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Reactions of metalloalkynes. New C_2 bonding mode in a trimetallic complex†‡

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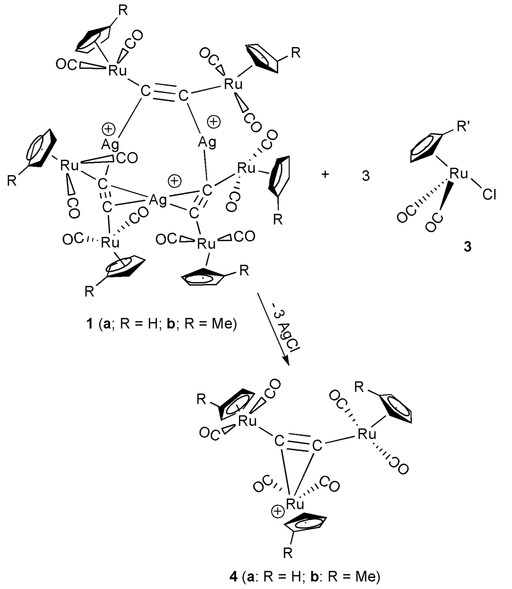
The reaction of the silver complexes [{{Ru(CO)$_2$(η-C$_5$H$_4$R)}$_2$(μ-C≡C)}$_3$Ag$_3$][BF$_4$]$_3$ (R = H or Me) with [RuCl(CO)$_2$(η-C$_5$H$_4$R)] at room temperature gave the new trimetallic complexes [{Ru(CO)$_2$(η-C$_5$H$_4$R)}$_3$(η^1:η^2-C≡C))][BF$_4$] which contain the C_2^{2-} ligand surrounded by ruthenium atoms; these complexes do not contain metal–metal bonds and were characterised by single crystal X-ray studies; the solid state structure is not retained in solution, where it is found to be fluxional on the NMR timescale and the dynamic process postulated could be described as 'bearing-like'.

The chemistry of even and odd numbered carbon bridges[1–3] is of interest as a matter of scientific curiosity coupled with potential application as molecular wires[4–15] and in a number of important materials related fields.[16–19] One subset of that series, containing the C_2^{2-} ligand,[20–24] has presented a number of different bonding modes[25–27] for M_nC_2 (n = 2, 3, 4 and 5). However, to the best of our knowledge the only known example for n = 3[25] contains metal–metal bonds.

The reaction of [Ag$_3$({Ru(CO)$_2$(η-C$_5$H$_4$R)}$_2$(μ-C≡C))$_3$](BF$_4$)$_3$ **1** (R = H, **a**; R = Me, **b**), (Scheme 1) (prepared from [{Ru(CO)$_2$(η-C$_5$H$_4$R)}$_2$(μ$_2$-C≡C)] **2** (R = H, **a**;[20] R = Me, **b**), and AgBF$_4$ in the appropriate ratio) with three equivalents of [RuCl(CO)$_2$(η-C$_5$H$_5$)] **3**, gave complexes **4** in excellent yield accompanied by the precipitation of AgCl.

These novel complexes represent a new bonding mode for the C_2^{2-} ligand bound to three metal atoms. Conceptually simpler routes to complexes **4** were explored employing the reaction of **2** with [Ru(solvent)(CO)$_2$(η-C$_5$H$_5$)]$^+$. However, the seemingly simple abstraction of chloride from electron poor [RuCl(CO)$_2$(η-C$_5$H$_5$)], in the presence of tetrahydrofuran, using AgBF$_4$ or TlBF$_4$ was unsucessful. Although [Ru(NCMe)(CO)$_2$(η-C$_5$H$_5$)][PF$_6$][28] did react with **2a**, it gave an intractable mixture of products, presumably cationic, which we were not able to separate, and complex **3a** did not appear to be among the products. In an attempt to rationalise this chemistry and given the problems encountered in the abstraction of Cl$^-$ using silver ions we investigated the reaction of [RuCl(CO)$_2$(η-C$_5$H$_5$)] **3**, with AgBF$_4$ in the presence of **2a**, which gave complex **4a** in good yield. The mechanism appears to involve the intermediacy of **1a** enroute to **4a** and the precipitation of AgCl. It is unclear why this reaction and the direct reaction of **1a** with [RuCl(CO)$_2$(η-C$_5$H$_5$)] is so facile but presumably the labile Ag$^+$ ion in an array like that of complex **1a** is more 'naked', possessing a greater charge density than the aggregates formed by AgBF$_4$ in tetrahydrofuran. The notion of 'simple' halide abstraction by metal ions is obviously a naïve picture of the reality of this type of reaction. In the case of [RuCl(CO)$_2$(η-C$_5$H$_5$)] a complex aggregate must be formed with AgBF$_4$ that leads to products other than that expected. This silver adduct route is a reliable route to the preparation of the trimetallic compounds **4**.



Scheme 1 Synthesis of complex **4**.

The spectroscopic data were insufficient to unequivocally assign the structure of the complex. The carbide carbon signals were not observed in the ^{13}C NMR spectrum but singlets were observed for the carbonyl and cyclopentadienyl ligands. Excellent crystals were obtained from dichloromethane–diethyl ether of both **4a** and **4b**, and the results of an X-ray structural determination[29] of the former are presented in Fig. 1. The compound crystallised in in the centrosymmetric space group $P1$ with a complete molecule devoid of any intrinsic symmetry comprising the asymmetric unit. The result clearly shows that the cation contains a C_2 unit bound to three Ru(CO)$_2$(η-C$_5$H$_5$) fragments. Two of these ruthenium atoms are bound in η^1 fashion with distances to the ethynediyl moiety of 2.065(6) [Ru(1)–C(1)] and 2.044(6) Å [Ru(3)–C(2)]. The third ruthenium atom, Ru(2), is bound in an η^2 fashion to the ethynediyl carbons in an unsymmetrical manner with Ru(2)–C(1) and Ru(2)–C(2) being 2.324(5) and 2.388(5) Å, respectively.

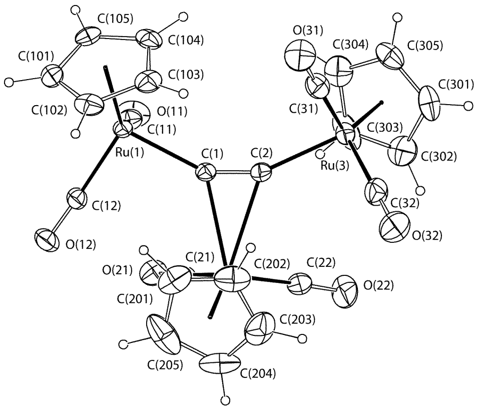


Fig. 1 ORTEP diagram of the cation in **4a**.

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† Electronic supplementary information (ESI) available: Synthesis and characterisation of complexes **4a** and **4b**. See http://www.rsc.org/suppdata/cc/b1/b110930h/

‡ This paper constitutes Part 4 of the series.

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The C≡C^{2-} unit is not appreciably lengthened relative to the ethynediyl starting materials[20,30] where the distance of 1.206(9) Å is comparable with the 1.222(9) Å for **2a**. However, the ethynediyl portion of the molecule is bent which is consistent with accepted models for metal π-bound alkynes. The deviation from linearity is significant with angles of 152.5(4) and 155.2(5)° for Ru(1)–C(1)–C(2) and Ru(2)–C(2)–C(1), respectively. One possible canonical component invokes a metallacyclopropene-type structure but the lack of lengthening of the C≡C^{2-} bond suggests structure **4a**, Scheme 1, as best fitting the available data. The geometries of the $Ru(CO)_2(\eta\text{-}C_5H_4R)$ units are unexceptional.

The solution state structure of complexes **4** was probed by variable temperature ^1H NMR studies. One signal for all of the cyclopentadienyl ligands was observed between room temperature and −90 °C (in CD_2Cl_2 or d_6-acetone); the compounds precipitated from solution below this temperature hampering the collection of the low-temperature limiting spectrum. Two signals in a 2 : 1 ratio would be expected if there was no mechanism for exchanging the σ- and π-bound ruthenium atoms on the NMR timescale.

One such mechanism for the exchange invokes the rotation of the C≡C^{2-} unit within a triangle defined by the three formally positive ruthenium atoms, Fig. 2, or *vice versa*. This motion is reminiscent of the action of a mechanical bearing. The fluxional motion of acetylide fragments[25,31] has been observed previously in the binuclear complex $[\{Fe(CO)_2(\eta\text{-}C_5Me_5)\}_2(\mu\text{-}C{\equiv}CH)]^+$ **5**. The dynamic behaviour of **5** was investigated by solution NMR measurements and interpreted as a 1,2-shift of the hydrogen atom on the carbide bridge[25] *via* an intermediate (Fig. 3) similar to **A**. One can view such an intermediate as formally analogous to complexes **4** and as exemplifying a coordination compound of the hydrogen ion.

In this and previous work we have shown that the carbide ligand is able to adopt a diversity of bonding modes depending on the environment in which it finds itself and in the present case we have found a new $M_3(C_2)$ mode which does not contain metal–metal bonds. This work and others involving the C_2^{2-} dianion has shown it to be relatively labile, with the multimetallic complexes containing this ligand presumably adopting solid state structures influenced by crystal-packing forces.

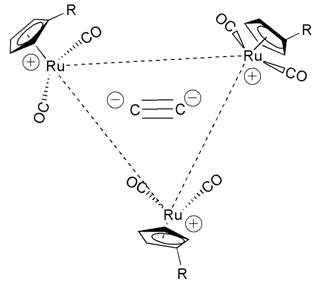

Fig. 2 Proposed mechanism of exchange for **4**.

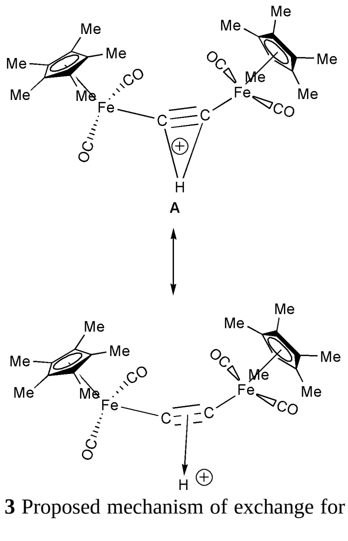

Fig. 3 Proposed mechanism of exchange for **5**.

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Notes and references

1 R. Schennach, D. G Naugle, D. Cocke, R. Dembinski and J. A. Gladysz, *Vacuum*, 2000, **56**(2), 115.
2 H. Lang, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 547; W. Beck, B. Niemer and M. Wieser, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 923.
3 U. H. F. Bunz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 969.
4 T. Bartik, B. Bartik, M. Brady, R. Dembinski and J. A. Gladysz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 414.
5 B. Bartik, R. Dembinski, T. Bartik, A. M. Arif and J. A. Gladysz, *New J. Chem.*, 1997, **21**, 739.
6 S. B. Falloon, W. Q. Weng, A. M. Arif and J. A. Gladysz, *Organometallics*, 1997, **16**, 2008.
7 M. Brady, W. Q. Weng, Y. L. Zhou, J. W. Seyler, A. J. Amoroso, A. M. Arif, M. Bohme, G. Frenking and J. A. Gladysz, *J. Am. Chem. Soc.*, 1997, **119**, 775.
8 S. B. Falloon, A. M. Arif and J. A. Gladysz, *Chem. Commun.*, 1997, **21**, 629.
9 T. Bartik, W. Q. Weng, J. A. Ramsden, S. Szafert, S. B. Falloon, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1998, **120**, 11071.
10 W. Q. Weng, J. A. Ramsden, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1993, **115**, 3824.
11 A. Vidalferran, C. M. Muller and J. Sanders, *J. Chem. Soc., Chem. Commun.*, 1994, **7**, 2657.
12 M. Uno and P. H. Dixneuf, *Angew. Chem., Int. Ed.*, 1998, **37**, 1714.
13 D. Touchard, S. Guesmi, M. Bouchaib, P. Haquette, A. Daridor and P. H. Dixneuf, *Organometallics*, 1996, **15**, 2579.
14 D. Touchard, P. Haquette, A. Daridor, L. Toupet and P. H. Dixneuf, *J. Am. Chem. Soc.*, 1994, **116**, 11157.
15 I. R. Whittall, M. G. Humphrey and D. C. R. Hockless, *Organometallics*, 1995, **14**, 3970.
16 I. R. Whittall, M. P. Cifuentes, M. J. Costigan, M. G. Humphrey, S. C. Goh, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1994, **471**, 193.
17 H. Lang, S. Blau, G. Rheinwald and G. Wildermuth, *J. Organomet. Chem.*, 1995, **489**, 21.
18 M. S. Khan, A. K. Kakkar, N. J. Long, J. Lewis, P. Raithby, P. Nguyen, T. B. Marder, F. Wittmann and R. H. Friend, *J. Mater. Chem.*, 1994, **4**, 1227.
19 M. D. Ward, *Chem. Ind. (London)*, 1996, **15**, 568.
20 G. A. Koutsantonis and J. P. Selegue, *J. Am. Chem. Soc.*, 1991, **113**, 2316.
21 G. A. Koutsantonis, J. P. Selegue and J.-G. Wang, *Organometallics*, 1992, **11**, 2704.
22 L. T. Byrne, C. S. Griffith, G. A. Koutsantonis, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1998, **21**, 1575.
23 L. T. Byrne, C. S. Griffith, J. P. Hos, G. A. Koutsantonis, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1998, **565**, 259.
24 C. S. Griffith, G. A. Koutsantonis, B. W. Skelton and A. H. White, *Chem. Commun.*, 1998, **7**, 1805.
25 M. Akita and Y. Morooka, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 420.
26 M. I. Bruce, *Coord. Chem. Rev.*, 1997, **166**, 91.
27 D. Miguel, M. Moreno, J. Perez and V. Riera, *J. Am. Chem. Soc.*, 1998, **120**, 417.
28 A. Jungbauer and H. Behrens, *Z. Naturforsch., Teil B*, 1978, **33**, 1083.
29 *Crystal data* for **4a**: $C_{23}H_{15}BF_4O_6Ru_3$, M_r = 777.4, triclinic, space group $P1$, a = 14.292(3), b = 10.397(3), c = 9.281(3) Å, α = 93.04(3), β = 103.04(2), γ = 107.29(2)°, V = 1272 Å^3, $T \approx$ 295 K, R = 0.052 for 5065 'observed' ($I > 3\sigma(I)$) single counter absorption corrected diffractometer reflections ($2\theta_{max}$ = 56°). CCDC reference number 175273. See http://www.rsc.org/suppdata/cc/b1/b110930h/ for crystallographic data in CIF or other electronic format.
30 M. Appel, W. Beck, J. R. Phillips and W. C. Trogler, *Organometallics*, 1990, **9**, 1296.
31 M. Akita, A. Takabuchi, M. Terada, N. Ishii, M. Tanaka and Y. Morooka, *Organometallics*, 1994, **13**, 2516.