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LETTER

# A heterometallic cluster with extreme hydride content: $H_{24}Cu_6Re_4(PPh_3)_8{}^{2+}$

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The synthesis of heterometallic polyhydride clusters has led to impressive accomplishments [1, 2], but still holds challenges to full characterization, due to (among other reasons) high molecular weight, fluxionality and the low X-ray scattering power of hydrogen. It is a general principle that copper, silver or gold is one of the metal elements typically present. Moreover, the atom ratio of this Group I metal to the second metal can be varied, always with major structural change. Thus, $H_3IrP_3$ (P = tertiary phosphine) and $Cu(NCMe)_4{}^+$ can be combined to produce linear $P_3HIr(\mu\text{-}H)_2Cu(\mu\text{-}H)_2IrHP_3{}^+$ [3] as well as trigonal bipyramidal $(P_3Ir)_2(MeCNCu)_3(\mu\text{-}H)_6{}^{3+}$ [4]. When $ReH_5(PMePh_2)_3$ is reacted with $Cu(NCMe)_4{}^+$, linear $[H_2(PMePh_2)_3Re(\mu\text{-}H)_3]_2Cu^+$ is formed [5]. We report here the preferred stoichiometry and unusual closed polyhedral aggregation adopted when $Cu(NCMe)_4{}^+$ reacts with the $d^0$ compound $ReH_7(PR_3)_2$.

## Experimental

### *Syntheses*

Solid $Cu(MeCN)_4PF_6$ (0.0272 g, 0.072 mmol) was added to $ReH_7(PMe_2Ph)_2$ (0.017 g, 0.037 mmol) in 3 ml THF. The yellow solid which precipitates was filtered, washed ($Et_2O$) and dried *in vacuo*. $^1H$ NMR (in $CD_3CN$): −5.42 (t, $J$ = 15 Hz), 1.83 (d, PMc), 7.45 (m, Ph). $^{31}P\{^1H\}$ NMR (in $CD_3CN$): −25.0(s). The $PMePh_2$ and $PPh_3$ analogs were made the same way. For the $PMePh_2$ analog, $^1H$ NMR ($CD_3CN$): −5.14 (t, $J$ = 15 Hz), 1.86 (br, PMe), 7.32 (m, Ph). $^{31}P\{^1H\}$ NMR (in $CD_3CN$): −4.72(s). For the $PPh_3$ analog, $^1H$ NMR (in $CD_3CN$): −4.8 (br t, $J$ = 15 Hz), 7.07 and 7.25 (m, Ph). $^{31}P\{^1H\}$ NMR (in $CD_3CN$): +18.56(s).

### *X-ray diffraction study*

A crystal of dimension 0.2×0.3×0.3 mm was transferred to a goniostat and quickly cooled (due to ready solvent loss) to −154 °C. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited tetragonal symmetry and systematic extinctions consistent with space group $P4_2/n$. Crystal data for $Cu_6[ReH_x(PPh_3)_2]_4(PF_6)(X)\cdot 2CH_3CN$ (at −154 °C): $a = b = 18.889(4)$, $c = 42.800(18)$ Å with $Z = 4$; $D_{calc} = 1.50$ gm/cm$^3$. Data collection ($6° < 2\theta < 45°$) was carried out ($\lambda = 0.71069$ Å) in the usual manner [6]. Direct methods and heavy atom Fourier techniques revealed all atoms of the cation, which is located on a two-fold axis which passes through Cu5 and Cu6. Also located in general positions were an acetonitrile molecule and a poorly defined $PF_6{}^-$ ion. In addition, electron density (well removed from the cation) consistent with $OH^-$ or $F^-$ was also present and could be refined, but distinction between these two species was not possible based on the data. (This problem has been encountered earlier in gold cluster chemistry [7].) $R(F) = 0.0939$ and $R_w(F) = 0.0867$ for 5272 observed ($> 3\sigma$) reflections and anisotropic thermal parameters on metals, P and F. Hydride hydrogens were not evident in difference Fourier maps. See also 'Supplementary material'.

## Results and discussion

The stoichiometry of the reaction of $ReH_7P_2$ (P = $PMe_2Ph$, $PMePh_2$ and $PPh_3$) with $[Cu(NCMe)_4]PF_6$ in THF was established by monitoring ($^{31}P$ NMR) a titration of the former with the latter. This revealed that complete consumption of $ReH_7P_2$ requires 1.5–2.0 mol of copper. At the 2:1 stoichiometry, a yellow solid precipitates. There is no gas evolution or deposition of copper metal during the reaction. Crystals of the $PPh_3$ compound were grown from MeCN, and a single crystal X-ray study revealed the $[Cu_6(ReH_xP_2)_4]^{n+}$ cation (Fig. 1 and Tables 1 and 2), together with anions which suggest a cation charge of $n = 2$, and thus $x = 6$. The balanced reaction is thus eqn. (1). The cation has crystallographic $C_2$ symmetry, consistent with the

$$4ReH_7P_2 + 6Cu(MeCN)_4{}^+ \longrightarrow Cu_6(ReH_6P_2)_4{}^{2+} + 4H^+ \quad (1)$$

observation of only one $^{31}P\{^1H\}$ NMR signal at both +25 and −80 °C. The hydride resonance of all three compounds at 25 °C is a triplet ($J$(PH) = 15 Hz), in-

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TABLE 1. Fractional coordinates[a] (×10$^4$) and isotropic thermal parameters[b] (×10) for $Cu_6[H_6Re(PPh_3)_2]_4^{2+}$

| | $x$ | $y$ | $z$ | $B_{iso}$ |
|---|---|---|---|---|
| Re(1) | 7566(1) | 1109(1) | 8431.4(3) | 17 |
| Re(2) | 8880(1) | 2510(1) | 9345.0(3) | 15 |
| Cu(3) | 8258(2) | 1762(2) | 8893(1) | 18 |
| Cu(4) | 6797(2) | 1754(2) | 8885(1) | 18 |
| Cu(5) | 7500* | 2500* | 8481(1) | 22 |
| Cu(6) | 7500* | 2500* | 9293(1) | 18 |
| P(7) | 8563(5) | 613(4) | 8152(2) | 28 |
| P(8) | 6588(5) | 650(4) | 8113(2) | 25 |
| P(9) | 9342(4) | 3522(4) | 9622(2) | 19 |
| P(10) | 9350(4) | 1506(4) | 9639(2) | 20 |
| C(11) | 8940(18) | 1006(18) | 7802(9) | 35(7) |
| C(12) | 9514(20) | 703(19) | 7654(9) | 40(8) |
| C(13) | 9799(21) | 1035(21) | 7404(10) | 48(9) |
| C(14) | 9553(27) | 1693(27) | 7296(12) | 68(12) |
| C(15) | 8967(29) | 1995(30) | 7427(14) | 82(14) |
| C(16) | 8626(26) | 1652(26) | 7685(12) | 68(12) |
| C(17) | 9413(16) | 586(17) | 8352(8) | 27(6) |
| C(18) | 9822(18) | −23(19) | 8405(9) | 37(7) |
| C(19) | 10488(18) | −22(19) | 8519(8) | 36(7) |
| C(20) | 10782(21) | 644(22) | 8626(12) | 56(9) |
| C(21) | 10419(18) | 1265(18) | 8574(10) | 40(8) |
| C(22) | 9715(18) | 1259(17) | 8448(8) | 33(7) |
| C(23) | 8428(15) | −324(15) | 8013(7) | 20(6) |
| C(24) | 8333(15) | −474(15) | 7711(7) | 21(6) |
| C(25) | 8197(15) | −1192(15) | 7620(7) | 23(6) |
| C(26) | 8137(14) | −1689(14) | 7830(7) | 18(5) |
| C(27) | 8231(15) | −1550(15) | 8160(7) | 19(6) |
| C(28) | 8389(15) | −845(15) | 8257(7) | 22(6) |
| C(29) | 6258(17) | −275(17) | 8182(8) | 30(7) |
| C(30) | 6649(15) | −742(15) | 8343(7) | 19(5) |
| C(31) | 6356(15) | −1456(15) | 8376(7) | 21(6) |
| C(32) | 5689(17) | −1634(17) | 8266(8) | 29(7) |
| C(33) | 5278(18) | −1093(18) | 8107(9) | 37(8) |
| C(34) | 5558(16) | −401(16) | 8065(8) | 25(6) |
| C(35) | 5760(19) | 1154(18) | 8157(9) | 35(8) |
| C(36) | 5507(25) | 1524(25) | 7889(12) | 66(11) |
| C(37) | 4853(30) | 1862(29) | 7923(15) | 83(14) |
| C(38) | 4539(26) | 1890(26) | 8212(13) | 67(12) |
| C(39) | 4785(17) | 1579(17) | 8516(8) | 32(7) |
| C(40) | 5479(15) | 1193(15) | 8451(7) | 21(6) |
| C(41) | 6755(20) | 643(20) | 7696(9) | 41(8) |
| C(42) | 6633(15) | 71(15) | 7491(8) | 23(6) |
| C(43) | 6751(18) | 87(18) | 7171(8) | 33(7) |
| C(44) | 6970(22) | 682(23) | 7047(11) | 55(10) |
| C(45) | 7102(29) | 1328(30) | 7228(13) | 81(14) |
| C(46) | 6961(26) | 1292(26) | 7543(13) | 71(12) |
| C(47) | 8772(13) | 3913(13) | 9927(6) | 11(5) |
| C(48) | 8875(16) | 4633(16) | 10013(7) | 25(6) |
| C(49) | 8482(14) | 4978(14) | 10226(7) | 18(5) |
| C(50) | 7932(20) | 4559(20) | 10371(9) | 43(8) |
| C(51) | 7803(17) | 3893(18) | 10296(8) | 31(7) |
| C(52) | 8199(14) | 3597(14) | 10060(7) | 17(5) |
| C(53) | 9486(14) | 4291(14) | 9363(7) | 18(5) |
| C(54) | 8865(16) | 4632(16) | 9259(7) | 26(6) |
| C(55) | 8956(15) | 5193(15) | 9066(7) | 23(6) |
| C(56) | 9593(17) | 5466(17) | 8969(8) | 31(7) |
| C(57) | 10228(20) | 5128(20) | 9083(9) | 44(8) |
| C(58) | 10172(15) | 4529(14) | 9270(7) | 18(5) |
| C(59) | 10186(14) | 3405(14) | 9821(7) | 18(5) |
| C(60) | 10285(17) | 3609(17) | 10131(8) | 30(7) |
| C(61) | 10964(14) | 3525(13) | 10277(6) | 13(5) |
| C(62) | 11529(18) | 3209(17) | 10107(8) | 33(7) |
| C(63) | 11445(14) | 3026(14) | 9799(7) | 17(5) |
| C(64) | 10730(14) | 3130(15) | 9648(7) | 19(5) |
| C(65) | 9129(14) | 1435(14) | 10056(7) | 15(5) |
| C(66) | 9068(15) | 2045(15) | 10245(7) | 22(6) |
| C(67) | 8946(16) | 1968(17) | 10566(8) | 29(6) |
| C(68) | 8906(18) | 1273(19) | 10703(9) | 39(8) |
| C(69) | 8948(17) | 673(17) | 10525(8) | 30(7) |
| C(70) | 9089(17) | 752(17) | 10207(8) | 31(7) |
| C(71) | 10307(15) | 1403(15) | 9629(7) | 20(6) |
| C(72) | 10686(16) | 1431(16) | 9364(8) | 25(6) |
| C(73) | 11393(18) | 1393(18) | 9352(9) | 34(7) |
| C(74) | 11790(16) | 1232(15) | 9643(7) | 23(6) |
| C(75) | 11468(20) | 1138(20) | 9923(10) | 45(9) |
| C(76) | 10672(16) | 1244(16) | 9923(8) | 28(6) |
| C(77) | 9005(15) | 652(14) | 9487(7) | 19(5) |
| C(78) | 8297(19) | 506(19) | 9547(9) | 37(8) |
| C(79) | 7988(17) | −120(17) | 9421(8) | 32(7) |
| C(80) | 8397(20) | −571(20) | 9208(10) | 43(8) |
| C(81) | 9095(16) | −385(16) | 9161(8) | 27(6) |
| C(82) | 9424(15) | 238(15) | 9288(7) | 21(6) |

[a]Parameters marked with an asterisk were not varied. [b]Isotropic values for those atoms refined anisotropically are calculated according to ref. 8.

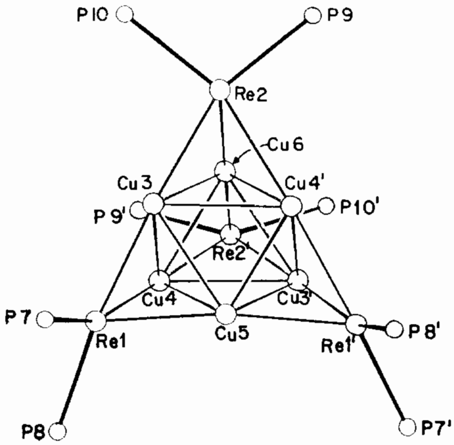

Fig. 1. ORTEP drawing of the cation $Cu_6[ReH_6(PPh_3)_2]_4^{2+}$. Carbon atoms have been deleted for clarity. Hydride hydrogens were not located. A crystallographic $C_2$ axis passes through Cu5 and Cu6.

dicating that hydride migration occurs, but is localized within the coordination sphere of each individual rhenium; no global hydride migration occurs. The $^1H$ NMR of $Cu_6[ReH_6(PPh_3)_2]_4^{2+}$ in $CD_2Cl_2$ at −70 °C shows two broad resonances at −2.7 and −5.7 ppm, which we assign to bridging and terminal hydrides*. Since the P–Re–P angles in this cation (100–103°) are similar

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*The integration of these resonances could not be reliably obtained because of low solubility at −70 °C. However, the −5.7 ppm resonance appears to have greater intensity.

TABLE 2. Selected bond distances (Å) and angles (°) in the ion $Cu_6[ReH_6(PPh_3)_2]_4^{2+}$

| | |
|---|---|
| Cu(3)–Re(1)–Cu(4) | 61.64(11) |
| Cu(3)–Re(1)–Cu(5) | 60.24(13) |
| Cu(3)–Re(1)–P(7) | 99.44(23) |
| Cu(3)–Re(1)–P(8) | 160.45(25) |
| Cu(4)–Re(1)–Cu(5) | 57.96(12) |
| Cu(4)–Re(1)–P(7) | 160.76(24) |
| Cu(4)–Re(1)–P(8) | 98.81(24) |
| Cu(5)–Re(1)–P(7) | 117.53(21) |
| Cu(5)–Re(1)–P(8) | 111.13(20) |
| P(7)–Re(1)–P(8) | 100.0(3) |
| Cu(3)–Re(2)–Cu(4)′ | 62.64(11) |
| Cu(3)–Re(2)–Cu(6) | 59.72(13) |
| Cu(3)–Re(2)–P(9) | 159.27(22) |
| Cu(3)–Re(2)–P(10) | 97.03(21) |
| Cu(4)′–Re(2)–Cu(6) | 58.34(12) |
| Cu(4)′–Re(2)–P(9) | 96.93(21) |
| Cu(4)′–Re(2)–P(10) | 159.66(21) |
| Cu(6)–Re(2)–P(9) | 114.06(20) |
| Cu(6)–Re(2)–P(10) | 113.65(20) |
| P(9)–Re(2)–P(10) | 103.30(27) |
| Re(1)–Cu(3)–Re(2) | 175.13(15) |
| Re(1)–Cu(3)–Cu(4)′ | 115.71(16) |
| Re(1)–Cu(3)–Cu(5) | 59.30(10) |
| Re(1)–Cu(3)–Cu(6) | 117.38(14) |
| Re(2)–Cu(3)–Cu(4)′ | 59.76(10) |
| Re(2)–Cu(3)–Cu(5) | 116.04(14) |
| Re(2)–Cu(3)–Cu(6) | 59.16(10) |
| Cu(4)–Cu(3)–Cu(4)′ | 88.15(15) |
| Cu(4)–Cu(3)–Cu(5) | 57.11(12) |
| Cu(4)–Cu(3)–Cu(6) | 57.80(12) |
| Cu(5)–Cu(3)–Cu(6) | 81.98(15) |
| Re(1)–Cu(4)–Re(2)′ | 174.85(14) |
| Re(1)–Cu(4)–Cu(3) | 58.44(10) |
| Re(1)–Cu(4)–Cu(5) | 59.61(10) |
| Re(1)–Cu(4)–Cu(6) | 116.73(14) |
| Re(2)′–Cu(4)–Cu(3) | 117.16(15) |
| Re(2)–Cu(4)′–Cu(5) | 116.32(14) |
| Re(2)–Cu(4)′–Cu(6) | 58.64(10) |
| Cu(3)–Cu(4)–Cu(3)′ | 91.83(15) |
| Cu(3)′–Cu(4)–Cu(5) | 59.00(12) |
| Cu(3)′–Cu(4)–Cu(6) | 58.02(12) |
| Cu(5)–Cu(4)–Cu(6) | 83.81(15) |
| Re(1)–Cu(5)–Re(1)′ | 170.74(24) |
| Re(1)–Cu(5)–Cu(3)′ | 126.86(16) |
| Re(1)–Cu(5)–Cu(4) | 62.43(9) |
| Cu(3)–Cu(5)–Cu(3)′ | 97.16(24) |
| Cu(3)′–Cu(5)–Cu(4) | 64.47(15) |
| Cu(4)–Cu(5)–Cu(4)′ | 96.51(25) |
| Re(2)–Cu(6)–Re(2)′ | 170.22(25) |
| Re(2)–Cu(6)–Cu(3)′ | 126.43(16) |
| Re(2)′–Cu(6)–Cu(4) | 63.02(9) |
| Cu(3)–Cu(6)–Cu(3)′ | 98.88(25) |
| Cu(3)′–Cu(6)–Cu(4)′ | 63.56(15) |
| Cu(4)–Cu(6)–Cu(4)′ | 95.87(25) |
| Re(1)–Cu(3) | 2.671(4) |
| Re(1)–Cu(4) | 2.713(4) |
| Re(1)–Cu(5) | 2.6399(14) |
| Re(1)–P(7) | 2.419(9) |
| Re(1)–P(8) | 2.454(9) |
| Re(2)–Cu(3) | 2.667(4) |
| Re(2)–Cu(4)′ | 2.729(4) |
| Re(2)–Cu(6) | 2.6154(14) |
| Re(2)–P(9) | 2.414(8) |
| Re(2)–P(10) | 2.442(8) |
| Cu(3)–Cu(4) | 2.759(5) |
| Cu(3)–Cu(4)′ | 2.806(5) |
| Cu(3)–Cu(5) | 2.665(5) |
| Cu(3)–Cu(6) | 2.631(5) |
| Cu(4)–Cu(5) | 2.594(5) |
| Cu(4)–Cu(6) | 2.607(5) |

to that in $Cp_2Y(THF)H_6Re(PPh_3)_2$ [9], we propose that each $ReH_6(PPh_3)_2$ unit in $Cu_6(ReH_6P_2)_4^{2+}$ has a dodecahedral geometry. This geometry furnishes up to three hydrides for bridging each Re to a triangular face of the $Cu_6$ polyhedron. This placement of four $ReH_6P_2$ units on a $Cu_6$ fragment closely mimics the structure of $Cu_6[Fe(CO)_4]_4^{-2}$ [10], in which the average Cu/Cu separation is 2.62 Å (compare 2.55 in copper metal), 2.508 Å in $[HCuP(NMe_2)_3]_6$ [11] and 2.453 Å in $H_8Cu_8(Ph_2P(CH_2)_3PPh_2)_4$ [11].

The $Cu_6$ polyhedron is accurately described an an octahedron moderately compressed along an idealized $C_4$ axis (which goes through Cu5 and Cu6). The inter-equatorial Cu–Cu distances range from 2.759(5) to 2.806(5) Å. The four axial/equatorial distances range from 2.594(5) to 2.665(5) Å. These distances compare to the value (2.626(3) Å) in the raft-like $Cu_3Os_3H_9(PMe_2Ph)_9$ [12]. The Re–Cu distances range from 2.667(4) to 2.729(4) Å for equatorial coppers and 2.615(1) to 2.640(1) Å for the axial coppers Cu6 and Cu5, respectively. These distances are comparable to those in $Re_4Cu_2H_{14}(PMe_2Ph)_8$ [13] and $Re_4Cu_2H_{16}(PMe_2Ph)_8^{2+}$ [5].

Much of our earlier work on copper-containing heterobimetallic molecules has required the coupling of neutral polyhydrides with the highly basic [13–15] alkoxide ligand of $(CuO^tBu)_4$. Alternatively, we have coupled metal halides with anionic polyhydrides, $MH_mL_n^-$ [9, 16]. The ability of the reagent $Cu(NCMe)_4^+$ to 'assemble' polyhydride molecules into hydride-bridged clusters is a quite general third alternative synthetic procedure [3–5]. However, while such reactions with $H_3IrP_3$ or $ReH_5P_3$ proceed without hydrogen loss (as either $H^+$ or $H_2$), the higher valent $ReH_7P_2$ displays Bronsted acid behavior (eqn. (1)). We feel that proton transfer is associated with the larger aggregation in this latter case (i.e. $Ir_2Cu_3$ [4], but $Re_4Cu_6$, not $Re_2Cu_3$); the high charge on the 'intact' hypothetical species like $Cu_6(ReH_7P_2)_4^{6+}$ enhances its Bronsted acidity. The same proton dissociation behavior is shown on condensation of neutral metal hydrides with sources of $Au(PR_3)^+$ [1]. The mechanism by which the electrophile $Cu^+$ enhances Bronsted acidity of a polyhydride is also of interest [17]. Coordinated $H_2$ is known to possess considerable Brønsted acidity [18], and $H_2$ is produced by one-electron oxidation [19], or by addition of $H^+$ [18] or an electrophile [17] to a metal hydride. We propose that addition of $Cu^+$ to the $d^0$ complex $ReH_7P_2$ might be expected to promote intramolecular redox chemistry to form $Cu^IRe^V(H)_5(H_2)P_2^+$. It thus seems that $H_2$ complexes may mediate the synthetic chemistry reported here. This hypothesis also naturally explains why the number of protons produced in eqn. (1) matches exactly the rhenium content (i.e. four) in the product.

## Supplementary material

A listing of positional parameters, thermal parameters and all bond distances and angles are available from the authors upon request.

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