# New Group IB Metal Chemistry. Part 6.[1] Reactions of Copper(I) Acetylides with Chloro(η-cyclopentadienyl)bis(triphenylphosphine)-ruthenium and *cis*-Tricarbonylchlorobis(triphenylphosphine)rhenium

By **Omar M. Abu Salah** and **Michael I. Bruce**,*† Department of Inorganic Chemistry, The University, Bristol BS8 1TS

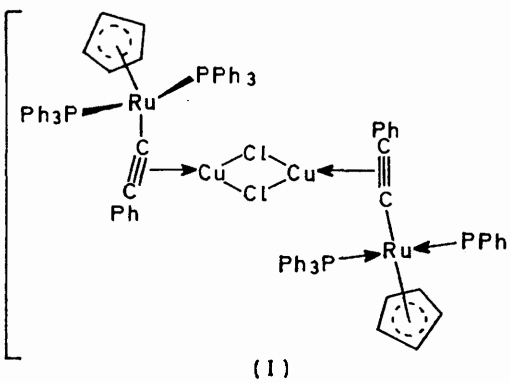
Reactions between $[RuCl(PPh_3)_2(C_5H_5)]$ and $Cu(C_2R)$ afford $[RuCuCl(C_2R)(PPh_3)_2(C_5H_5)]$ [R = Me, Ph (I), or *p*-$MeC_6H_4$], $[RuCu(C_2R)_2(PPh_3)(C_5H_5)]$ (R = *p*-$MeC_6H_4$ or *p*-$FC_6H_4$), $[\{RuCu(C_2C_6F_5)_2(PPh_3)(C_5H_5)\}_2]$ and $[Ru(C_2R)(PPh_3)_2(C_5H_5)]$ (R = *p*-$FC_6H_4$ or $C_6F_5$). Treatment of (I) with $MeC(CH_2PPh_2)_3$ (tde) gives $[Ru(C_2Ph)(PPh_3)_2(C_5H_5)]$ and [CuCl(tde)]; $Fe_2(CO)_9$ and (I) react to give the trinuclear cluster $[Fe_2Ru(C_2Ph)(CO)_6(PPh_3)(C_5H_5)]$. Similar reactions between *cis*-$[ReCl(CO)_3(PPh_3)_2]$ and $Cu(C_2R)$ afford $[ReCuCl(C_2Ph)(CO)_3(PPh_3)_2]$, $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$, and $[Re(C_2C_6F_5)(CO)_3(PPh_3)_2]$.

WE have recently reported reactions between substituted copper(I) arylacetylides, $Cu(C_2R)$ (R = Ph, $C_6H_4Me$-*p*, $C_6H_4F$-*p*, or $C_6F_5$) and cyclopentadienyliron carbonyl halides,[2,3] and of some of these with $[MCl(CO)(PPh_3)_2]$ (M = Rh or Ir),[4] to give unusual complexes containing copper. We have now extended these studies to ruthenium and rhenium. Preliminary reports have appeared concerning some of these results.[5,6]

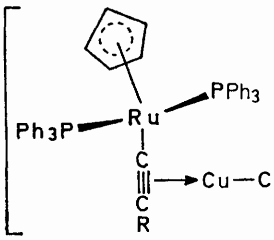
## RESULTS AND DISCUSSION

The chemistry of $[RuCl(PPh_3)_2(C_5H_5)]$ has recently been shown[7,8] to differ significantly from that of $[RuCl(CO)_2(C_5H_5)]$.[9,10] The reaction between $[RuCl(PPh_3)_2(C_5H_5)]$ and $Cu(C_2Ph)$ afforded two isomers of a 1 : 1 adduct. The first isolated (least soluble) is not soluble enough for solution spectroscopic and osmometric studies and may be a dimer (I) or oligomer of the more-soluble form. The latter was obtained as yellow crystals, shown to have the monomeric structure (II; R = Ph) by a single-crystal *X*-ray structure determination.[5] In solution, also, osmometric measurements indicated that the complex is monomeric, in contrast to $[\{FeCuCl(C_2Ph)(CO)_2(C_5H_5)\}_2]$.[2,3] In chlorinated solvents slow decomposition occurs. In the i.r. spectrum two bands were present in the ν(C≡C) region, while the $^1H$ n.m.r. spectrum contained resonances in the aromatic region and also a sharp singlet at τ 5.4, assigned to the $C_5H_5$ protons.

The ruthenium complex has a strong tendency to remain solvated on crystallisation, and indeed the structure determination revealed a molecule of acetone associated with each molecule of complex. In most respects the geometry of the copper–phenylacetylide group in (II; R = Ph) and the iron–copper complex mentioned above is similar. Steric crowding of the copper atom by the triphenylphosphine ligands attached to ruthenium may prevent dimerisation by formation of Cu–Cl–Cu bridges as found in the iron complex. Considering the complexed acetylene as occupying one co-ordination site, the copper is linear two-co-ordinate and few examples of this geometry have been structurally characterised; however, discrete $[CuCl_2]^-$ ions have been found in $[Ph_2P(O)CH_2CH_2NHEt_2][CuCl_2]$[11] and $[CuCl\{N_6P_6(NMe_2)_{12}\}][CuCl_2]$.[12]



(I)



(II) R = Ph, *p*-$MeC_6H_4$, or Me

The η-complexed copper(I) chloride may be removed from (II; R = Ph) by reaction with the tridentate 1,1,1-tris(diphenylphosphinomethyl)ethane (tde) as the complex [CuCl(tde)]. The complex $[Ru(C_2Ph)(PPh_3)_2(C_5H_5)]$ (III; R = Ph) could be isolated from the mother liquor in *ca.* 60% yield. No reaction occurred when a non-chelating phosphine, such as $PPh_3$, was used.

---

† *Present address:* Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001.

[1] Part 5, O. M. Abu Salah and M. I. Bruce, *J. Organometallic Chem.*, 1974, **87**, C15.

[2] M. I. Bruce, R. Clarke, J. Howard, and P. Woodward, *J. Organometallic Chem.*, 1972, **42**, C107.

[3] O. M. Abu Salah and M. I. Bruce, *J.C.S. Dalton*, 1974, 2302.

[4] O. M. Abu Salah, M. I. Bruce, M. R. Churchill, and S. A. Bezman, *J.C.S. Chem. Comm.*, 1972, 858.

[5] O. M. Abu Salah, M. I. Bruce, R. E. Davis, and N. V. Raghavan, *J. Organometallic Chem.*, 1974, **64**, C48.

[6] O. M. Abu Salah, M. I. Bruce, and A. D. Redhouse, *J.C.S. Chem. Comm.*, 1974, 855.

[7] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 2376.

[8] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 106.

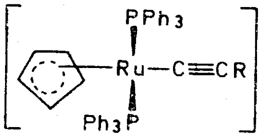
[9] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2158.

[10] T. Blackmore, M. I. Bruce, J. D. Cotton, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2931.

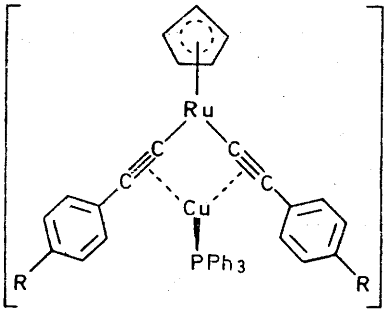
[11] M. G. Newton, H. D. Caughman, and R. C. Taylor, *Chem. Comm.*, 1970, 1227; *J.C.S. Dalton*, 1974, 258.

[12] W. C. Marsh and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 1482.

Complex (III; R = Ph) is air stable in the solid state, but decomposes slowly in solution. In the i.r. spectrum a sharp ν(C≡C) band appeared *ca.* 100—150 cm$^{-1}$ higher than found for (II; R = Ph). The mass spectrum contained a weak molecular ion and other ions formed by loss of PPh$_3$, Ph, and the acetylide unit.



(III) R = Ph, *p*-FC$_6$H$_4$, or C$_6$F$_5$



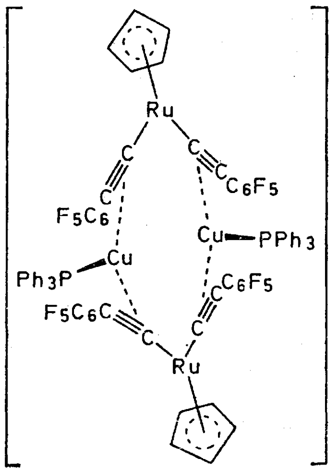
(IV) R = Me or F

The reactions of the various copper acetylides with the ruthenium chloride complex are more complex than indicated above, however. Further studies have indicated that two isomeric forms of (II) can be isolated, using their differing solubilities as a basis for separation. The more-soluble isomer forms yellow-orange blocks and may be a non-solvated form of (II).

With copper(I) *p*-tolylacetylide the major product was a halogen-free complex of stoicheiometry [RuCu-(C$_2$C$_6$H$_4$Me-*p*)$_2$(PPh$_3$)(C$_5$H$_5$)], (IV; R = Me), which was accompanied by the 1 : 1 adduct (II; R = *p*-MeC$_6$H$_4$) formed in less than 10% overall yield. Using Cu-(C$_2$C$_6$H$_4$F-*p*), the complex (IV; R = F) was the major product, but was accompanied by small amounts of [Ru-(C$_2$C$_6$H$_4$F-*p*)(PPh$_3$)$_2$(C$_5$H$_5$)], (III; R = *p*-FC$_6$H$_4$). No 1 : 1 adduct was isolated from this reaction. The i.r. spectra of (IV; R = Me or F) contained broad medium-intensity ν(C≡C) bands at *ca.* 1 950 cm$^{-1}$, suggesting that both acetylenic bonds are η bonded to copper in each complex. Osmometric molecular-weight determinations agreed with a monomeric formulation for both complexes, and the n.m.r. spectra indicated that in each complex the two arylacetylide groups were in similar environments. Thus, the methyl groups resonated as a sharp singlet at τ 7.86, while the fluorine signal was a multiplet at 117 p.p.m. A likely structure for complexes (IV) is the zwitterion aggregate illustrated. Although we were unable to obtain direct *X*-ray structural confirmation of this, the assignments follow from the identical environments found for the acetylide groups, the lowering of the ν(C≡C) frequency, and the similar structures found for [RhAg$_2$(C$_2$C$_6$F$_5$)$_5$(PPh$_3$)$_3$] [13] and [ReCu(C$_2$C$_6$F$_5$)$_2$(CO)$_3$-(PPh$_3$)] (see below).[6] The two ions forming the aggregate, [Cu(PPh$_3$)]$^+$ and [Ru(C$_2$Ar)$_2$(C$_5$H$_5$)]$^-$, are bonded to each other *via* copper–acetylide η-type bonds; no metal–metal bond is present and the formal oxidation states are Cu$^{I}$ and Ru$^{II}$.

Complex (III; R = *p*-FC$_6$H$_4$) was identified by the usual methods, and particularly significant was the sharp ν(C≡C) band at *ca.* 100 cm$^{-1}$ higher than found in (IV; R = F). The $^1$H n.m.r. spectrum contained a complex multiplet for the aryl protons, with a sharp singlet at τ 5.26 for the C$_5$H$_5$ group. The mass spectrum is similar to that of (III; R = Ph).

The reaction between [RuCl(PPh$_3$)$_2$(C$_5$H$_5$)] and copper(I) pentafluorophenylacetylide afforded moderate yields of a crimson-red tetranuclear complex, characterised as [{RuCu(C$_2$C$_6$F$_5$)$_2$(PPh$_3$)(C$_5$H$_5$)}$_2$], (V). The i.r. spectrum contained two broad ν(C≡C) bands at 2 025 and 1 870 cm$^{-1}$, while the $^1$H n.m.r. spectrum showed only one sharp peak at τ 5.11 for the C$_5$H$_5$ protons. The $^{19}$F n.m.r. spectrum contained only the three characteristic signals for the C$_6$F$_5$ groups, indicating that all four were in identical environments. The crystals were not suitable for an *X*-ray structure determination, but on the basis of the data given we propose structure (V) for this complex. Again the major feature is the zwitterionic aggregate of [Cu(PPh$_3$)]$^+$ cations and [Ru(C$_2$C$_6$F$_5$)$_2$(C$_5$H$_5$)]$^-$ anions held together by the copper–acetylide η interaction. A longer reaction time afforded some [Ru(C$_2$C$_6$F$_5$)-(PPh$_3$)$_2$(C$_5$H$_5$)], (III; R = C$_6$H$_5$), as yellow crystals. The ν(C≡C) band appeared at 2 100 cm$^{-1}$.



(V)

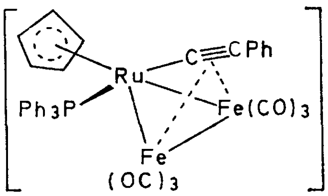
The monomeric 1 : 1 adduct [RuCuCl(C$_2$Me)(PPh$_3$)$_2$-(C$_5$H$_5$)] (II; R = Me) was obtained from Cu(C$_2$Me) and the ruthenium chloride. It was identified by analytical and spectroscopic methods; the i.r. spectrum contained a ν(C≡C) band at 1 980 cm$^{-1}$, and the methyl resonance in the $^1$H n.m.r. spectrum appeared as a triplet as a result of coupling to the two phosphorus atoms. In reactions where halide-free complexes were isolated, the copper derivatives [Cu$_2$Cl$_2$(PPh$_3$)$_3$] or [{CuCl(PPh$_3$)}$_4$] were also isolated. It may be that elimination of

---

[13] O. M. Abu Salah, M. I. Bruce, M. R. Churchill, and B. G. deBoer, *J.C.S. Chem. Comm.*, 1974, 688.

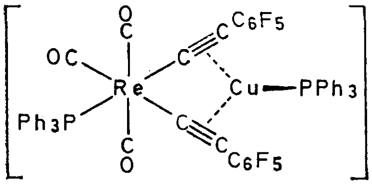
$[CuCl(PPh_3)]$, and its subsequent tetramerisation, is the means whereby a vacant co-ordination site can be created about the ruthenium atom, which might then add a further molecule of the copper(I) acetylide to form the zwitterionic complexes.

Reaction between (II; R = Ph) and $Fe_2(CO)_9$ afforded the heterotrinuclear cluster $[Fe_2Ru(C_2Ph)(CO)_6(PPh_3)(C_5H_5)]$, (VI). The i.r. spectrum contained only terminal ν(CO) bands, in contrast to the related complex $[Fe_3(C_2Ph)(CO)_7(H_5C_5)]$ which exhibits a bridging ν(CO) band at 1 870 $cm^{-1}$.[3] The mass spectrum did not contain a molecular ion, but significant peaks corresponding to $[Ru(C_2Ph)(CO)(PPh_3)(C_5H_5)]^+$, $[Ru(PPh_3)(C_5H_5)]^+$, and $[Fe(CO)_n(PPh_3)]^+$ ($n$ = 0—3) originated from this complex. A plausible structure for this complex is (VI), in which the major feature of interest is the interaction of the metal acetylide with the $Fe_2(CO)_6$ group. Metal–metal bonding involving all metal atoms is consistent with the deep colour of (VI), and enables each metal to conform to the effective atomic number rule.

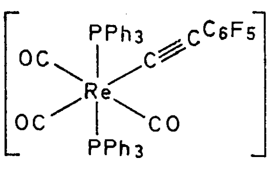


(VI)

*Rhenium Complexes*.—The reaction between $Cu(C_2C_6F_5)$ and *cis*-$[ReCl(CO)_3(PPh_3)_2]$ gave three products, characterised as $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$, (VII), $[Re(C_2C_6F_5)(CO)_3(PPh_3)_2]$, (VIII), and $[\{CuCl(PPh_3)\}_4]$. Complex (VII) formed pale yellow crystals, the i.r. spectrum of which was complicated in the 2 000 $cm^{-1}$ region; the $^{19}F$ n.m.r. spectrum contained only three resonances, characteristic of one type of $C_6F_5$ group. In contrast to most of the copper-containing complexes described above, (VII) was sufficiently volatile to give a mass spectrum which contained a $m/e$ 1 240 parent-ion cluster. A single-crystal *X*-ray determination[6] of (VII) revealed the structure illustrated, in which a $[Cu(PPh_3)]^+$ cation is attached to the $[Re(C_2C_6F_5)_2(CO)_3(PPh_3)_2]^-$ anion by the usual copper–acetylide η interaction.[6] No metal–metal bond is present and both metal atoms attain the favoured 18-electron configuration. The mother liquor from crystallisation of (VII) afforded white crystals of composition $[Re(C_2C_6F_5)(CO)_3(PPh_3)_2]$, (VIII). The i.r. spectrum contained three ν(CO) bands, characteristic of a *mer*-$M(CO)_3$ group, and a weak band at 2 015 $cm^{-1}$ assigned to the uncomplexed ν(C≡C) vibration. It is likely that this complex has structure (VIII) with mutually *trans* phosphine ligands, although a *cis* arrangement is also possible.

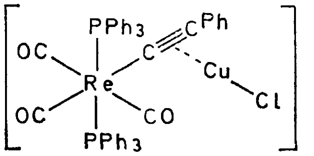


(VII)



(VIII)

A different result was obtained in the reaction with $Cu(C_2Ph)$, when a 1 : 1 adduct (IX) formed. The ν(CO) region of the i.r. spectrum contained bands with a similar pattern to that of *cis*-$[ReCl(CO)_3(PPh_3)_2]$ together with two bands assigned to η-bonded acetylide. We were not able to determine whether the complex is a monomer or dimer, but it seems clear that the structure corresponds to that found for $[RuCuCl(C_2Ph)(PPh_3)_2(C_5H_5)]$[5] (if a monomer) or $[\{FeCuCl(C_2Ph)(CO)_2(C_5H_5)\}_2]$[2] (if a dimer).



(IX)

Both the formation and structures of the complexes described above merit some comment. The simple acetylides are envisaged as resulting from a metathetical reaction (1) and the formation of the copper(I) chloride

$$[L_nMCl] + Cu(C_2R) \longrightarrow [L_nM(C_2R)] + CuCl \quad (1)$$

adducts, previously found with $[\{FeCuCl(C_2Ph)(CO)_2(C_5H_5)\}_2]$, follows. In contrast to most copper(I)–acetylene adducts, the strength of the copper–acetylide η bond is considerable, the complexes remaining unaffected when treated with triphenylphosphine which is normally able to displace a number of other ligands from CuCl complexes. In the presence of excess of acetylide a new type of addition–elimination reaction occurs [equation (2)]. This reaction is probably facilitated by

$$[L_nM(C_2R)] + Cu(C_2R) \longrightarrow [L_{n-1}M(C_2R)_2Cu] + L \quad (2)$$

dissociation of one of the tertiary phosphine ligands which migrates to the copper atom, or perhaps by elimination of LCuCl from the initial 1 : 1 adduct. The reaction may be considered to be simple complex-ion formation [equation (3)] accompanied by redistribution of ligands to preserve the original co-ordination numbers.

$$[L_nM(C_2R)] + Cu(C_2R) \longrightarrow [CuL]^+ + [L_{n-1}M(C_2R)_2]^- \quad (3)$$

Reactions of this type have been encountered previously in copper chemistry.[14] Thus addition of a tertiary phosphine such as $PMe_3$ to $[\{Cu(C_2Ph)\}_n]$ affords the complex $[Cu(C_2Ph)(PMe_3)]$ which is a tetramer in the solid state.[15] This consists of $[Cu(PMe_3)_2]^+$ and $[Cu(C_2Ph)_2]^-$ ions forming an aggregate *via* η bonding from the anionic acetylide to the cationic copper atom, in a

---

[14] G. E. Coates and C. Parkin, *J. Inorg. Nuclear Chem.*, 1961, **22**, 59.

[15] P. W. R. Corfield and H. M. M. Shearer, *Acta Cryst.*, 1966, **21**, 957.

similar fashion to that found for complex (VII) in the present work. Few copper halide adducts of alkynes are known, those of cycloalkynes such as cyclo-octyne being reported in 1972,[16] while other complexes of metal acetylides which have been structurally characterised are limited to the simple acetylides $[\{M(C_2R)\}_n]$ and tertiary phosphine derivatives $[\{M(C_2R)(PR_3)\}_n]$ (M = Cu or Ag) and $[Fe_2(CO)_6(C_2Ph)(PPh_2)]$,[17] in addition to complexes mentioned above.

## EXPERIMENTAL

Spectra were recorded using Perkin-Elmer 457 (i.r.), Varian Associates HA 100 (n.m.r.; $^1H$ at 100 MHz, $^{19}F$ at 94.14 MHz), and A.E.I.–G.E.C. MS 902 (mass; at 70 eV) * instruments. M.p., analytical, i.r. and n.m.r. data are listed in the Table.

M.p., analytical, i.r., and n.m.r. data

| Complex | M.p. ($\theta_c$/°C) | Analyses [a]/% C | H | X | P | Cu | Other | M [a] | $\bar{\nu}$(C≡C)/cm$^{-1}$ | Chemical shifts [$\tau$($^1$H) or p.p.m. ($^{19}$F)] Ph [b] | $C_5H_5$ | Other | Solvent |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $[\{RuCuCl(C_2Ph)(PPh_3)_2(C_5H_5)\}]_n$ (I) | 202—206 | 66.15<br>(66.05) | 4.65<br>(4.05) | Cl 3.75<br>(4.0) | 6.9<br>(7.0) | | Ru 10.5<br>(11.4) | | | | | | |
| $[RuCuCl(C_2Ph)(PPh_3)_2(C_5H_5)]$ (II; R = Ph) | 185—188<br>(decomp.) | 66.15<br>(66.05) | 4.55<br>(4.05) | Cl 4.1<br>(4.0) | | 6.7<br>(7.15) | | 860 [c]<br>(890) | 1 979w, 1 934m [d] | 2.8(m) | 5.4(s) | | e |
| $[Ru(C_2Ph)(PPh_3)_2(C_5H_5)]$ (III; R = Ph) | 205<br>(decomp.) | 74.1<br>(74.25) | 5.35<br>(5.05) | | | | | 792 [f]<br>(792) | 2 076m [g] | 2.7(m) | 5.69(s) | | e |
| $[RuCu(C_2C_6H_4Me)_2(PPh_3)(C_5H_5)]$ (IV; R = Me) | 150—152 | 68.3<br>(68.1) | 4.85<br>(4.7) | | 4.15<br>(4.3) | 8.9<br>(8.8) | | 718 [c]<br>(721) | 1 957m,br [g] | 2.32—2.54(m), 3.5(m) | 5.44(s) | Me 7.86(s) | e |
| | | | | | | | | | | 2.32—2.76(m), 3.5(m) | 5.46(s) | 7.88(s) | h |
| $[RuCuCl(C_2C_6H_4Me)(PPh_3)_2(C_5H_5)]$ (II; R = p-$MeC_6H_4$) | 182—185<br>(decomp.) | 66.15<br>(66.45) | 4.85<br>(4.55) | | 6.8<br>(6.65) | 7.15<br>(7.05) | | 919 [c]<br>(904) | 1 945w, 1 902vw,br [g] | 2.85(m), 3.26(m) | 5.42(m) | Me 7.76(s) | e |
| $[RuCu(C_2C_6H_4F)_2(PPh_3)(C_5H_5)]\cdot\frac{1}{3}OEt_2$ (IV; R = F) | 183—187<br>(decomp.) | 64.5<br>(64.2) | 4.3<br>(4.1) | F 5.5<br>(5.05) | 4.15<br>(4.1) | | | 719 [i]<br>(729) | 1 960m, 1 918vw [g] | 2.35(m), 2.48(m) | 5.26(s) | F 117 | |
| $[Ru(C_2C_6H_4F)(PPh_3)_2(C_5H_5)]$ (III; R = p-$FC_6H_4$) | 187—190 | 72.7<br>(72.65) | 5.15<br>(4.8) | | | | | 809 [f]<br>(809) | 2 076s [d] | | | | |
| $[\{RuCu(C_2C_6F_5)_2(PPh_3)(C_5H_5)\}_2]$ (V) | 209—211 | 53.6<br>(53.5) | 2.2<br>(2.3) | F 21.2<br>(21.75) | 3.5<br>(3.55) | 7.25<br>(7.25) | | 1 596 [c]<br>(1 745) | 2 034m, 1 915w,br, 1 874m,br [d] | 3.62(m) | 5.11(s) | $F^{2,6}$ 141.75,<br>$F^{3,5}$ 165.05,<br>$F^4$ 160.75 | e |
| $[Ru(C_2C_6F_5)(PPh_3)_2(C_5H_5)]$ (III; R = $C_6F_5$) | 142 | 66.75<br>(66.65) | 4.25<br>(3.95) | | | | | 882 [f]<br>(882) | 2 101m, 2 066s, 2 034(sh) [g] | 2.65(m) | 5.62(s) | $F^{2,6}$ 142.9,<br>$F^{3,5}$ 166.3,<br>$F^4$ 165.7 | j |
| $[RuCuCl(C_2Me)(PPh_3)_2(C_5H_5)]$ (II; R = Me) | 168<br>(decomp.) | 64.0<br>(63.8) | 5.05<br>(4.6) | | 7.15<br>(7.6) | 7.2<br>(7.65) | | 833 [c]<br>(878) | 1 982w [g] | 2.82(m) | 5.51(s) | Me 8.21(t) [J(PMe) 1.75 Hz] | e |
| | | | | | | | | | $\nu$(C≡C) + $\nu$(CO) | | | | |
| $[Fe_2Ru(C_2Ph)(CO)_6(PPh_3)(C_5H_5)]$ (VI) | 145—151<br>(decomp.) | 54.9<br>(55.0) | 3.05<br>(3.1) | | 3.4<br>(3.85) | Fe 14.95<br>(13.85) | Ru 11.1<br>(12.4) | | 2 066vs, 2 049s, 2 022w, 2 007m, 1 974m, 1 944vs [k] | | | | |
| $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$ (VII) | 209—211<br>(decomp.) | 53.2<br>(53.2) | 2.5<br>(2.45) | F 15.6<br>(15.3) | 5.2<br>(5.0) | 5.3<br>(5.15) | Re 14.2<br>(15.0) | 1 240 [f]<br>(1 240) | 2 051w, 2 021w, 2 006s, 1 957m, 1 943vs, 1 932vs [k] | 2.32(m), 2.70(m) | | $F^{2,6}$ 136.8,<br>$F^{3,5}$ 163.8,<br>$F^4$ 158.2 | j |
| $[Re(C_2C_6F_5)(CO)_3(PPh_3)_2]$ (VIII) | 196—200<br>(decomp.) | 57.05<br>(56.8) | 3.1<br>(3.0) | | | | | 968 [f]<br>(968) | 2 105w, 2 046m, 1 952vs, 1 932vs [k] | 2.26(m), 2.65(m) | | $F^{2,6}$ 141.8,<br>$F^{3,5}$ 165.5,<br>$F^4$ 162.15 | j |
| $[ReCuCl(C_2Ph)(CO)_3(PPh_3)_2]$ (IX) | | 56.2<br>(56.65) | 3.5<br>(3.5) | | | | | | 2 033vs, 1 997s, 1 970m, 1 941vs, 1 926vs [d] | | | | |

[a] Calculated values are given in parentheses. [b] Aromatic protons. [c] Osmometric, in $C_6H_6$. [d] In Nujol. [e] $CDCl_3$. [f] Mass spectrometric. [g] In $CHCl_3$. [h] $CS_2$. [i] Osmometric, in $CHCl_3$. [j] $(CD_3)_2CO$. [k] In cyclohexane.

Reactions were normally carried out in a nitrogen atmosphere. Chromatography was on columns of Florisil, initially packed in light petroleum (b.p. 40—60 °C). Solvents for reactions were normally dried over sodium, and distilled from calcium hydride before use.

*Reactions of* $[RuCl(PPh_3)_2(C_5H_5)]$.—(a) *With* $Cu(C_2Ph)$. A mixture of $[RuCl(PPh_3)_2(C_5H_5)]$ (363 mg, 0.5 mmol) and excess of $Cu(C_2Ph)$ (164 mg, 1.0 mmol) was heated under reflux in benzene (45 cm$^3$) for 20 h. Filtration and partial evaporation resulted in separation of yellow crystals of $[\{RuCuCl(C_2Ph)(PPh_3)_2(C_5H_5)\}]_n$ (I), ν(C≡C) in Nujol at 1 991m, 1 955(sh) and 1 946s cm$^{-1}$. Addition of light petroleum to the filtrate gave further crops of crystals which were of two types. Manual separation gave more (I), together with yellow-orange blocks of the more-soluble isomer, which on recrystallisation from acetone–light petroleum afforded the solvated complex $[RuCuCl(C_2Ph)(PPh_3)_2(C_5H_5)]\cdot OCMe_2$, (II; R = Ph). The total yield of (I) and (II) was 365 mg (82%). Acetone in the powdered crystalline sample was removed after several hours *in vacuo*, as indicated by analysis (Table). The single-crystal *X*-ray diffraction study [5] revealed the presence of acetone in the lattice.

(b) *With* $Cu(C_2C_6H_4Me$-p$)$. A mixture of the chloride (485 mg, 0.68 mmol) and the copper acetylide (250 mg, 1.4 mmol) was heated for 18 h under reflux in benzene. Filtration, evaporation, and crystallisation of the residue from acetone afforded orange crystals of $[RuCu(C_2C_6H_4Me$-p$)_2(PPh_3)(C_5H_5)]$, (IV; R = Me) (300 mg, 62%). On further concentration the filtrate afforded $[Cu_2Cl_2(PPh_3)_3]$ (110 mg, 36%), m.p. 240—242 °C (lit.,[18] 235—236 °C) (Found: C, 65.0; H, 4.45. Calc. for $C_{54}H_{45}Cl_2Cu_2P_3$: C, 65.58; H, 4.6%). Addition of light petroleum then resulted in formation of yellow blocks of $[RuCuCl(C_2C_6H_4Me$-p$)(PPh_3)_2(C_5H_5)]$, (II; R = p-$MeC_6H_4$) (45 mg, 7%).

(c) *With* $Cu(C_2C_6H_4F$-p$)$. Reaction between $[RuCl(PPh_3)_2(C_5H_5)]$ (363 mg, 0.5 mmol) and $Cu(C_2C_6H_4F$-p$)$ (183 mg, 1 mmol) in refluxing benzene (40 cm$^3$) for 6 h similarly gave orange $[RuCu(C_2C_6H_4F$-p$)_2(PPh_3)(C_5H_5)]$, (IV; R = F) (230 mg, 56%). Further fractional crystallisation gave $[\{CuCl(PPh_3)\}_4]$ (50 mg, 28%) and yellow $[Ru(C_2C_6H_4F$-p$)(PPh_3)_2(C_5H_5)]$, (III; R = p-$FC_6H_4$) (20 mg, 5%).

(d) *With* $Cu(C_2C_6F_5)$. The reaction between the ru-

---

* 1 eV ≈ 1.60 × 10$^{-19}$ J.

[16] G. Wittig and S. Fischer, *Chem. Ber.*, 1972, **105**, 3542.

[17] H. A. Patel, R. G. Fischer, A. J. Carty, D. V. Naik, and G. J. Palenik, *J. Organometallic Chem.*, 1973, **60**, C49.

[18] G. Costa, G. Pellizer, and F. Rubessa, *J. Inorg. Nuclear Chem.*, 1964, **26**, 961.

thenium complex (363 mg, 0.5 mmol) and $Cu(C_2C_6F_5)$ (254 mg, 1.0 mmol) in refluxing benzene for 7 h gave a crimson-red solution. Filtration, evaporation, and crystallisation afforded $[\{CuCl(PPh_3)\}_4]$ (81 mg, 45%) as the first crop, m.p. 237—240 °C (lit.,[19] 240 °C) (Found: C, 59.95; H, 4.2. Calc. for $C_{18}H_{15}ClCuP$: C, 59.8; H, 4.15%). The second fraction was crimson-red $[\{RuCu(C_2C_6F_5)_2(PPh_3)(C_5H_5)\}_2]$, (V) (145 mg, 33%). A third, yellow, product which sometimes contaminated (V) could not be isolated pure on recrystallisation.

When the reaction with $[RuCl(PPh_3)_2(C_5H_5)]$ (250 mg, 0.35 mmol) and $Cu(C_2C_6F_5)$ (170 mg, 0.62 mmol) was carried out in refluxing benzene (35 cm$^3$) for 13 h the original crimson-red colour changed to red-brown. Filtration, concentration, and addition of light petroleum effected separation of white crystals of $[\{CuCl(PPh_3)\}_4]$. Evaporation of the filtrate and recrystallisation (diethyl ether—light petroleum) afforded $[Ru(C_2C_6F_5)(PPh_3)_2(C_5H_5)]$, (III; $R = C_6F_5$).

(e) *With* $Cu(C_2Me)$. The ruthenium complex (363 mg, 0.5 mmol) and $Cu(C_2Me)$ (102 mg, 1.0 mmol) were heated under reflux in benzene (40 cm$^3$) for 20 h. Filtration, evaporation, and crystallisation (acetone–light petroleum) afforded $[RuCuCl(C_2Me)(PPh_3)_2(C_5H_5)]$, (II; R = Me) (245 mg, 55%).

*Reaction between* (II; R = Ph) and $MeC(CH_2PPh_2)_3$.—The complex (200 mg) was stirred with an equimolar amount of $MeC(CH_2PPh_2)_3$ (tde) in benzene (50 cm$^3$) at room temperature overnight, after which time a white precipitate had separated. Evaporation, extraction of the residue with diethyl ether, and crystallisation afforded yellow crystals of $[Ru(C_2Ph)(PPh_3)_2(C_5H_5)]$, (III; R = Ph) (103 mg, 60%). The residue was recrystallised (dichloromethane–light petroleum) to give white [CuCl(tde)] (94 mg, 60%), identified by comparison with an authentic sample (m.p. and mixed m.p. 340—341 °C) (Found: C, 67.65; H, 5.2. $C_{41}H_{39}ClCuP_3$ requires C, 68.0; H, 5.35%), $\tau$ (in $CDCl_3$) 2.34, 3.00(m) (30 H, $PPh_2$), 7.64(m) (6 H, $PCH_2$), and 8.52(m) (3 H, $CMe$).

*Reaction between* (II; R = Ph) *and* $Fe_2(CO)_9$.—A mixture of the complex (200 mg, 0.22 mmol) and $Fe_2(CO)_9$ (200 mg, 0.55 mmol) in benzene (40 cm$^3$) was stirred at room temperature for 18 h. The red-brown mixture resulting was filtered, reduced in volume, and chromatographed (silica gel). The major product was contained in an orange band eluted with light petroleum–diethyl ether (1 : 1). Repeated crystallisation of this fraction afforded successively complex (II; R = Ph) (15 mg, 7.5% recovery), $[Fe_2Ru(C_2Ph)(CO)_6(PPh_3)(C_5H_5)]$, (VI) (25 mg, 15%), with $\nu$(CO) at 2 066vs, 2 049s, 2 022w, 2 007m, 1 974m, and 1 944vs cm$^{-1}$, and $[Fe(CO)_4(PPh_3)]$ (30 mg, 35%), m.p. 197—200 °C (lit.,[18] 202 °C) (Found: C, 61.95; H, 3.7. Calc. for $C_{22}H_{15}FeO_4P$: C, 61.45; H, 3.5%), $\nu$(CO) (in cyclohexane) at 2 054s, 1 984s, and 1 948vs cm$^{-1}$; *m/e* (relative intensity, assignment) 430 (3.5, $P^+$), 402 (4.0, $[P - CO]^+$), 374 (7.0, $[P - 2CO]^+$), 346 (11, $[P - 3CO]^+$), and 318 (100, $[P - 4CO]^+$).

*Reactions of* cis-$[ReCl(CO)_3(PPh_3)_2]$.—(a) *With* $Cu(C_2C_6F_5)$. A mixture of $Cu(C_2C_6F_5)$ (200 mg, 0.79 mmol) and *cis*-$[ReCl(CO)_3(PPh_3)_2]$ (276 mg, 0.33 mmol) was heated under reflux in tetrahydrofuran (30 cm$^3$) for 24 h. The resulting yellow-brown solution was filtered, evaporated, and extracted with diethyl ether to give $[\{CuCl(PPh_3)\}_4]$ (45 mg, 37%). Concentration of the mother liquor afforded pale yellow crystals of $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$, (VII) (85 mg, 21%), $\nu$(CO) (in Nujol) at 2 060w, 2 036w, 2 011vs, 1 956vs, and 1 923vs cm$^{-1}$; *m/e* (relative intensity, assignment) 1 240 (vw, $P^+$), 1 212 (vw, $[P - CO]^+$), 1 184 (vw, $[P - 2CO]^+$), 1 156 (vw, $[P - 3CO]^+$), 986, (w, $[Re(C_2C_6F_5)(CO)_3(PPh_3)_2]^+ \equiv P'^+$), 958 (w, $[P' - CO]^+$), 930 (w, $[P' - 2CO]^+$), 902 (w, $[P' - 3CO]^+$), 894 (m, $[1\,156 - PPh_3]^+$), 752 (m, $[Re(C_2C_6F_5)(CO)_4PPh_3]^+ \equiv P''^+$), 724 (w, $[P'' - CO]^+$), 696 (m, $[P'' - 2CO]^+$), 668 (w, $[P'' - 3CO]^+$), and 640 (m, $[P'' - 4CO]^+$). At *m/e* 262 and below, intense ions formed by fragmentation of $PPh_3$ (from thermal decomposition) were present. The above results were obtained with some difficulty, and suggest that thermal decomposition of (VII) to (VIII) and $[Re(C_2C_6F_5)(CO)_4(PPh_3)]$ occurred in the spectrometer source. A third product was isolated by chromatography of the filtrate, and crystallisation of the fraction eluted with benzene–light petroleum (1 : 9) from diethyl ether–light petroleum gave white crystals of $[Re(C_2C_6F_5)(CO)_3(PPh_3)_2]$, (VIII) (22 mg, 6%).

(b) *With* $Cu(C_2Ph)$. A mixture of *cis*-$[ReCl(CO)_3(PPh_3)_2]$ (140 mg, 0.17 mmol) and $Cu(C_2Ph)$ (140 mg, 0.85 mmol) was heated under reflux in benzene (40 cm$^3$) for 6.5 h. Filtration, evaporation, and crystallisation (diethyl ether) of the residue afforded white crystals of $[ReCuCl(C_2Ph)(CO)_3(PPh_3)_2]$, (IX) (110 mg, 65%), $\nu$ (in Nujol) at 2 033vs, 1 997s, 1 970m, 1 941vs, and 1 926vs cm$^{-1}$.

We thank the International Copper Research Association (INCRA) Inc., New York, for support.

[4/2711 *Received*, 30*th December*, 1974]

---

[19] F. H. Jardine, L. Rule, and A. G. Vohra, *J. Chem. Soc.* (*A*), 1970, 238.