DALTON
COMMUNICATION

Decarboxylation reactions of alkyne-carboxylic acids as a route to multiply bonded $[Re_2]^{n+}$ μ-alkyne and μ-carbyne complexes

Jitendra K. Bera, Phillip E. Fanwick and Richard A. Walton*

Department of Chemistry, Purdue University, 1393 Brown Building, West Lafayette, IN 47907-1393, USA. E-mail: rawalton@purdue.edu

Received 13th October 2000, Accepted 30th November 2000
First published as an Advance Article on the web 21st December 2000

Multiply bonded organometallic complexes $Re_2(\mu\text{-}Cl)(\mu\text{-}\eta^2\text{-}HCCH)Cl_4(\mu\text{-}dppm)_2$ (2) and $Re_2(\mu\text{-}Cl)(\mu\text{-}CCH_2CH_3)Cl_4(\mu\text{-}dppm)_2$ (3) are formed upon refluxing $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-}dppm)_2$ (1) with $HO_2CC{\equiv}CCO_2H$ and $CH_3C{\equiv}CCO_2H$, respectively; these reactions are believed to proceed *via* the *in situ* formation of the corresponding metal alkynoates and the crystal structures of 2 and 3 show that the Re–Re distances of 2.6567(5) and 2.5277(6) Å are in accord with Re–Re bond orders of 1.5 and 2, respectively.

The carbonation reactions of Grignard and organolithium reagents to form metal carboxylates have been studied in considerable detail,[1] while the reverse reaction, namely, the decarboxylation of metal carboxylates, has been utilized extensively in the synthesis of organometallic complexes (eqn. 1).[2]

$$[M]\text{–}O_2CR \longrightarrow [M]\text{–}R + CO_2 \qquad (1)$$

This strategy has included the use of metal alkynoates[2a,3] which can be used as precursors to metal alkynyl derivatives. Although carboxylate groups (RCO_2) are known to bridge a wide variety of multiply bonded dimetal units (M_2),[4] attempts to synthesize organometallic complexes using the appropriate dimetal alkynoates and alkenoates have not previously been reported. We now describe the first examples of the synthesis of multiply bonded dimetal organometallics that contain $[Re_2]^{n+}$ cores, where $n = 5$ or 8, by this decarboxylation method using both $HO_2CC{\equiv}CCO_2H$ and $CH_3C{\equiv}CCO_2H$.

Although the preformed metal alkynoate precursors for the decarboxylation syntheses were not isolated, their *in situ* synthesis was readily achieved by the reactions of the paramagnetic acetate complex $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-}dppm)_2$ (**1**)[5] with the corresponding alkynoic acid. A green coloured paramagnetic complex **2** was obtained upon refluxing complex **1** with acetylenedicarboxylic acid in ethanol.† A cyclic voltammetric (CV) measurement of **2** in 0.1 M $Bu^n{}_4NPF_6$–CH_2Cl_2 shows the presence of a reversible one-electron oxidation [$E_{\frac{1}{2}}$(ox)] and a reversible one-electron reduction [$E_{\frac{1}{2}}$(red)] at +0.54(70) and −0.49(70) V,‡ *vs.* Ag/AgCl, respectively.

Confirmation of the identity of complex **2** comes from an X-ray crystal structure determination.§ The molecular structure, which can be described by the representation $Re_2(\mu\text{-}Cl)(\mu\text{-}\eta^2\text{-}HCCH)Cl_4(\mu\text{-}dppm)_2$, is depicted in Fig. 1 together with the atomic numbering scheme. The distance Re–Re′ is 2.6567(5) Å. The acetylene molecule bridges the two metal centers in an η^2 fashion; the Re–C distances span the range 2.205(15)–2.244(20) Å, and the C–C distance of the η^2-HCCH ligand is 1.31(2) Å. A formal Re–Re bond order of 1.5 would accord with an 18-electron count for the Re centres and the μ-η^2-HCCH ligand behaving as a 4-electron donor.[6] Support for the formulation of this product comes from its mass spectrum (using ESI) which has prominent peaks for $[M]^+$ and $[M - Cl]^+$ at $m/z = 1343$ and 1308, respectively, with the experimental isotopic patterns matching the calculated ones in each case.

When the reaction of **1** was carried out with 2-butynoic acid in either methanol or ethanol, a similar green coloured complex **3** was obtained.¶ While we originally anticipated that the complex would be $Re_2(\mu\text{-}Cl)(\mu\text{-}\eta^2\text{-}HCCCH_3)Cl_4(\mu\text{-}dppm)_2$, *i.e.* analogous to **2**, CV measurement showed $E_{\frac{1}{2}}$(ox) and $E_{\frac{1}{2}}$(red) at +0.90(65) and −0.68(65) V,‡ respectively, behaviour quite different from that observed for **2**. Also unlike **2**, complex **3** was found to be diamagnetic with a sharp singlet in its $^{31}P\text{-}\{^1H\}$ NMR spectrum at δ −16.9. The ^1H NMR resonances for the bridgehead methylene protons of the μ-dppm ligands appear as multiplets centered at δ +3.20 (2H) and +3.80 (2H), while a triplet and quartet were observed at δ +2.01 (3H) and +5.95 (2H), respectively, confirming the presence of an ethyl group.

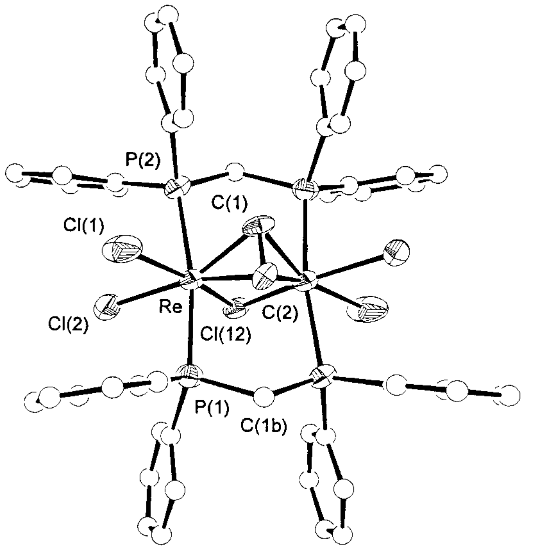

Fig. 1 ORTEP[14] representation of the structure of **2** with the important atoms labeled. The thermal ellipsoids are drawn at the 40% level except for the carbon atoms of the dppm ligand which are circles of arbitrary radius. Some important bond distances (Å) and bond angles (°) are as follows: Re–Re′ 2.6567(5), Re–C(1) 2.205(15), Re–C(2) 2.244(20), Re′–C(1) 2.224(14), Re′–C(2) 2.208(19), C(1)–C(2) 1.31(2), Re–Cl(12) 2.351(5), Re′–Cl(12) 2.312(5), Re–Cl(1) 2.3954(18), Re–Cl(2) 2.4058(19); Re–C(1)–Re′ 73.7(4), Re–C(2)–Re′ 73.3(6), Re–Cl(12)–Re′ 69.46(15). Note: Re′ is the unlabeled Re atom.

The structural identity of complex **3** was confirmed by the X-ray single crystal structure which showed it to be the μ-alkylidyne complex $Re_2(\mu\text{-}Cl)(\mu\text{-}CCH_2CH_3)Cl_4(\mu\text{-}dppm)_2$.§ The molecular structure of complex **3** is shown in Fig. 2 together with the atomic numbering scheme. The basic core is somewhat similar to complex **2**. However, instead of it being a μ-η^2-alkyne complex, the structural parameters involving the carbon-containing unit show it to be a symmetrically bridging alkylidyne complex. The distances Re(1)–C(11) and Re(2)–C(11) are 1.946 (11) and 1.938 (11) Å, respectively, which are much longer than expected (1.70–1.76 Å) for a terminal Re≡C (sp) triple bond,[7] but shorter than a rhenium–vinylidene (Re=C) unit {*e.g.* 2.046(8) Å in *trans*-[ReCl(=C=CHPh)(dppe)$_2$]}.[8] Since the atom C(11) bridges the two rhenium centers in a symmetrical fashion, a formal Re–C bond order of 1.5 should be present in this alkylidyne complex. The distances C(11)–C(12)

DOI: 10.1039/b008265l

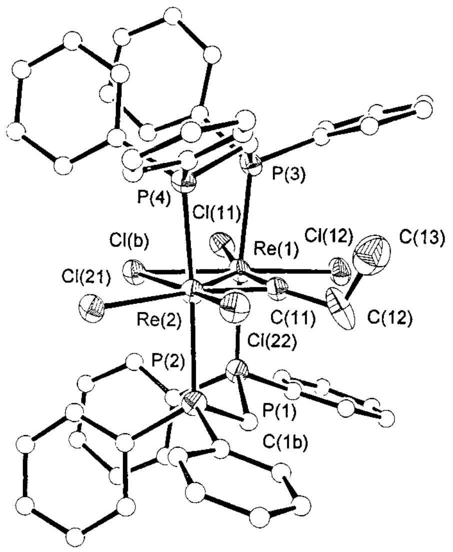

Fig. 2 ORTEP[14] representation of the structure of **3** with the important atoms labeled. The thermal ellipsoids are drawn at the 40% level except for the carbon atoms of the dppm ligand which are circles of arbitrary radius. Some important bond distances (Å) and bond angles (°) are as follows: Re(1)–Re(2) 2.5277(6), Re(1)–C(11) 1.946(11), Re(2)–C(11) 1.938(11), C(11)–C(12) 1.544(19), C(12)–C(13) 1.49(2), Re(1)–Cl(b) 2.419(3), Re(2)–Cl(b) 2.412(3); Re(1)–C(11)–Re(2) 81.2(4), C(11)–C(12)–C(13) 109.7(16), Re(1)–Cl(b)–Re(2) 63.10(7).

and C(12)–C(13) are 1.544(19) and 1.49(2) Å, respectively, typical of C–C single bonds. The angle C(11)–C(12)–C(13) is 109.7(16)°, which accords with the sp^3-hybridized nature of C(12). Consistent with these results we find a high abundance peak at *m*/*z* = 1323 in the electrospray mass spectrum of **3**, assigned to $[M - Cl]^+$ with the correct isotopic distribution pattern; the parent ion peak $[M]^+$ was not observed.

It should be noted that a large excess of acid was used in both reactions in order to prevent the competing known thermal reduction of $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ to $Re_2Cl_4(\mu\text{-dppm})_2$.[5] The amount of acid was varied from 7–10 equivalents without changing the nature and yields of **2** and **3**.

The reactions of **1** with alkynoic acids most likely proceed *via* the corresponding metal alkynoates. Several stable dimetal-carboxylates have been prepared recently by this method, including the complexes $Re_2(\mu\text{-}O_2C\text{-}4\text{-}C_5H_5N)Cl_4(\mu\text{-dppm})_2$ and $[Re_2Cl_4(\mu\text{-dppm})_2]_2(\mu\text{-}O_2C\text{-}1,4\text{-}C_6H_4CO_2)$ which have been structurally characterized.[9] This implies that the mechanism involves the *in situ* formation of metal alkynoates derived from $HO_2CC{\equiv}CCO_2H$ and $CH_3C{\equiv}CCO_2H$, which are relatively unstable and undergo thermal decarboxylation to form **2** and **3**, respectively.

Since the yields of **2** and **3** never exceed 50%, and these products contain one more chlorine atom than the number present in the starting material $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ (**1**), some portion of **1** must be sacrificed in these reactions. Note that the addition of free Cl^- (as $[Bu_4{}^nN]Cl$) to these reaction mixtures did not significantly affect the yields of **2** and **3** indicating that the mechanism is probably quite complex. It is possible that the conversion of **1** to the μ-alkylidyne complex **3** may proceed through the intermediacy of $Re_2(\mu\text{-}Cl)(\mu\text{-}\eta^2\text{-}HC{\equiv}CCH_3)Cl_4(\mu\text{-dppm})_2$, structurally analogous to **2**, which then converts to **3** *via* an alkyne→alkylidyne rearrangement, in which the excess acid present in the reaction mixture is the source of the extra hydrogen atom.[10]

Additional studies are underway in order to establish further details of the mechanisms of these reactions and examine the scope of this chemistry as it relates to other multiply bonded systems.

Acknowledgement

We thank the John A. Leighty Endowment Fund for support of this work.

Notes and references

† A mixture of $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ (**1**) (0.108 g, 0.08 mmol) and acetylenedicarboxylic acid (0.091 g, 0.80 mmol) was refluxed in ethanol for one day. The green product was separated from the dark coloured solution by filtration, washed with fresh ethanol (3 × 5 mL) and diethyl ether (3 × 5 mL) and dried under vacuum. Yield: 52 mg (48%). Anal. calc. for $C_{52}H_{46}Cl_5P_4Re_2$: C, 46.45; H, 3.45; Cl, 13.18. Found: C, 46.66; H, 3.62; Cl, 12.98%. Magnetic moment (300 K): $\mu_{eff} = 1.71\ \mu_B$.

‡ The values in parentheses are for ΔE_p (*i.e.*, $E_{p,a} - E_{p,c}$) in mV.

§ Single crystals of complexes **2** and **3** were grown from $1,2\text{-}C_2H_4Cl_2\text{–}Et_2O$ and $CH_2Cl_2\text{–}Pr^i{}_2O$, respectively. The data were collected at a temperature of 150 (**2**) or 173 K (**3**) with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer. Lorentz and polarization corrections were applied to the data and an empirical absorption correction using SCALEPACK was applied.[11] The structures were solved using the structure solution program PATTY in DIRDIF92.[12] The remaining atoms were located in successive difference Fourier syntheses. Hydrogen atoms were included in the refinements but restrained to ride on the atoms to which they are bonded. The dirhenium unit of **2** is located about a crystallographic inversion center thereby leading to a disorder between the bridging HCCH and Cl ligands; this disorder was resolved satisfactorily. Refinements were performed using SHELX-97.[13] Crystallographic drawings were done using the program ORTEP.[14]

Crystal data for **2**: $C_{52}H_{46}Cl_5P_4Re_2$, $M = 1344.51$, monoclinic $C2/c$ (no. 15), $a = 22.9626(4)$, $b = 10.8638(3)$, $c = 21.7099(6)$ Å, $\beta = 118.7103(12)°$, $V = 4750.0(4)$ Å^3, $Z = 4$, $D_c = 1.880$ g cm^{-3}, $\mu = 5.616$ mm^{-1}, 20529 reflections (5025 unique, $R_{int} = 0.058$) with $2\theta = 55.0°$, 305 variables, $R = 0.041$ [3703 data, $I > 2\sigma(I)$], $wR(F_0^2) = 0.088$, GoF = 1.024.

Crystal data for $\mathbf{3}\cdot 4CH_2Cl_2\cdot 0.66H_2O$: $C_{57}H_{58.32}Cl_{13}O_{0.66}P_4Re_2$, $M = 1711.15$, monoclinic, $P2_1/c$ (no. 14), $a = 12.4448(3)$, $b = 18.7581(5)$, $c = 27.8011(8)$ Å, $\beta = 101.5817(19)°$, $V = 6357.8(5)$ Å^3, $Z = 4$, $D_c = 1.785$ g cm^{-3}, $\mu = 4.546$ mm^{-1}, 54443 reflections (16031 unique, $R_{int} = 0.073$) with $2\theta = 57.0°$, 705 variables, $R = 0.081$ [10018 data, $I > 2\sigma(I)$], $wR(F_0^2) = 0.168$, GoF = 1.047. CCDC reference number 186/2294. See http://www.rsc.org/suppdata/dt/b0/b008265l/ for crystallographic files in .cif format.

¶ A procedure similar to that described for **2** was employed using 0.104 g (0.08 mmol) of $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ (**1**) and 2-butynoic acid 0.065 g (0.80 mmol) in refluxing methanol or ethanol. Yield: 50 mg (46%). Anal. calc. for $C_{53}H_{49}Cl_5P_4Re_2$: C, 46.82; H, 3.63; Cl, 13.04. Found: C, 47.33; H, 3.67; Cl, 12.94%.

1 B. J. Wakefield, *Comprehensive Organometallic Chemistry*, vol. 7, Pergamon Press, Oxford, 1982, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, ch. 44, pp. 38–39; B. J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon Press, Oxford, 1974, ch. 9, pp. 124–126.

2 (*a*) G. B. Deacon, S. J. Faulks and G. N. Pain, *Adv. Organomet. Chem.*, 1986, **25**, 237; (*b*) R. C. Mehrotra and R. Bohra, *Metal Carboxylates*, Academic Press, New York, 1983.

3 T. Tsuda, Y. Chujo and T. Saegusa, *Chem. Commun.*, 1975, 963.

4 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, 2nd edn., Oxford University Press, Oxford, UK, 1993.

5 A. R. Cutler, D. R. Derringer, P. E. Fanwick and R. A. Walton, *J. Am. Chem. Soc.*, 1988, **100**, 5024.

6 M. H. Chisholm, K. Folting, J. C. Huffman and I. P. Rothwell, *J. Am. Chem. Soc.*, 1982, **104**, 4389.

7 (*a*) D. A. Kort, K.-Y. Shih, W. Wu, P. E. Fanwick and R. A. Walton, *Organometallics*, 1995, **14**, 448; (*b*) M. Leeaphon, A. L. Ondracek, R. J. Thomas, P. E. Fanwick and R. A. Walton, *J. Am. Chem. Soc.*, 1995, **117**, 9715.

8 A. J. L. Pombeiro, S. S. P. R. Almeida, M. F. C. G. Silva, J. C. Jeffrey and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1989, 2381.

9 J. K. Bera, P. E. Fanwick and R. A. Walton, manuscript in preparation.

10 For other examples of the conversion of alkynes to alkylidynes. (*a*) H. Werner, *J. Organomet. Chem.*, 1994, **475**, 45; (*b*) M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197 and references therein; (*c*) Ref. 7(*b*).

11 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1996, **276**, 307.

12 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF92 Program System, Technical Report, Crystallography Laboratory, Univ. of Nijmegen, The Netherlands, 1992.

13 G. M. Sheldrick, SHELX-97, A Program for Crystal Structure Refinement, Univ. of Gottingen, Germany, 1997.

14 C. K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA, 1976.