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A New Type of Tweezer Complex Involving a Rhenium–Rhenium Multiple Bond That Enforces an Unusual Structure in a Dipalladium(II) Unit

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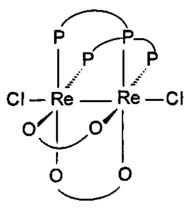
The substitution of the μ-acetato ligands in *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (**1**, dppm $=$ $Ph_2PCH_2PPh_2$) and *trans*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppE})_2$ (**2**, dppE $=$ $Ph_2PC({=}CH_2)PPh_2$) by $[4\text{-}Ph_2PC_6H_4CO_2]^-$ occurs with retention of stereochemistry to give *cis*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}PPh_2)_2Cl_2(\mu\text{-dppm})_2$ (**3**) and *trans*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}PPh_2)_2Cl_2(\mu\text{-dppE})_2$ (**6**), respectively. The uncoordinated phosphine groups in complexes **3** and **6** have been used to form mixed-metal assemblies with Au(I) and Pd(II), including the Re_2Pd_2 complex *cis*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}PPh_2)_2Cl_2(\mu\text{-dppm})_2(Pd_2Cl_4)$ (**5**), in which the planar $[(P)ClPd(\mu\text{-}Cl)_2PdCl(P)]$ unit has the unusual cis structure. The crystal structures of **3** and **5** have been determined.

We have shown that the triply bonded complex *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (**1**, PP $=$ $Ph_2PCH_2PPh_2$ (dppm))[1,2] reacts with bridging dicarboxylic acids such as terephthalic acid and *trans*-1,4-cyclohexanedicarboxylic acid to form supramolecular triangles $[cis\text{-}Re_2Cl_2(\mu\text{-dppm})_2(\mu\text{-}O_2CRCO_2)]_3$, where R $=$ C_6H_4 or C_6H_{10}, and with 1,1′-ferrocene dicarboxylic acid to give the trimetallic complex *cis*-$Re_2Cl_2(\mu\text{-dppm})_2[(\mu\text{-}O_2CC_5H_4)_2Fe]$.[3] In addition, the acetate ligands of **1** can be displaced by isonicotinic acid to give *cis*-$Re_2(\mu\text{-}O_2CC_5H_4N)_2Cl_2(\mu\text{-dppm})_2$ that can be used to obtain a new type of molecular square composed of alternating triply bonded dirhenium(II) and mononuclear platinum(II) units at the corners.[4] We now address two questions. (1) What are the stereochemical and structural consequences of using an unsymmetrical linker ligand such as $[4\text{-}Ph_2PC_6H_4CO_2]^-$, in which the non-carboxylate donor group (in this case a phosphine) is not part of a delocalized ring system, as is the case with the N atom of the isonicotinate bridging ligand? (2) Will the displacement of the acetate groups in trans isomers of type **2** proceed with the retention of this trans structure? To this end we have examined the reactions of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (**1**)[1,2] and *trans*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppE})_2$ (**2**, PP $=$ $Ph_2PC({=}CH_2)PPh_2$ (dppE))[5] with $4\text{-}Ph_2PC_6H_4CO_2H$, a reagent that serves as a prototype for other substituted benzoic acids of the type $4\text{-}XC_6H_4CO_2H$.



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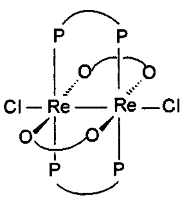

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The reaction of **1** with 4-(diphenylphosphino)benzoic acid[6] in refluxing ethanol affords red crystalline *cis*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}PPh_2)_2Cl_2(\mu\text{-dppm})_2$ (**3**) in almost quantitative yield.[7] The $^{31}P\{^1H\}$ NMR spectrum of **3** (recorded in $CDCl_3$) shows singlets at $\delta = -4.6$ and $\delta = -10.0$ that are assigned to the uncoordinated P atoms of the cis pair of $[4\text{-}Ph_2PC_6H_4CO_2]^-$ ligands and to the μ-dppm ligands, respectively; the corresponding resonances for free $4\text{-}Ph_2PC_6H_4CO_2H$ and **1** in $CDCl_3$ are at $\delta = -4.1$ and $\delta = -8.9$, respectively. Confirmation of the structure of **3** was established by X-ray crystallography (see Figure 1).[8] The distance Re(1)−Re(2) is 2.304(2) Å and is very similar to the $Re{\equiv}Re$ distance in **1** (2.3151(7) Å).[1]

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(1) Cutler, A. R.; Derringer, D. R.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1988**, *110*, 5024.

(2) Derringer, D. R.; Buck, E. A.; Esjornson, S. M. V.; Fanwick, P. E.; Walton, R. A. *Polyhedron* **1990**, *9*, 743.

(3) (a) Bera, J. K.; Angaridis, P.; Cotton, F. A.; Petrukina, M. A.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 1515. (b) Bera, J. K.; Fanwick, P. E.; Walton, R. A. Unpublished results.

(4) Bera, J. K.; Smucker, B. W.; Walton, R. A.; Dunbar, K. R. *Chem. Commun.* **2001**, 2562.

(5) Kuang, S.-M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **2000**, *300−302*, 434.

(6) This ligand was prepared by a procedure similar to that used to obtain $2\text{-}Ph_2PC_6H_4CO_2H$. Hoots, J. B.; Rauchfuss, T. B.; Wrobleski, D. A. *Inorg. Synth.* **1982**, *21*, 175.

(7) Synthesis of *cis*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}PPh_2)_2Cl_2(\mu\text{-dppm})_2$ (**3**): A mixture of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ (**1**) (133 mg, 0.10 mmol) and $Ph_2P\text{-}4\text{-}C_6H_4CO_2H$ (80 mg, 0.25 mmol) was refluxed in 50 mL of EtOH for 3 days. The cooled reaction mixture was filtered, and the insoluble red crystals were washed with ethanol (2 × 5 mL) and diethyl ether (2 × 5 mL); yield 170 mg, 92%. Anal. Calcd for $C_{92}H_{84}Cl_2O_6P_6Re_2$ (i.e., **3**·2EtOH): C, 57.71; H, 4.42. Found: C, 57.43; H, 4.12.

10.1021/ic0112084 CCC: $22.00

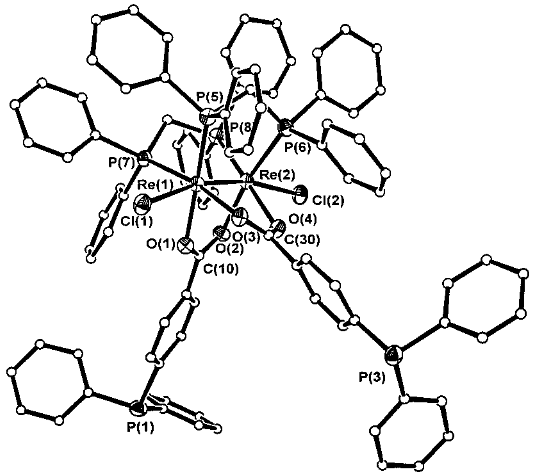

Figure 1. ORTEP representation of the structure of the dirhenium molecule *cis*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}PPh_2)_2Cl_2(\mu\text{-dppm})_2$ as present in the crystals of **3**·2EtOH. Thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)−Re(2) 2.3040(2), Re(1)−O(1) 2.144(3), Re(1)−O(3) 2.150(3), Re(1)−Cl(1) 2.5562(11), Re(2)−O(2) 2.129(3), Re(2)−O(4) 2.141(3), Re(2)−Cl(2) 2.5347(11); O(1)−Re(1)−O(3) 80.04(11), P(5)−Re(1)−P(7) 94.06(4), Re(2)−Re(1)−Cl(1) 167.05(3), O(2)−Re(2)−O(4) 78.43(11), P(6)−Re(2)−P(8) 93.10(4), Re(1)−Re(2)−Cl(2) 167.37(3).

The potential of using **3** as a precursor to mixed-metal assemblies is shown by its reactions with AuCl(tht)[9] to afford red *cis*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}PPh_2)_2Cl_2(\mu\text{-dppm})_2(AuCl)_2$ (**4**)[10] and with $Pd(COD)Cl_2$[11] to give the Re_2Pd_2 complex *cis*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}PPh_2)_2Cl_2(\mu\text{-dppm})_2(Pd_2Cl_4)$ (**5**).[12] The complexation of the free phosphine groups in **3** by Au(I) was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy which showed that a $CDCl_3$ solution of **4** had a pair of singlets at $\delta = +33.5$ and $\delta = -9.9$, the most downfield resonance being assigned to the coordinated PPh_2 groups. The identity of **5**, which was insoluble in polar and nonpolar organic solvents, was established by X-ray crystallography (see Figure 2).[13] The Re−Re distance of 2.3295(6) Å is lengthened slightly (by up to 0.025 Å) relative to the Re−Re distances in **1**[1] and **3** (Figure 1) but is still typical of a Re≡Re bond. The coordination of the P atoms of **3** to a $[Pd_2(\mu\text{-}Cl)_2Cl_2]$ unit creates a Re_2Pd_2 assembly in **5** that is quite distinct from the Re_2Pt_2 supramolecular square that has been obtained with the use of the isonicotinate complex *cis*-$Re_2(\mu\text{-}O_2CC_6H_4N)_2Cl_2(\mu\text{-dppm})_2$.[4] The formation of **5** is of additional note because it involves **3** behaving as a chelating phosphine to form a planar dipalladium(II) species of the type $(R_3P)ClPd(\mu\text{-}Cl)_2PdCl(PR_3)$ in which the phosphines are cis to one another. To our knowledge only the trans isomers of $Pd_2(\mu\text{-}Cl)_2Cl_2(PR_3)_4$ (where PR_3 represents a wide range of phosphine ligands[14] as well as phosphites[15]) have previously been structurally characterized. The insertion of the $[ClPd(\mu\text{-}Cl)_2PdCl]$ unit between the pair of cis Ph_2P groups in **3** leads to a large increase in this nonbonding P···P distance from 4.975 Å in **3** to 6.757 Å in **5**. However, the O−Re−O "corner" angles in **5** (i.e., O(31)−Re−O(32) = 75.2(2)°) are actually smaller than in **3** (O(1)−Re(1)−O(3) = 80.04(11)° and O(2)−Re(1)−O(4) = 78.43(11)°), reflecting the flexibility of the $[4\text{-}Ph_2PC_6H_4CO_2]^-$ linker ligands.

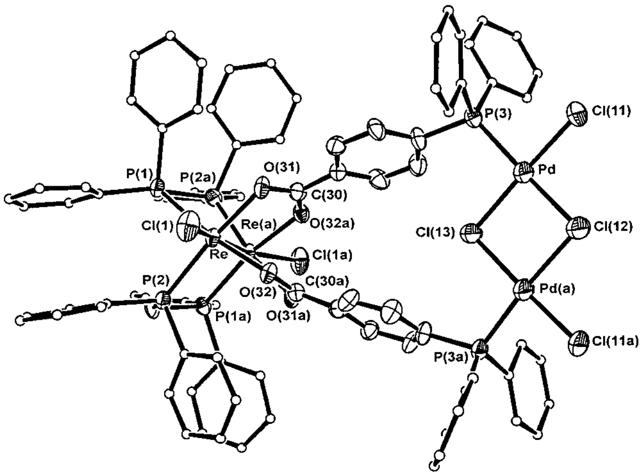

Figure 2. ORTEP representation of the structure of the Re_2Pd_2 complex *cis*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}PPh_2)_2Cl_2(\mu\text{-dppm})_2(Pd_2Cl_4)$ (**5**). This molecule contains a crystallographic 2-fold rotational axis that contains atoms Cl(12) and Cl(13) and bisects the Re−Re bond. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppm ligands and diphenylphosphino groups, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: Re−Re(a) 2.3295(6), Re−O(31) 2.134(5), Re−O(32) 2.167(5), Re−Cl(1) 2.517(2), Pd−P(3) 2.212(2), Pd−Cl(11) 2.268(2), Pd−Cl(12) 2.365(3), Pd−Cl(13) 2.332(2); O(31)−Re−O(32) 75.2(2), P(1)−Re−P(2) 93.23(7), Re(a)−Re−Cl(1) 166.54(6), P(3)−Pd−Cl(11) 86.65(9), Cl(13)−Pd−Cl(12) 86.88(9), Pd−Cl(12)−Pd(a) 92.29(14), Pd−Cl(13)−Pd(a) 93.94(12).

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(8) Crystal data for **3**·2EtOH (150 K): space group $P2_1/n$ (No. 14) with $a = 17.8968(2)$ Å, $b = 31.8530(4)$ Å, $c = 18.6342(2)$ Å, $\beta = 97.5326(8)°$, $V = 10531.1(4)$ Å^3, $Z = 4$, $d_{calcd} = 1.208$ g cm^{-3}, μ(Mo Kα) = 2.510 mm^{-1}; 81907 reflections were measured of which 23730 were unique. A cutoff $F_o^2 > 2\sigma(F_o^2)$ was used for *R*-factor calculations to give $R(F_o) = 0.043$, $R_w(F_o^2) = 0.096$ and GOF = 0.953. Asymmetric unit contains two molecules of EtOH, one of which is disordered but satisfactorily modeled; the C and O atoms of both solvent molecules were refined with anisotropic thermal parameters.

(9) Uson, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 86.

(10) Synthesis of *cis*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}PPh_2)_2Cl_2(\mu\text{-dppm})_2(AuCl)_2$ (**4**): A solution of **3** (91 mg, 0.05 mmol) and AuCl(tht) (32 mg, 0.10 mmol) in 45 mL of dichloromethane was stirred at 25 °C for 2 h, the solvent evaporated slowly, and the red microcrystals of **4** were washed with diethyl ether (2 × 5 mL); yield 100 mg (88%). Anal. Calcd for $C_{88}H_{72}Au_2Cl_4O_4P_6Re_2$: C, 46.21; H, 3.17; Cl, 6.20. Found: C, 46.50; H, 3.25; Cl, 6.44.

(11) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 52.

(12) Synthesis of *cis*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}PPh_2)_2Cl_2(\mu\text{-dppm})_2(Pd_2Cl_4)$ (**5**): A solution of $Pd(COD)Cl_2$ (16 mg, 0.056 mmol) in 5 mL of dichloromethane was added to one of **3** (45.5 mg, 0.025 mL) in 30 mL of acetonitrile. This mixture was left undisturbed for 3 days to produce orange crystals of **5**, which were filtered off and washed with dichloromethane (2 × 10 mL); yield 26 mg (48%). Incomplete thermal decomposition of this very stable product prevented us from obtaining satisfactory elemental microanalyses.

(13) Crystal data for **5** (170 K): space group $C2/c$ (No. 15) with $a = 19.0226(4)$ Å, $b = 17.4693(4)$ Å, $c = 25.2040(7)$ Å, $\beta = 109.5935(10)°$, $V = 7890.6(6)$ Å^3, $Z = 4$, $d_{calcd} = 1.833$ g cm^{-3}, μ(Mo Kα) = 3.920 mm^{-1}; 30158 reflections were measured of which 8910 were unique. A cutoff $F_o^2 > 2\sigma(F_o^2)$ was used for *R*-factor calculations to give $R(F_o) = 0.049$, $R_w(F_o^2) = 0.116$ and GOF = 1.025.

(14) (a) Coles, S. J.; Faulds, P.; Hursthouse, M. B.; Kelly, D. G.; Ranger, G. C.; Toner, A. J.; Walker, N. M. *J. Organomet. Chem.* **1999**, *586*, 234. (b) Slawin, A. M. Z.; Woollins, J. D.; Zhang, Q. *Inorg. Chem. Commun.* **1999**, *2*, 386. (c) Dyer, P. W.; Dyson, P. J.; James, S. L.; Suman, P.; Davies, J. E.; Martin, G. M. *Chem. Commun.* **1998**, 1375. (d) Chaloner, P. A.; Dewa, S. Z.; Hitchcock, P. B. *Acta Crystallogr., Sect. C* **1995**, *51*, 232. (e) Ang, H. G.; Cai, Y. M.; Kwik, W. L.; Rheingold, A. L. *Chem. Commun.* **1990**, 1580. (f) Newkome, G. R.; Evans, D. W.; Fronczek, F. R. *Inorg. Chem.* **1987**, *26*, 3500.

(15) (a) Cobley, C. J.; Ellis, D. D.; Orpen, A. G.; Pringle, P. G. *J. Chem. Soc., Dalton Trans.* **2000**, 1101. (b) Grigsby, W. J.; Nicholson, B. K. *Acta Crystallogr., Sect. C* **1992**, *48*, 362.

Although the complex *trans*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ isomerizes cleanly to the more thermodynamically stable cis isomer **1**,[1,2] the related trans isomer of $Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppE})_2$ (**2**)[5] is stable thermally and undergoes carboxylate exchange with 4-$Ph_2PC_6H_4CO_2H$ to afford *trans*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-4-}PPh_2)_2Cl_2(\mu\text{-dppE})_2$ (**6**).[16] Complex **6** has CV electrochemical properties that are similar to those of the parent complex **2** (for **6** $E_{1/2}(\mathrm{ox}) = +1.05$ V and $E_{1/2}(\mathrm{ox}) = -0.23$ V vs Ag/AgCl in 0.1 M $n\text{-}Bu_4NPF_6-CH_2Cl_2$) but quite different from those for cis isomers of this type.[1,2] The $^{31}P\{^1H\}$ NMR spectrum of **6** (recorded in $CDCl_3$) shows singlets at $\delta = +29.9$ (dppE ligands) and $\delta = -3.7$ (uncoordinated PPh_2 groups). The reaction of **6** with AuCl(tht), using a procedure similar to that for the analogous reaction of AuCl(tht) with **3**,[10] gives the mixed-metal complex *trans*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-4-}PPh_2)_2Cl_2(\mu\text{-dppE})_2(AuCl)_2$ (**7**), which has a CV similar to that of **6** and a $^{31}P\{^1H\}$ NMR spectrum (recorded in $CDCl_3$) with singlets at $\delta = +34.2$ (2P, coordinated PPh_2 groups) and $\delta = +33.9$ (4P, dppE ligands), confirming that both PPh_2 groups are coordinated to Au(I).

The trans structure of **6** is supported by the isolation of *trans*-$Re_2(\mu\text{-}O_2CC_{10}H_6N)_2Cl_2(\mu\text{-dppE})_2$ (**8**) from the reaction of **2** with quinoline-4-carboxylic acid with use of the same procedure as that used to prepare **6** from **2**.[16] The CV properties of **6** and **8** are very similar, and the single-crystal X-ray structure determination of **8** has confirmed its structure. Full details of this structure, along with the results of studies aimed at linking trans complexes like **8** into mixed-metal polymeric chains, will be reported in due course.

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Supporting Information Available: X-ray crystallographic files for **3**·2EtOH and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Synthesis of *trans*-$Re_2(\mu\text{-}O_2CC_6H_4\text{-4-}PPh_2)_2Cl_2(\mu\text{-dppE})_2$ (**6**): A procedure similar to that described for the preparation of **3**[7] was used to react **2** with 4-$Ph_2PC_6H_4CO_2H$. Brown microcrystals of **6** were obtained upon recrystallization of the crude product from CH_2Cl_2/Et_2O; yield 55%. Anal. Calcd for $C_{91}H_{74}Cl_4O_4P_6Re_2$ (i.e., **6**·CH_2Cl_2): C, 56.58; H, 3.86. Found: C, 56.72; H, 3.87.