Group IB Metal Chemistry. Part 3.[1] Reactions between Bromo- and Chloro-dicarbonyl-π-cyclopentadienyliron and Copper Acetylides

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

Reactions between $[(\pi\text{-}C_5H_5)Fe(CO)_2X]$ (X = Cl, Br) and CuC_2R (R = Ph, $p\text{-}MeC_6H_4$, $p\text{-}FC_6H_4$, or C_6F_5) afford the complexes $[\{(\pi\text{-}C_5H_5)Fe(CO)_2(C_2R)CuX\}_2]$. In these, the iron acetylide group is π-bonded to copper; the complexes are dimeric via copper–halogen bridges. An alternative method of synthesis is from the acetylide and the copper(I) halide in acetone. Reactions between these complexes and $[Fe_2(CO)_9]$ afford trinuclear $[(\pi\text{-}C_5H_5)Fe_3(C_2R)(CO)_7]$.

TRANSITION-METAL ACETYLIDES have been known for many years, and the major features of their chemistry have been described.[2] Although the analogous Group IB derivatives have found extensive application in organic synthesis, there have been no reported uses in the sphere of organotransition-metal chemistry. This paper describes some initial results obtained during a wide-ranging study of the interactions of copper and silver acetylides with a variety of transition-metal complexes.

The normally insoluble yellow copper(I) phenylacetylide dissolves readily in boiling tetrahydrofuran or acetone containing $[(\pi\text{-}C_5H_5)Fe(CO)_2Cl]$ to give an orange solution. Concentration readily affords well-formed air-stable orange crystals of a 1 : 1 adduct (I), moderately soluble in benzene, ether, or acetone. A similar bromo-complex was obtained from the corresponding reaction using $[(\pi\text{-}C_5H_5)Fe(CO)_2Br]$. Other related compounds were formed when substituted copper(I) phenylacetylides were used.

The structure of complex (I) has been determined by a single-crystal X-ray diffraction study,[3] as the dimeric structure illustrated. This appears to be the first occasion on which a discrete, simple, acetylene–copper π-complex has been structurally characterised. The polymeric copper phenylacetylide and several tertiary phosphine derivatives are well-known examples of complexes containing copper bonded in this way, but contain other less well-defined interactions between the acetylenic carbons and the copper atoms. Neither phenyl- nor diphenyl-acetylene form simple π adducts with copper halides; cyclo-octyne has been reported to form the compounds C_8H_{12},CuX (X = Cl, Br).[4]

Under high resolution, the two ν(CO) bands are close doublets (separation 6—12 cm⁻¹), the relative intensities of the two pairs of lines varying with concentration (in $CHCl_3$). This phenomenon may result from some dissociation of the dimer occurring in solution, which is supported by osmometric molecular weight determinations, e.g. M 450 in chloroform. Of interest also is the general stability of the adduct, especially in solution, which we find to be greater than that of the free acetylide complex $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Ph)]$.
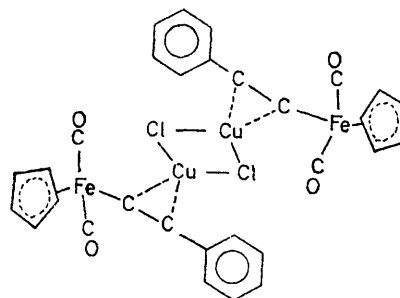
Complexes of type (I) may also be made directly from

the appropriate copper(I) halide and the acetylide in acetone, and representative examples were so prepared using $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2R)]$ (R = Me, Ph). Yields of between 85 and 90% would be obtained in this way.

(I)

The reaction between complex (I) and $[Fe_2(CO)_9]$, investigated as a reaction to remove the complexed CuCl, afforded a copper mirror, and deep purple crystals of $[(\pi\text{-}C_5H_5)Fe_3(C_2Ph)(CO)_7]$.‡ The same complex was also obtained from a reaction between the uncomplexed iron acetylide and $[Fe_2(CO)_9]$. This trinuclear complex was characterised by analysis and from its mass spectrum, which showed a parent ion at m/e 530 (most intense peak of an Fe_3 pattern). Other ions include those corresponding to the usual stepwise loss of seven carbonyl groups. The i.r. spectrum contained six terminal ν(CO) bands in the region 2070—1960 cm⁻¹, together with one band at 1870 cm⁻¹. The ¹H n.m.r. spectrum had only the resonances arising from C_6H_5 and C_5H_5 groups.

A plausible structure for complex (II) is shown, with the iron-bonded acetylide group interacting with the two other iron atoms; all three metal atoms form a triangular cluster. The intense colour of the complex suggests some metal–metal interaction to be present. Although structure (II) satisfies the E.A.N. rule, the single low ν(CO) band is unusual, and we suggest that the single CO group attached to the $Fe(C_5H_5)$ group may also interact to a degree, i.e. asymmetrically, with the other two iron atoms as in (IIa) {cf. $[(C_5H_5)_2Rh_2Fe_2(CO)_8]$ with one bridging and two asymmetric CO groups having ν(CO) below 1900 cm⁻¹ at 1849 and 1788 cm⁻¹}. In this case

---

¹ M. I. Bruce, D. M. Abu Salah, R. E. Davis, and N. V. Raghavan, *J. Organometallic Chem.*, 1974, **65**, C48 is considered to be Part 2.

² See, for example: M. L. H. Green, ' Organometallic Compounds,' Methuen, London, vol. 2, The Transition Elements, pp. 271—280.

³ M. I. Bruce, R. Clark, J. Howard, and P. Woodward, *J. Organometallic Chem.*, 1972, **42**, C107.

⁴ G. Wittig and S. Fischer, *Chem. Ber.*, 1972, **105**, 3542.

we assign a total of six electrons to the Fe–CO and two Fe–Fe bonds, with a non-integral number of electrons

(II)

(IIa)

(IIb)
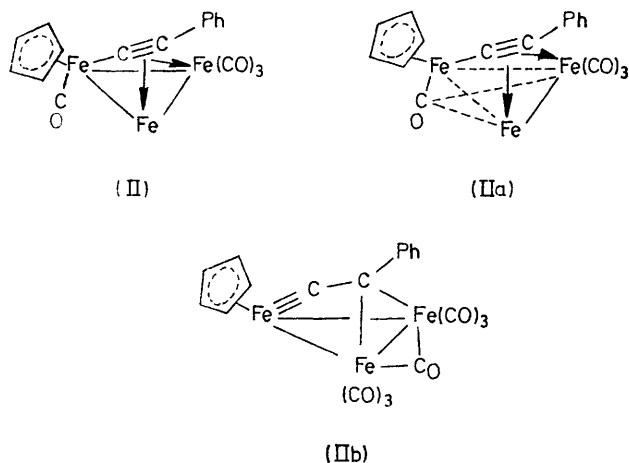
being associated with both Fe–Fe and Fe–CO interactions.

During the course of our work, several complexes obtained from transition-metal alkynyls and iron, cobalt, and nickel carbonyls and including complex (II), were reported by Japanese workers.[5] However, we do not at this stage have any evidence to support their view of the structure of (II), which involves an Fe–C triple bond (IIb).

[5] K. Yasafuku and H. Yamazaki, *Bull. Chem. Soc. Japan*, 1972, **45**, 2664.

During an attempted preparation of [(π-C₅H₅)Fe(CO)₂(C₂Ph)] by the Grignard route, in which the hydrolysis step was carried out using dilute HCl, the product was not the expected acetylide, but contained a ν(acyl CO) band in the i.r. spectrum, in addition to the characteristic ν(CO) bands from the (π-C₅H₅)Fe(CO)₂ group. We briefly examined the reaction between the iron acetylide and dilute HCl, and obtained the same product in over 50% yield. The ^{1}H n.m.r. spectrum contained resonances at τ 2·78m (5H, C₆H₅), 5·25s (5H, C₅H₅), and 5·90s (2H, CH₂), and the mass spectrum contained ions at m/e 296, 268, 240, and 212, together with strong ions at m/e 205 ([C₅H₅Fe(CO)₃]$^+$) and 91 ([C₇H₇]$^+$). These data suggested that an acid-catalysed addition of water to the acetylide had occurred, and the identity of the complex as the phenylacetyl derivative [(π-C₅H₅)Fe(CO)₂COCH₂Ph] was confirmed by its independent synthesis from [(π-C₅H₅)Fe(CO)₂]$^-$ and PhCH₂COCl.

The formation of complexes of this type has been reported previously by Jolly and Pettit,[6] who observed the formation of [(π-C₅H₅)Fe(CO)₂COEt] in a similar reaction using [(π-C₅H₅)Fe(CO)₂(C₂Me)].

We have found the most convenient route to the methylacetylide, [(π-C₅H₅)Fe(CO)₂(C₂Me)], to be the reaction between the chloride and the Grignard reagent. Previously this compound has been prepared indirectly by rearrangement of [(π-C₅H₅)Fe(CO)₂CH₂C₂H] on acid

[6] P. W. Jolly and R. Pettit, *J. Organometallic Chem.*, 1968, **12**, 491.

TABLE 1
M.p. and analytical data (%)

Complex	M.p. (t/°C)	Found (calc.)					
		C	H	F or Cl	Cu	Other	M ^{a}
[{(C₅H₅)Fe(CO)₂(C₂Ph)CuCl}₂] (I)	160—162d	47·9 (47·75)	2·65 (2·65)	9·2 (Cl) (9·4)	16·1 (16·8)	Fe 13·85 (14·85)	450 ^{b} (757)
[{(C₅H₅)Fe(CO)₂(C₂p-tol)CuCl}₂]	158—159d	49·5 (49·2)	3·15 (3·1)	9·65 (Cl) (9·1)			674 (782)
[{(C₅H₅)Fe(CO)₂(C₂C₆H₄F)CuCl}₂]	158—162d	45·75 (45·55)	2·5 (2·3)	5·4 (F) (4·8)	15·55 (16·1)		
[{(C₅H₅)Fe(CO)₂(C₂C₆F₅)CuCl}₂]	170—173d	38·9 (38·6)	1·55 (1·7)	19·05 (F) (20·35)	13·05 (13·6)		
[{(C₅H₅)Fe(CO)₂(C₂Me)CuCl}₂]	145—147	37·8 (38·1)	2·55 (2·6)	11·15 (Cl) (11·25)	19·8 (20·2)		525 (630)
[{(C₅H₅)Fe(CO)₂(C₂Ph)CuBr}₂]	153—154d	42·5 (42·45)	2·25 (2·4)				633 (843)
[(C₅H₅)Fe₃(C₂Ph)(CO)₇] (II)	136—138d	46·0 (45·3)	1·95 (1·9)				530 ^{c} (530)
[(C₅H₅)Fe(CO)₂C₂Me]	95—96	55·65 (55·55)	3·75 (3·7)				216 ^{c} (216)

^{a} In benzene unless otherwise stated. ^{b} CHCl₃. ^{c} Mass spectrometric.

TABLE 2
I.r. (cm^{-1}), and n.m.r spectra

Complex	ν(CO) ^{a}	N.m.r.^{b}	Solvent
[{(C₅H₅)Fe(CO)₂(C₂Ph)CuCl}₂]	2061vs, 2053vs, 2013vs, 2003vs	τ 2·6m (5H, C₆H₅), 4·58s (5H, C₅H₅)	(CD₃)₂CO
[{(C₅H₅)Fe(CO)₂(C₂p-tol)CuCl}₂]	2060vs, 2054vs, 2013vs, 2004vs	τ 2·74m (4H, C₆H₄), 4·58s (5H, C₅H₅), 7·69 (3H, Me)	(CD₃)₂CO
[{(C₅H₅)Fe(CO)₂(C₂C₆H₄F)CuCl}₂]	2054vs, 2005vs	τ 2·44m, 2·94m (4H, C₆H₄), 4·57 (5H, C₅H₅) F 114·3tt (J_{HF}, 5·4, 8·4 Hz)	(CD₃)₂CO
[{(C₅H₅)Fe(CO)₂(C₂C₆F₅)CuCl}₂]	2061vs, 2012vs	τ 4·85s (5H, C₅H₅) F 138·3(F₂₆), 159(F₄), 164·3(F₃₅)	CDCl₃
[{(C₅H₅)Fe(CO)₂(C₂Me)CuCl}₂]	2058vs, 2051vs, 2012vs, 2002vs	τ 4·90s (5H, C₅H₅), 7·88 (3H, Me)	CDCl₃
[{(C₅H₅)Fe(CO)₂(C₂Ph)CuBr}₂]	2055vs, 2049vs, 2010vs, 2001vs		

^{a} In CHCl₃. ^{b} ^{19}F Chemical shifts in p.p.m. upfield from internal CFCl₃.

alumina, or directly from NaC_2Me and $[(\pi\text{-}C_5H_5)Fe(CO)_2Br]$ (1% yield).[6]

EXPERIMENTAL

Spectra were obtained using Perkin-Elmer 257 (infrared), Varian HA100 (^1H and ^{19}F n.m.r.), and AEI MS902 (mass) instruments. Solvents were dried and distilled before use, and reactions were carried out in a nitrogen atmosphere. Chromatography was on columns of Florisil, initially packed in light petroleum.

Copper(I) acetylides were prepared by reacting the appropriate acetylene with an ammoniacal ethanolic solution of copper(I) chloride. The iron acetylides were made by the Grignard route in ca. 50% yield.

Reactions of $[(\pi\text{-}C_5H_5)Fe(CO)_2Cl]$.—(a) *Copper(I) phenyl-acetylide.* A mixture of $[(\pi\text{-}C_5H_5)Fe(CO)_2Cl]$ (2·12 g, 10 mmol) and CuC_2Ph (1·65 g, 10 mmol) in acetone (150 ml) was refluxed for 6 h, during which time most of the acetylide dissolved, while the colour of the solution changed from red to deep orange. Filtration, concentration, and addition of light petroleum afforded well-formed orange crystals of the dimeric adduct $[\{(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Ph)CuCl\}_2]$ (I) (1·69 g, 42%). Addition of light petroleum to the concentrated mother liquor resulted in precipitation of further amounts of the complex (1).

Alternatively, chromatography of the mother liquors gave amounts of ferrocene (10%), diphenylbuta-1,4-diyne (1%), and some complex (I), eluted with ether.

(b) *Copper(I) p-tolylacetylide.* A similar reaction to (a), using $CuC_2C_6H_4Me\text{-}p$ in tetrahydrofuran for 6 h, afforded the adduct $[\{(\pi\text{-}C_5H_5)Fe(CO)_2(C_2C_6H_4Me\text{-}p)CuCl\}_2]$ (810 mg, 27%), crystallised from an acetone–light petroleum mixture. Chromatography of the mother liquor gave small amounts of ferrocene (9%) and di-p-tolylbuta-1,4-diyne, m.p. 182—184° (lit.,[7] 183—183·2°) (Found: C, 93·7; H, 6·15%; M, 230. Calc. for $C_{18}H_{14}$: C, 93·8; H, 6·2%; M, 230) (1%).

(c) *Copper(I) p-fluorophenylacetylide.* This reaction was carried out as in (a) using $CuC_2C_6H_4F\text{-}p$ (182 mg, 1 mmol) in tetrahydrofuran (50 ml) for 4 h, gave the adduct $[\{(\pi\text{-}C_5H_5)Fe(CO)_2(C_2C_6H_4F\text{-}p)CuCl\}_2]$ (73 mg, 16%). In contrast to the other reactions, relatively higher yields of ferrocene (34%) and di-p-fluorophenylbuta-1,4-diyne (25%), m.p. 193—193·5° (Found: C, 80·95; H, 3·45%; M, 238. Calc. for $C_{16}H_8F_2$: C, 80·7; H, 3·35%; M, 238); ^{19}F n.m.r. (CDCl$_3$): 106·1 p.p.m. (triplet of triplets, J_{HF} 5·5, 8·5 Hz).

(d) *Copper(I) pentafluorophenylacetylide.* A mixture of $[(\pi\text{-}C_5H_5)Fe(CO)_2Cl]$ (212 mg, 1 mmol) and $CuC_2C_6F_5$ (254 mg, 1 mmol) was refluxed in tetrahydrofuran (40 ml) for 2 h. Evaporation of solvent and recrystallisation of the residue from ether, afforded $[\{(\pi\text{-}C_5H_5)Fe(CO)_2(C_2C_6F_5)CuCl\}_2]$ (83 mg, 20%).

Preparation of $[\{(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Ph)CuBr\}_2]$.—A mixture of $[(\pi\text{-}C_5H_5)Fe(CO)_2Br]$ (1·0 g, 3·9 mmol) and CuC_2Ph (0·65 g, 3·9 mmol) in tetrahydrofuran (40 ml) was refluxed for 24 h to give an orange-brown solution. Evaporation of the filtered solution gave a brown oil which was recrystallised from aqueous acetone. The resulting fine orange-yellow plates of $[\{(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Ph)CuBr\}_2]$ were filtered off, and washed with light petroleum (170 mg, 10%).

Reactions of Copper(I) Halides.—(a) *With* $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Ph)]$. Copper(I) chloride (99 mg, 1 mmol) and the iron acetylide (278 mg, 1 mmol) were refluxed in deoxygenated acetone (35 ml) for 5½ h. Filtration and addition of light petroleum to the concentrated filtrate gave yellow crystals of complex (I) (320 mg, 85%), identical with the complex prepared from $[(\pi\text{-}C_5H_5)Fe(CO)_2Cl]$ and CuC_2Ph as described above.

Using copper(I) bromide (146 mg, 1 mmol) and the iron acetylide (278 mg, 1 mmol) in a similar reaction for 20 h afforded $[\{(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Ph)CuBr\}_2]$ (160 mg, 38%).

(b) *With* $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Me)]$. A similar reaction between copper(I) chloride (99 mg, 1 mmol) and $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Me)]$ (216 mg, 1 mmol), carried out for 100 min, afforded yellow $[\{(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Me)CuCl\}_2]$ (271 mg, 86%).

Preparation of $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Me)]$.—A slow stream of MeC_2H was bubbled into a solution of Bu^nMgBr [from Bu^nBr (5·4 g, 45 mmol) and magnesium turnings (2 g) in tetrahydrofuran (20 ml)] at 40—50 °C. A further 20 ml solvent was added, and the whole added to $[(\pi\text{-}C_5H_5)Fe(CO)_2Cl]$ (5·0 g, 23 mmol) in tetrahydrofuran (25 ml) at −78 °C. After warming to room temperature, and hydrolysis with 5% aqueous NH_4Cl, conventional work-up procedures gave $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Me)]$ (2·2 g, 45%) as yellow crystals, m.p. 95—96 °C.

Action of Dilute HCl *on* $[(\pi\text{-}C_5H_5)Fe(CO)_2C_2Ph.]$—A solution of $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2Ph)]$ (278 mg, 1 mmol) in tetrahydrofuran (20 ml) was treated with 5% aqueous HCl (30 ml) and stirred for 4 h. The mixture was extracted with ether, the extract dried, solvent removed, and the residue sublimed. Chromatography of the sublimate afforded a yellow fraction with light petroleum–ether (9 : 1), identified as $[(\pi\text{-}C_5H_5)Fe(CO)_2COCH_2Ph]$ (150 mg, 51%), m.p. 77·5—78° (Found: C, 60·85; H, 4·05. $C_{15}H_{12}FeO_3$ requires C, 60·8; H, 4·0%); i.r.: $\nu(CO)$ in cyclohexane at 2022vs and 1962vs cm^{-1}.

The same complex was prepared by a reaction between $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ {from $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2]$ (710 mg, 2 mmol) and sodium amalgam} and $PhCH_2COCl$ (620 mg, 4 mmol) in tetrahydrofuran (75 ml). After 2·5 h, removal of solvent, sublimation, and chromatography as above gave $[(\pi\text{-}C_5H_5)Fe(CO)_2COCH_2Ph]$ (430 mg, 36%), identical in all respects with the above product.

Preparation of $[(\pi\text{-}C_5H_5)Fe(C_2Ph)(CO)_7]$ (II).—(a) Di-iron enneacarbonyl (819 mg, 2·25 mmol) was added to complex (I) (566 mg, 1·5 mmol) in benzene (120 ml), and the mixture was stirred for 2—3 h. After this time, all the $[Fe_2(CO)_9]$ had reacted to give a deep red-brown solution, and a bright copper mirror had been deposited on the wall of the flask. After filtration and evaporation, an ether extract of the residue was chromatographed. Light petroleum–ether mixtures eluted a red-brown band, from which dark red-purple, almost black, crystals of the cluster complex (II) were obtained (60 mg, 7·5%). In solution, rapid decomposition occurred in air after about 10 min, with separation of a copious brown precipitate.

(b) A mixture of $[(C_5H_5)Fe(CO)_2(C_2Ph)]$ (278 mg, 1 mmol) and $[Fe_2(CO)_9]$ (264 mg, 1 mmol) in benzene (40 ml) was stirred for 12 h at room temperature. Filtration, evaporation, and recrystallisation of the residue from ether afforded complex (II) (115 mg, 27%); $\nu(CO)$ in cyclohexane: 2068vs, 2027vs, 2008vs, 1996m, 1978m, 1966s, and 1870m cm^{-1}.

[7] Y. S. Zal'kind and B. M. Fundylev, *J. Gen. Chem. U.S.S.R.*, 1939, **9**, 1725.