Rhenium Complexes

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Saturated Versus Unsaturated: Ligand Addition to the Saturated Metal Site in an Unsaturated Binuclear Metal Complex**

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In memory of F. Albert Cotton

Coordination asymmetry in binuclear metal systems is a feature that can impart unusual properties and reactivity to the metal atoms.[1] Coordination asymmetry is most pronounced when the metal atoms have different coordination numbers. Mixed-valence states have been observed in binuclear coordination complexes.[2] Coordination asymmetry may be important to the reactivity of metalloenzymes having bimetallic active sites.[3] We have recently shown how an unsaturated metal atom can activate a neighboring metal atom toward organic transformations.[4]

Coordinative unsaturation in homodinuclear metal systems is usually expressed in the form of multiple bonds between the metal atoms.[5] We now wish to report an unusual metal–metal bonded dirhenium carbonyl complex that not only exhibits its unsaturation in the form of the classical "vacant" coordination site, but also expresses its reactivity in an unexpected manner.

The reaction of $[Re_3(CO)_{12}(\mu\text{-}H)_3]$[6] with $PtBu_3$ at 127 °C provided the new dirhenium compound $[Re_2(CO)_6(PtBu_3)(\mu\text{-}PtBu_2)(\mu\text{-}H)]$ (**1**) in 31 % yield. Compound **1** was characterized crystallographically (Figure 1). The molecule contains two rhenium atoms separated by a normal single-bond distance, Re1−Re2 3.1083(3) Å.[7] The Re−Re bond is bridged by a $PtBu_2$ ligand and one hydrido ligand, H1, ^1H NMR, $\delta = -4.46$ ppm.[8] The most unusual feature about the structure of **1** is the distribution of the remaining ligands. Re1 has four CO ligands giving it a saturated 18-electron configuration, while Re2 has only two CO ligands and one $PtBu_3$ ligand giving it an unsaturated 16-electron configuration. The unsaturation on Re2 is clearly evident in the form of a vacant coordination site *trans* to the carbonyl ligand C21–O21.

The availability of this vacant site was demonstrated by the reversible reaction of **1** with CO to yield the compound $[Re_2(CO)_7(PtBu_3)(\mu\text{-}PtBu_2)(\mu\text{-}H)]$ (**2**) in 97 % yield. An ORTEP diagram of the molecular structure of **2** is shown in Figure 2. Compound **2** is structurally similar to **1** in every respect except that it contains an additional CO ligand on Re2, C23−O23, *trans* to C21−O21. The Re−Re single bond is only nominally longer than that in **1**, Re1−Re2 3.1781(2) Å. When solutions of **2** were heated to reflux in heptane solvent, **2** was converted back into **1** in 96 % yield.

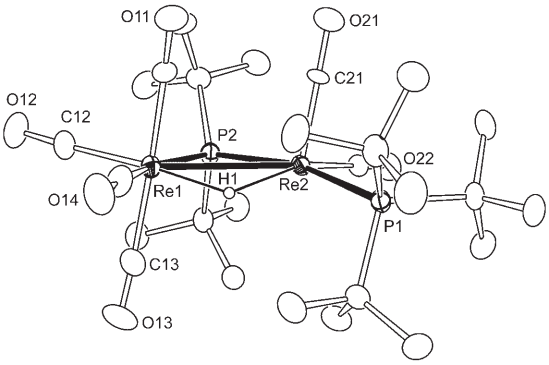

Figure 1. An ORTEP diagram of the molecular structure of **1**; thermal ellipsoids set at 30 % probability.

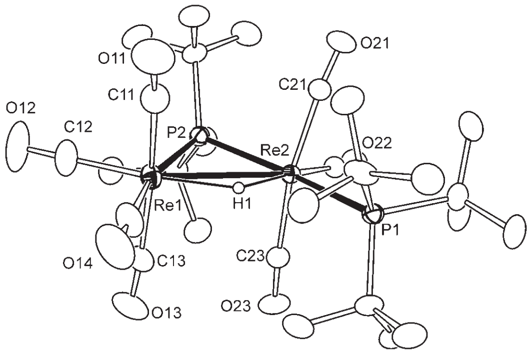

Figure 2. An ORTEP diagram of the molecular structure of **2**; thermal ellipsoids set at 30 % probability.

To examine the nature of the electronic structure of **1** further, Fenske–Hall molecular orbitals were calculated.[9] A diagram of the lowest unoccupied molecular orbital (LUMO) in **1** is shown in Figure 3. This orbital shows a large component on Re2 that clearly represents the vacant site.

Compound **1** also readily adds other donor molecules as ligands. For example, when dissolved in acetonitrile (NCMe), the solution becomes colorless immediately. When these solutions were concentrated and cooled, the compound

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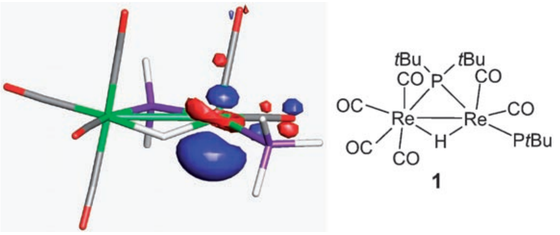


Figure 3. Fenske–Hall lowest unoccupied molecular orbital (LUMO) of **1** (see text for details); stick model: Re green, P purple, C gray, H white, O red.

$[Re_2(CO)_6(NCMe)(PtBu_3)(\mu\text{-}PtBu_2)(\mu\text{-}H)]$ (**3**) was obtained as crystals in 82% yield (Figure 4). Compound **3** is structurally similar to **2** except there is an NCMe ligand on Re1 in the place of one of the CO ligands. Interestingly, there is a CO ligand in the former vacant site next to the $PtBu_3$ ligand.

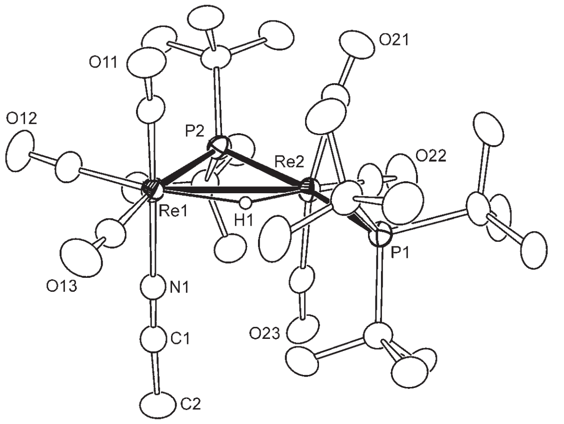
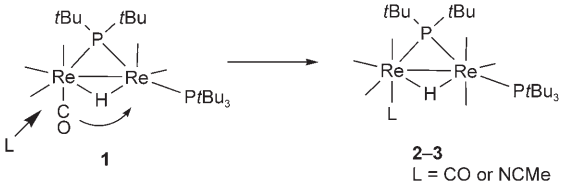


Figure 4. An ORTEP diagram of the molecular structure of **3**; thermal ellipsoids set at 30% probability. Re1–Re2 3.1808(2) Å.

It appears that one of the CO ligands on Re1 has been shifted to Re2 in the course of the NCMe addition (Scheme 1). Facile shifts of CO ligands between metal atoms are well known.[10] Indeed, the CO ligands in **1** are dynamically active and exchange between the metal atoms occurs rapidly on the NMR time scale at 100 °C (see the Supporting Information).



Scheme 1. Ligand addition/shift; CO ligands shown as ——.

What is even more surprising is that the CO addition to **1** to form **2** evidently proceeds by a similar CO addition/shift mechanism. This idea was confirmed by monitoring the addition of CO to **1** by using a sample of CO enriched with ^{13}CO. The ^{13}C NMR spectrum of this sample of **2** showed a single strong resonance at $\delta = 187$ ppm (Figure 5a). An analysis of the complete ^{13}C NMR spectrum of **2** prepared independently has allowed unambiguous site assignments to all of the CO ligands (see Figure 5b).[11] The resonance at 187.2 ppm is attributed to the sites of the two equivalent CO ligands C11–O11 and C13–O13 on Re1.

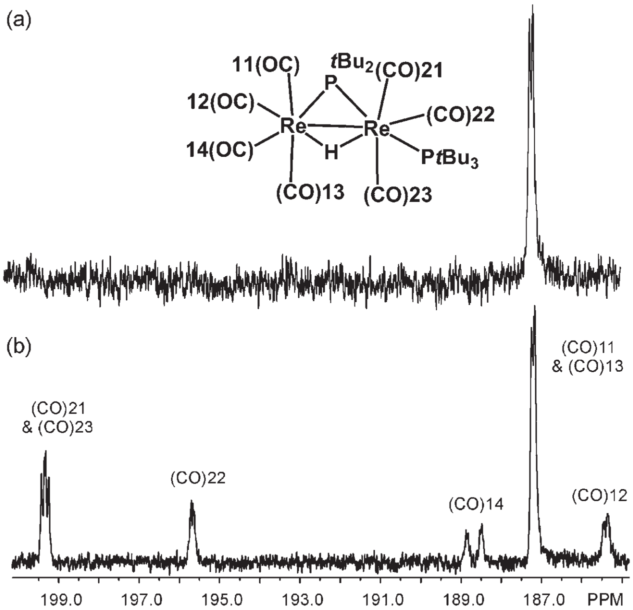


Figure 5. a) $^{13}C\{^1H\}$ NMR spectrum of a sample of **2** formed by the addition of CO enriched with ^{13}CO. b) A $^{13}C\{^1H\}$ NMR spectrum of **2** having all CO sites enriched with ^{13}CO.

These combined results demonstrate that even a reaction as simple as a ligand addition to an apparent vacant site on a metal atom, may not be as simple and straightforward as it could be, especially when two or more metal atoms are involved and facile transfer of ligands between the metal atoms can readily occur.[12]

Experimental Section

1: Under an atmosphere of nitrogen, $[Re_3(CO)_{12}(\mu\text{-}H)_3]$ (50.3 mg, 0.056 mmol) and $PtBu_3$ (50 μL, 0.201 mmol) were dissolved in octane (20 mL). The reaction mixture was heated to reflux for 6 h. The solvent was removed in vacuo, and the products were separated by thin-layer chromatography (TLC) by using a 5:1 hexane/methylene chloride solvent mixture to yield, in order of elution: 15.4 mg (31% yield) of orange **1**, and 5.3 mg of a yellow band (currently being characterized). Spectral data for **1**: IR ν_{CO} (in hexane): $\tilde{\nu} = 2079$ (s), 1993 (vs), 1969 (vs), 1954 (vs), 1923 (s), 1850 cm^{-1} (s). ^1H NMR (400 MHz, $[D_8]$toluene, RT, TMS): $\delta = 1.37$ (d, $^3J(P,H) = 14$ Hz, 18 H; CH_3), 1.24 (d, $^3J(P,H) = 12$ Hz, 27 H; CH_3), -4.46 ppm (dd, $^2J(P,H) = 12$ Hz, $^2J(P,H) = 5$ Hz, hydride 1 H). $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$toluene, RT, 85% *ortho*-H_3PO_4): $\delta = 139.68$ (d, $^2J(P,P) = 99$ Hz, 1P, $\mu\text{-}PtBu_2$), 84.31 ppm (d, $^2J(P,P) = 99$ Hz, 1*P*, $PtBu_3$). Mass spectrometry EI/MS *m*/*z* 888. The isotope pattern is consistent with the presence of two rhenium atoms. Crystal data for **1**: $Re_2P_2O_6C_{26}H_{46}$, $M_r = 888.97$, orthorhombic, space group $Pna2_1$, $a = 21.1976(10)$, $b = 17.2257(8)$, $c = 8.8901(4)$ Å, $V = 3246.2(3)$ Å^3, $Z = 4$, $T = 294$ K, $Mo_{K\alpha} = 0.71073$ Å, GOF = 1.078 The final $R1(F^2)$ was 0.0279 for 7338 reflections $I > 2\sigma(I)$.

2: Carbon monoxide gas (1 atm) was bubbled through a solution of **1** (15.4 mg, 0.017 mmol) in hexane (20 mL). Within a few minutes the orange solution turned to yellow and then almost colorless. The CO gas was purged through this solution for a total of 10 min and an IR spectrum after this time indicated complete conversion of the starting material **1**. The solvent was removed in vacuo, and the product was separated by TLC by using a 5:1 hexane/methylene chloride solvent mixture to yield 15.4 mg (97%) of colorless **2**. Spectral data for **2**: IR ν_{CO} (in hexane): $\tilde{\nu} = 2079$ (m), 2018 (w), 1983 (m), 1974 (vs), 1953 (s), 1914 (m), 1908 cm^{-1} (m). ^1H NMR (400 MHz, $[D_8]$toluene, RT, TMS): $\delta = 1.53$ (d, $^3J(P,H) = 14$ Hz, 18H; CH_3), 1.38 (d, $^3J(P,H) = 12$ Hz, 27H; CH_3), -14.01 ppm (dd, $^2J(P,H) = 15$ Hz, $^2J(P,H) = 8$ Hz, hydride 1H). $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$toluene, RT, 85% *ortho*-H_3PO_4): $\delta = 120.84$ (d, $^2J(P,P) = 71$ Hz, 1P, μ-P*t*Bu_2), 63.05 ppm (d, $^2J(P,P) = 71$ Hz, 1P, P*t*Bu_3). Mass spectrometry EI/MS *m*/*z* 916. The isotope pattern is consistent with the presence of two rhenium atoms. Crystal data for **2**: $Re_2P_2O_7C_{27}H_{46}$, $M_r = 916.98$, monoclinic, space group $P2_1/c$, $V = 3307.88(14)$ Å^3, $a = 16.4619(4)$, $b = 11.8441(3)$, $c = 16.9897(4)$ Å, $\beta = 93.057(1)°$, $Z = 4$, $T = 294$ K, $Mo_{K\alpha} = 0.71073$ Å, GOF = 1.061. The final $R1(F^2)$ was 0.0254 for 7468 reflections $I > 2\sigma(I)$.

Conversion of **2** into **1**: Compound **2** (15.0 mg, 0.016 mmol) in heptane (10 mL) was heated to reflux for 30 min. The IR spectrum at this time showed complete conversion of the starting material **2** into **1**. The solvent was removed in vacuo, and the product was separated by TLC by using a 5:1 hexane/methylene chloride solvent mixture to yield 14.0 mg (96%) of orange **1**.

3: Compound **1** (9.9 mg, 0.011 mmol) was dissolved in acetonitrile (approximately 0.6 mL) in a medium vial (1 dram size, 3.7 mL). The solution was then concentrated to about half the volume and placed in a freezer at −25°C for approximately 2 days to yield 8.5 mg (82% yield) of light yellow/colorless crystals of **3**. Spectral data for **3**: IR ν_{CO} (in acetonitrile): $\tilde{\nu} = 2018$ (w), 2000 (s), 1909 (vs), 1889 cm^{-1} (sh). ^1H NMR (400 MHz, CD_3CN, RT, TMS): $\delta = 1.60$ (d, $^3J(P,H) = 12$ Hz, 27H; CH_3), 1.50 (t, $^3J(P,H) = 13$ Hz, 18H; CH_3), -11.76 ppm (dd, $^2J(P,H) = 16$ Hz, $^2J(P,H) = 9$ Hz, hydride 1H). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN, RT, 85% *ortho*-H_3PO_4): $\delta = 114.09$ (d, $^2J(P,P) = 67$ Hz, 1P, μ-P*t*Bu_2), 65.26 ppm (d, $^2J(P,P) = 67$ Hz, 1P, P*t*Bu_3). In the ^1H NMR spectrum taken on a 300 MHz instrument, the triplet (overlapping doublet of doublets) splits into a doublet of doublets. Mass spectrometry ES^+/MS calcd for $[M^+]$, $[Re_2(CO)_6(NCMe)(PtBu_3)(\mu\text{-}PtBu_2)(\mu\text{-}H)]^+$: 929, found: 929. The isotope pattern is consistent with the presence of two rhenium atoms. NOTE: Compound **3** converts back into **1** when acetonitrile is removed. Crystal data for **3**: $Re_2P_2O_6N_1C_{28}H_{49}$, $M_r = 930.02$, monoclinic, space group $P2_1/c$, $V = 3392.63(19)$, $a = 11.0279(4)$, $b = 29.6026(10)$, $c = 10.7886(3)$ Å, $\beta = 105.577(1)°$, $Z = 4$, $T = 294$ K, $Mo_{K\alpha} = 0.71073$ Å, GOF = 1.101. The final $R1(F^2)$ was 0.0227 for 7412 reflections $I > 2\sigma(I)$. CCDC-650897 (**1**), CCDC-650898 (**2**), CCDC-650899 (**3**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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