types of organocopper complexes. The copper may be bonded within a heteronuclear cluster, as in $Ir_2Cu_4(PPh_3)_2(C_2Ph)_8$ [1], or formally π-bonded to the acetylenic group, as in $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Ph)CuCl]_2$.

The reactions of $(\pi\text{-}C_5H_5)Ru(PPh_3)_2Cl$ are distinctly different from those of the analogous iron dicarbonyl [3]. Treatment with copper phenylacetylide in benzene results in a smooth reaction, affording yellow crystals from hexane—acetone, m.p. 202-206° (decomp.), shown by the subsequent X-ray analysis to have stoichiometry $(\pi\text{-}C_5H_5)Ru(PPh_3)_2Cu(C_2Ph)Cl\cdot(CH_3)_2CO$ (I).

Crystals of the complex from acetone are monoclinic, $P2_1/c$, with a 12.914, b 22.111, c 16.534 Å, β 110.77°, $Z = 4$. Using the 5895 observed reflections of 6777 measured with Cu-K_α radiation, the structure was solved after location of the Ru and Cu atoms from a sharpened Patterson map. A heavy atom map based on these two atoms showed three peaks at about the correct height for P and Cl. The proximity of one of these to the copper atom indicated at this point that the structure included a terminal CuCl group. A subsequent map based on these five atomic positions revealed the entire structure, shown in Fig. 1. This structure, including one acetone molecule of solvation per complex

Fig. 1. Stereoscopic view of the molecular geometry of (π-C_5H_5)Ru(PPh_3)$_2$Cu(C_2Ph)Cl (I). For clarity only the phosphorus atoms, and the carbon atoms bonded to them, are shown for the PPh_3 ligands.

TABLE 1

METAL—ACETYLIDE—COPPER COMPLEX GEOMETRY $\mathrm{M—\underset{\searrow\ \swarrow}{C — C}— Ph}$
Cu

Bond lengths (Å)	M = Fe[a]	M = Ru[b]	Bond angles (deg.)	M = Fe[a]	M = Ru[b]
M—C	1.89(2)	2.016(9)	M—C—C	162(2)	172.6(8)
C—C	1.27(2)	1.25(1)	C—C—Ph	162(2)	165.0(1.0)
C—Ph	1.39(2)	1.46(1)	C—C—Cu	71.5(1.0)	70.9(6)
C—Cu	1.99(2)	2.01(1)		71.5(1.0)	70.9(6)
	1.99(2)	2.04(1)	C—Cu—C	37(1)	35.9(4)

[a] Ref. 2. [b] This work.

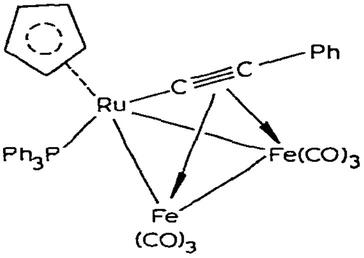
molecule, has now been refined to a conventional *R* value of 0.082 and a weighted *R* value of 0.074. This represents, to our knowledge, the only crystal structure which has been studied containing acetylide—CuCl groups which are only terminally π-bonded.

Of some interest is the coordination about the copper atom, which differs from that found in [(π-C_5H_5)Fe(CO)$_2$(C_2Ph)CuCl]$_2$. Whereas the latter forms a chlorine-bridged dimer, containing trigonal copper(I), the ruthenium complex is a monomer, with linear two-coordinate copper(I). The coordination of the triple bond to copper is similar in both complexes (Table 1), when differences in covalent radii of iron (1.34Å) and ruthenium (1.49Å) are taken into account.

The precise reasons for the differences between the two complex structures are not apparent at present, although steric crowding by the triphenylphosphine ligands preventing the formation of a Cu_2Cl_2 bridge is a likely explanation.

We have examined the reactions of this complex with reagents which readily react with carbon—carbon triple bonds. Thus the reaction between (π-C_5H_5)Ru(PPh_3)$_2$(C_2Ph)CuCl and $Fe_2(CO)_9$ affords a new cluster complex identified as (π-C_5H_5)Fe_2Ru(C_2Ph)(CO)$_6$(PPh_3) (II). This complex is obtained as dark red crystals, m.p. 149-151° (decomp.), and shows only terminal ν(CO) bands, at 2066s, 2049s, 2022w, 2007(sh), 1994s(br) and 1976s cm^{-1}.

A structure consistent with this formula, and the method of preparation, is shown. The major feature is the acetylide group bridging two iron atoms, whilst still attached to the third metal atom. In addition, the three metal atoms interact to give a heteronuclear triatomic cluster. Other complexes were obtained from similar reactions between various metal carbonyls and the iron—,



(II)

ruthenium— and iridium—copper complexes mentioned above. Some of these for example, $(\pi\text{-}C_5H_5)Fe_3(C_2Me)(CO)_7$, can also be obtained using the uncomplexed acetylides, and thus are similar to those reported recently by Yasufuku and Yamazaki [4].

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