

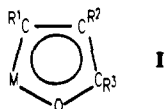
## Use of Dirhenium Complexes as Templates for the Reductive Coupling of Carbon Monoxide with Alkynes through C-O Bond Formation. Synthesis and Characterization of 3-Metallafuran Complexes

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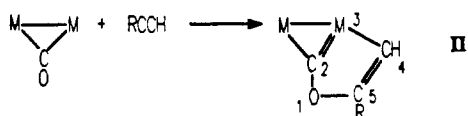
The literature on metallacyclic complexes that contain a 2-metallafuran ring (I) is now very extensive, with many examples existing for the transition elements of groups VI-VIII.<sup>1,2</sup> The



synthetic methodologies used are quite varied, and many of these compounds have been structurally characterized by X-ray crystallography, from which it is apparent that the majority may be viewed as vinyl ketone-like (canonical form A), although the carbenoid structure B also makes a significant contribution in several of the compounds. In the present report we describe a



simple route to the first examples of 3-metallafuran complexes which involves formally the regiospecific addition of terminal alkynes RCCH to a bridging M(μ-CO)M unit as represented in II. This gives rise to a 2-metalated-3-metallafuran unit.



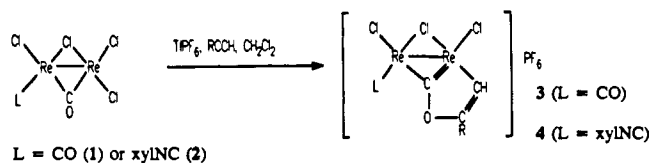
The edge-sharing bioctahedral dirhenium complexes  $\text{Re}_2(\mu\text{-Cl})(\mu\text{-CO})\text{Cl}_3(\text{L})(\mu\text{-dppm})_2$  (**1**, L = CO; **2**, L = xylNC; dppm =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ )<sup>3</sup> react with terminal alkynes  $\text{RC}\equiv\text{CH}$  (R = H, *n*-Pr, *n*-Bu, Ph, or *p*-tol) at room temperature in the presence of  $\text{TiPF}_6$  to afford a novel series of diamagnetic complexes ( $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-COC}(\text{R})\text{CH})\text{Cl}_2(\text{L})(\mu\text{-dppm})_2]\text{PF}_6$ ) in which the reductive coupling of a bridging CO ligand and the alkyne leads to unprecedented C-O bond formation and the generation of a 3-metallafuran ring. This is represented in the following reaction

(1) Selected examples of 2-metallafuran type complexes for groups VI-VIII: (a) Allen, S. R.; Green, M.; Norman, N. C.; Paddick, K. E.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1983**, 1625. (b) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055. (c) Alt, H. G.; Herrman, G. S.; Engelhardt, H. E.; Rogers, R. D. *J. Organomet. Chem.* **1987**, *331*, 329. (d) Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383. (e) Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1992**, *11*, 3505. (f) Stack, J. G.; Simpson, R. D.; Hollander, F. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1990**, *112*, 2716. (g) Garcia Alonso, F. J.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio Camellini, M. *Organometallics* **1992**, *11*, 370. (h) Allevi, C.; Garlaschelli, L.; Malatesta, M. C.; Ganazzoli, F. *Organometallics* **1990**, *9*, 1383.

(2) Bleeker, J. R., private communication. A report on novel iridafuran chemistry will be submitted shortly.

(3) (a) Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 3524. (b) Cotton, F. A.; Dunbar, K. R.; Price, A. C.; Schwotzer, W.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 4843.

(dppm ligands omitted).<sup>4</sup> These reactions are regiospecific to



give the substituent R in the 5-position.

The reactions of **4** with  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  and  $\text{NaBPh}_4$  can be used to prepare analogous  $[\text{BF}_4]^-$  and  $[\text{BPh}_4]^-$  salts of type **4**. The IR spectra of **3** and **4** (Nujol mulls) show  $\nu(\text{CO})$  and  $\nu(\text{CN})$  modes in the ranges 2032-2027 and 2162-2147  $\text{cm}^{-1}$ , respectively, for the terminal carbonyl and xyllyl isocyanide ligands. The reactions of acetylene with the  $^{13}\text{C}$ -labeled derivatives of **1** and **2** generate the labeled compounds  $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-}^{13}\text{COCHCH})\text{Cl}_2(\text{L})(\mu\text{-dppm})_2]\text{PF}_6$ , where L =  $^{13}\text{CO}$  or xylNC. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-}^{13}\text{COCHCH})\text{Cl}_2(^{13}\text{CO})(\mu\text{-dppm})_2]\text{PF}_6$  (recorded in  $\text{CD}_2\text{Cl}_2$ ) has singlets at  $\delta +189$  and  $+331$ , in accord with the presence of a terminally bound CO ligand and a bridging alkyldiyne carbon<sup>5</sup> that is generated from the bridging carbonyl ligand of **1**. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the analogous  $^{13}\text{C}$ -labeled derivative of **4** shows a similar alkyldiyne carbon resonance at  $\delta +339$ .

Confirmation of the identity of these complexes comes from an X-ray crystal structure determination on a compound of type **4** (L = xylNC, R = *p*-tol,  $[\text{BF}_4]^-$  as the anion).<sup>6,7</sup> The dirhenium cation has an edge-sharing bioctahedral geometry (Figure 1). The Re-Re distance (2.558(1) Å) is somewhat shorter than that in the complex  $[\text{Re}_2(\mu\text{-Br})(\mu\text{-HN}_2\text{C}_2\text{Me}_2)\text{Br}_2(\text{NCMe})(\mu\text{-dppm})_2]\text{PF}_6$  (2.666(1) Å),<sup>8</sup> which contains a nitrile-coupled ligand but overall has a structure similar to that of the CO/alkyne coupled product. The relative shortness of the Re-Re bond in **4** is probably due in part to the strong interaction between the bridging alkyldiyne carbon and the two Re atoms. Within the coupled  $\text{Re}(\mu\text{-COCC})\text{Re}$  unit (Figure 1), the alkyldiyne carbon atom C(4) appears to be bound asymmetrically to the two rhenium atoms (the distances are 1.99(2) and 1.88(2) Å), with the shorter of the two distances involving the rhenium atom (Re(2)) that is incorporated into the 3-metallafuran ring. The distances Re(2)-C(1), C(1)-C(2), and C(2)-O(3) of 2.10(3), 1.27(3), and 1.48(3) Å, respectively, are in accord with the 3-metallafuran ring having C as a major contribution to the overall structure.

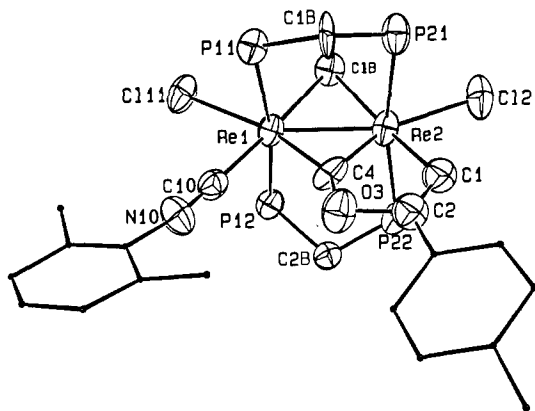
(4) A representative synthesis is as follows: a solution of **1** (0.100 g, 0.075 mmol) and  $\text{TiPF}_6$  (0.030 g, 0.086 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was treated with a slow stream of gaseous acetylene for 2 min. The resulting mixture was then stirred at room temperature for 2 h (this reaction time is critical), and the white precipitate (TIC) was filtered off. The brown filtrate was evaporated to dryness. The residue was extracted into 3 mL of  $\text{CH}_2\text{Cl}_2$  and diethyl ether (40 mL) was added to induce the precipitation of the title complex. After a period of ca. 10 min, the precipitate was filtered off, washed with diethyl ether (10 mL), and dried under vacuum; yield 0.080 g (72%). Anal. Calcd for  $\text{C}_{35}\text{H}_{49}\text{Cl}_3\text{F}_6\text{O}_2\text{P}_3\text{Re}_2$  (i.e.,  $[\text{Re}_2\text{Cl}_2(\mu\text{-COCHCH})(\text{CO})(\mu\text{-dppm})_2]\text{PF}_6\cdot\text{CH}_2\text{Cl}_2$ ): C, 42.36; H, 3.11. Found: C, 42.52; H, 3.07. The presence of a small amount of lattice  $\text{CH}_2\text{Cl}_2$  was confirmed by  $^1\text{H}$  NMR spectroscopy. IR spectrum:  $\nu(\text{CO})$  2032(s)  $\text{cm}^{-1}$ .

(5) (a) Chisholm, M. H.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5284. (b) Chisholm, M. H.; Huffman, J. C.; Heppert, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5116.

(6) Crystal data for  $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-COC}(\text{p-tol})\text{CH})\text{Cl}_2(\text{CNxyl})(\mu\text{-dppm})_2]\text{BF}_4\cdot 0.5\text{H}_2\text{O}$  (+20 °C): space group  $C2/c$ ;  $a = 37.402(8)$  Å,  $b = 15.302(4)$  Å,  $c = 28.578(8)$  Å,  $\beta = 119.06(3)^\circ$ ;  $V = 14\,296(15)$  Å<sup>3</sup>,  $Z = 8$ ,  $d_{\text{calcd}} = 1.504$  g/cm<sup>3</sup>; Enraf-Nonius diffractometer, Mo K $\alpha$  radiation; 9861 unique reflections with  $4^\circ < 2\theta < 45^\circ$  collected, 5158 reflections with  $I > 3.0\sigma(I)$  used in the refinement; all non-carbon atoms of the cation refined anisotropically, hydrogen atoms not included,  $[\text{BF}_4]^-$  anion disordered; empirical absorption correction applied ( $\mu = 36.93$   $\text{cm}^{-1}$ );  $R = 0.066$ ,  $R_w = 0.085$ , GOF = 1.715.

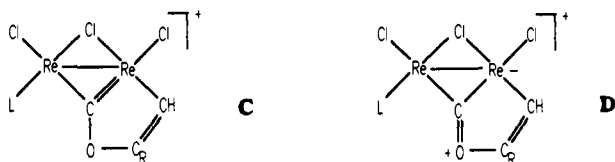
(7) The structures of  $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-COCHCH})\text{Cl}_2(\text{CO})(\mu\text{-dppm})_2]\text{PF}_6$  and  $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-COC}(\text{n-Pr})\text{CH})\text{Cl}_2(\text{CNxyl})(\mu\text{-dppm})_2]\text{PF}_6$  have also been determined. Both display the same connectivity as for the structure in Figure 1, but each possesses a crystallographic disorder that has impeded a full refinement of the structure. Details will be published in due course.

(8) Esjornson, D.; Derringer, D. R.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 2821.



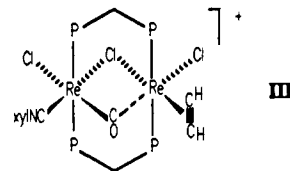
**Figure 1.** ORTEP representation of the structure of the  $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-COC}(p\text{-tol})\text{CH})\text{Cl}_2(\text{CNxyl})(\mu\text{-dppm})_2]^+$  cation with the phenyl groups of the dppm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level. Some important bond distances (Å) and bond angles (deg) are as follows:  $\text{Re}(1)\text{-Re}(2)$  2.558(1),  $\text{Re}(1)\text{-Cl}(11)$  2.429 (6),  $\text{Re}(1)\text{-Cl}(B)$  2.466 (6),  $\text{Re}(1)\text{-C}(4)$  1.99 (2),  $\text{Re}(1)\text{-C}(10)$  2.01 (3),  $\text{Re}(2)\text{-Cl}(2)$  2.406 (7),  $\text{Re}(2)\text{-Cl}(B)$  2.480 (6),  $\text{Re}(2)\text{-C}(1)$  2.10 (3),  $\text{Re}(2)\text{-C}(4)$  1.88 (2),  $\text{O}(3)\text{-C}(2)$  1.48 (3),  $\text{O}(3)\text{-C}(4)$  1.27 (3),  $\text{C}(1)\text{-C}(2)$  1.27 (3);  $\text{Re}(1)\text{-C}(4)\text{-Re}(2)$ , 82.8 (9),  $\text{Re}(2)\text{-C}(4)\text{-O}(3)$  131 (2),  $\text{C}(4)\text{-O}(3)\text{-C}(2)$  107 (2),  $\text{O}(3)\text{-C}(2)\text{-C}(1)$  114 (2),  $\text{C}(2)\text{-C}(1)\text{-Re}(2)$  117 (2),  $\text{C}(1)\text{-Re}(2)\text{-C}(4)$  72 (1).

However, the shortness of  $\text{C}(4)\text{-O}(3)$  (1.27(3) Å) relative to  $\text{C}(2)\text{-O}(3)$  implies that canonical form **D** also makes a significant contribution.



We have also isolated the  $\eta^2$ -alkyne complex  $[\text{Re}_2\text{Cl}_3(\text{CO})(\eta^2\text{-HCCH})(\text{CNxyl})(\mu\text{-dppm})_2]\text{PF}_6$  as orange microcrystals from the reaction of **2** with acetylene when short reaction times were used. Its subsequent conversion to the coupled product **4** when a dichloromethane solution was stirred at room temperature suggests that it is an intermediate in the conversion of **2** to **4**. It

is the logical species that would be formed upon labilizing (by the use of  $\text{TIPF}_6$ ) the terminal  $\text{Re}\text{-Cl}$  bond of **2**, which is cis to the bridging carbonyl ligand. The low frequency of the  $\nu(\text{CO})$  mode in the IR spectrum of this complex ( $1880\text{ cm}^{-1}$ ) accords with the presence of a semibridging carbonyl ligand, while the downfield shift of the acetylene resonance in its  $^1\text{H NMR}$  spectrum ( $\delta +13.4$  in  $\text{CD}_2\text{Cl}_2$ ) is consistent with the  $\eta^2\text{-HCCH}$  ligand behaving as a four-electron donor in such a metal-metal-bonded dirhenium complex.<sup>9,10</sup> We propose that this complex has a structure like that shown in **III**. The coupling of the  $\mu\text{-CO}$  and



$\text{RC}\equiv\text{CH}$  ligands to give the R group in the 4-position of the metallafuran ring will be disfavored because of the steric constraints imposed by the phenyl groups of the dppm ligands within the cleftlike pocket where the alkyne ligand coordinates and then couples with CO. In accord with this conclusion, we find that internal alkynes do not couple with the  $\mu\text{-CO}$  ligand of **1** and **2**. A full examination of the scope of this novel chemistry is underway, and complete details will be presented in due course.

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**Supplementary Material Available:** Listing of important atomic positional parameters for the structure of  $[\text{Re}_2(\mu\text{-Cl})(\mu\text{-COC}(p\text{-tol})\text{CH})\text{Cl}_2(\text{CNxyl})(\mu\text{-dppm})_2]\text{BF}_4\cdot 0.5\text{H}_2\text{O}$  (4 pages). Ordering information is given on any current masthead page.

(9) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

(10) Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *Organometallics* **1993**, *12*, 347.