Physical Properties. PDPL showed the following characteristics:[14] air-sensitive greenish black fine scales with a metallic luster; mp 155 °C dec; MS, *m/e* 350 (M^+, 38%); ^1H NMR (360 MHz, CS_2 and C_6D_{12})[13a] δ 4.42 (d, 4 H, J = 8.5 Hz, H-5, -6, -12, -13), 5.23 (d, 4 H, J = 8.5 Hz, H-4, -7, -11, -14), 5.54 (4 H, B part of an AB_2 system, J = 8 Hz, H-1, -3, -8, -10), 5.57 (2 H, A part of an AB_2 system, J = 8 Hz, H-2, -9); UV/vis λ_{max} (in THF)[13a] 666 (log ϵ 5.13), 636 (4.41), 610 (4.24), 544 sh (3.69), 4.68 (3.52), 442 (3.74), 400 (4.04), 346 (4.70), 324 (4.61), 309 (4.49), 282 (4.48), 230 nm sh (4.40). The striking feature is that the chemical shifts of all protons are at markedly upfield regions for a condensed conjugated hydrocarbon and are even at higher field by over 1 ppm than those of pyracylene (δ 6.01 and 6.52), which is regarded as a perturbed 12π-electron system.[15] Interestingly, the shifts can be compared to those of the outer protons of [24]annulene (δ 4.73),[16] and 3,11,16,24-tetra-*tert*-butyl-1,12,14-trisdehydro-[24]annulene (δ 4.70, 4.71, 5.00, and 5.14).[17,18] A reasonable explanation for the NMR finding resides in the presence of an induced paramagnetic ring current in PDPL, the highly antiaromatic molecule, which implies net energy destabilization with electron delocalization in this system.

Direct insight into the amphotericity of PDPL was obtained by electrochemical studies, and the results are summarized schematically in Figure 1. The CV measurement[13a] was carried out at −50 °C since no reversible cyclic voltammogram was obtained at room temperature due to its instability. For comparison, the corresponding data for some related compounds are included. Apparently, PDPL exhibits the smallest E_1^{sum} (0.99 V) and the highest E_1^{red} (−0.43 V) among the hydrocarbons reported so far.[4,19] The E^{red} values, which are comparable to that of well-known π-electron acceptors 1,4-benzoquinone (E_1^{red} = −0.38 V, E_2^{red} = −1.17 V)[20a,b] and 1,2-naphthoquinone (E_1^{red} = −0.46 V, E_2^{red} = −0.77 V),[20a] can be correlated to the feature that the LUMO of PDPL is a nonbonding MO (NBMO) that retains the characteristic of the NBMO of the phenalenyl in the Hückel level arguments.[21]

From the viewpoint of the electrochemical phenomena, PDPL is the potential hydrocarbon from which two types of solid complexes are isolated in which it behaves as a donor with a molecule and as an acceptor with another.[22] To test this possibility we attempted to prepare such complexes. Although PDPL forms 1:1 complexes with 2,4,7-trinitrofluorenone (greenish black solid, mp >360 °C) and tetracyanoquinodimethane (greenish black solid, mp 295 °C dec), our attempts to use donors to form complexes with PDPL have led to failure to date.[23] Further examinations are currently being pursued.

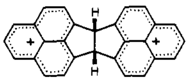
Acknowledgment. We thank Hideo Naoki (Suntory Institute for Bioorganic Research) for 360-MHz NMR measurement.

Registry No. 1, 86272-03-9; **2**, 83548-18-9; **3**, 86260-85-7; bis(phenalenyl) dication, 86260-88-0; PDPL·2,4,7-trinitrofluorenone, 86260-86-8; PDPL·tetracyanoquinodimethane, 86260-87-9.

Supplementary Material Available: Cyclic voltammograms and UV/vis spectra of BPLA (**1**), BPLE (**2**), and PDPL (**3**), ^1H NMR (360 MHz) of PDPL, and detailed experimental procedure for the preparation of PDPL (4 pages). Ordering information is given on any current masthead page.

---

[14] In concentrated sulfuric acid, PDPL was reversibly diprotonated at the two central carbon atoms of the pentalene skeleton to form the bis(phenalenyl) dication (i) characterized by ^1H NMR spectrum: δ 7.32 (s, 2 H),



i

8.95 (t, 2 H, J = 7.7 Hz), 9.37 (d, 4 H, J = 8.1 Hz), 9.75 (d, 4 H, J = 7.7 Hz), 9.91 (d, 4 H, J = 8.1 Hz).

[15] (a) Trost, B. M.; Bright, G. M. *J. Am. Chem. Soc.* **1967**, *89*, 4244. (b) Trost, B. M.; Bright, G. M.; Frihart, C.; Brittelli, D. *Ibid.* **1971**, *93*, 737. (c) Trost, B. M., ref 5a, p 243.

[16] Calder, I. C.; Sondheimer, F. *Chem. Commun.* **1966**, *904*. Sondheimer, F.; Calder, I. C.; Elix, J.; Gaoni, Y.; Garratt, P. J.; Grohmann, K.; DiMais, G.; Mayer, J. "Aromaticity"; The Chemical Society: London, 1967; Special Publication No. 21, p 75.

[17] Nakatsuji, S.; Akiyama, S.; Nakagawa, M. *Tetrahedron Lett.* **1976**, 2623.

[18] One of the valence-bond structures of PDPL consists of a peripheral 24π-electron array with two vinyl cross-links.

[19] (a) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970; Chapters 2 and 3. (b) For electrochemical studies on some pentalene derivatives see, for 1,9-dimethyldibenzo[*b,f*]pentalene (the peak potential of the first reduction E_{p1c}^{red} = −1.92 V and the peak potential of the first oxidation E_{p1a}^{ox} = 0.98 V vs. Ag/Ag^+ electrode): Wilner, I.; Becker, J. Y.; Rabinovitz, M. *J. Am. Chem. Soc.* **1979**, *101*, 395. See, for 1,3,5-tri-*tert*-butylpentalene (E_1^{red} = −1.45 V and E_1^{ox} = 0.75 V vs. SCE): Johnson, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 1461.

[20] (a) Nelsen, S. F.; Trost, B. M.; Evans, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 3034. (b) Butler, J. N. *J. Electroanal. Chem. Interfacial Electrochem.* **1967**, *14*, 89.

[21] PDPL can be classified as a typical pentalenoid molecule in which the HOMO lies close to the vacant nonbonding level in energy. See, for example, ref 15 and: Boyd, G. V. *Tetrahedron*, **1966**, *22*, 3409. The low-energy difference of the HOMO–LUMO separation is responsible for the extremely small E_1^{sum} value observed for PDPL.

[22] In the case of nonhydrocarbon molecules, such an amphoteric phenomenon in the solid state has already been demonstrated. (a) Sandman, D. J.; Richter, A. F. *J. Am. Chem. Soc.* **1979**, *101*, 7079. (b) Sandman, D. J.; Richter, A. F.; Warner, D. E.; Fekete, G. T. *Mol. Cryst. Liq. Cryst.* **1980**, *60*, 21. (c) Matsunaga, Y. *Nature (London)* **1966**, *211*, 182.

[23] We examined here tetrathiafulvalene, tetrathiotetracene, 5,10-dimethyldihydrophenazine, *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, 3,3-bis(dimethylamino)biphenyl, and 2,7-bis(dimethytlamino)pyrene as donors, all to no avail. We are grateful to Professor Soichi Misumi, Osaka University, for a generous gift of 2,7-bis(dimethylamino)pyrene(Natsume, B.; Nishikawa, N.; Kaneda, T.; Sakata, Y.; Misumi, S. *Chem. Lett.* **1981**, 601).

An Unprecedented Ligand Set and Coordination Geometry for Copper(I)

Larry F. Rhodes, John C. Huffman, and
Kenneth G. Caulton*

Department of Chemistry, Indiana University
Bloomington, Indiana 47405

Received March 3, 1983

Activation of thermally stable polyhydrido phosphine complexes has been one of our major research objectives.[1,2] With this in mind, the oxidation of MoH_4L_4 (L = PMe_2Ph (≡P) and $PMePh_2$ (≡P′)) by Ag(I) in MeCN was investigated[3] and shown to produce $MoH_2P_4(MeCN)_2^{2+}$ and $MoH_2P'_3(CH_3CN)_3^{2+}$ along with H_2 and Ag^0. Among the many mechanisms proposed for this reaction, the intermediacy of an inner-sphere electron-transfer precursor complex $[MoL_4H_4Ag]^+$ seemed most attractive. We now report the isolation of analogues of such an intermediate from the reaction of the milder oxidant Cu(I) with the isoelectronic (d^2) hydride ReH_5L_3 as well as the unusual outcome of electrophilic attack upon $Re_2H_8L_4$.

Addition of $Cu(MeCN)_4PF_6$ to a cooled (−70 °C) THF solution of $ReH_5P'_3$ followed by warming to room temperature results in precipitation of a colorless solid. NMR spectral assay of this reaction[4] indicates an unexpected 2:1 Re/Cu stoichiometry. Lack

---

[1] Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695–696.

[2] Green, M. A.; Huffman, J. C.; Caulton, K. G.; Rybak, W. K.; Ziolkowski, J. J. *J. Organomet. Chem.* **1981**, *218*, C39–C43.

[3] Rhodes, L. F.; Zubkowski, J. D.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1982**, *21*, 4185–4192.

[4] 220-MHz ^1H NMR (CD_3CN) (16 °C) δ −5.54 (quartet, J_{PH} = 17 Hz, 5 H)

0002-7863/83/1505-5137$01.50/0 © 1983 American Chemical Society

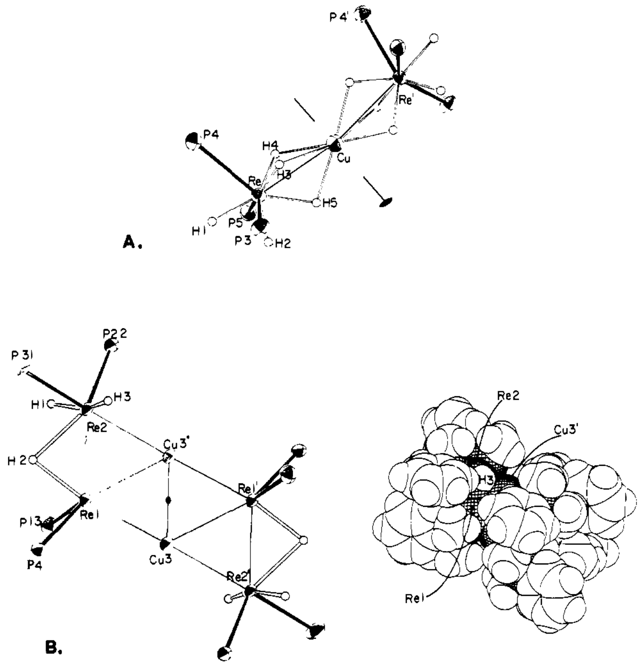


Figure 1. (A) ORTEP drawing of the inner coordination sphere of $[ReH_5(PMePh_2)_3]_2Cu^+$, showing the crystallographic C_2 axis through Cu. The dodecahedron about rhenium is composed of the trapezoids P3, P5, H3, and H4 and P4, H1, H2, and H5. (B) ORTEP and space-filling drawings of $[Re_2H_8(PMe_2Ph)_4]_2Cu_2^{2+}$ viewed perpendicular to the Re_4Cu_2 plane. The center of symmetry is shown as a solid dot. Only six of the 16 hydride ligands were located.

of H_2 evolution, integration of the ^1H NMR spectrum, and the absence of Cu^0 deposition suggest the formulation $[(ReH_5P'_3)_2Cu]PF_6$ (**1a**) for the colorless solid (eq 1). An X-ray

$$2ReH_5L_3 + Cu(MeCN)_4PF_6 \xrightarrow[-70\ °C]{THF} [(ReH_5L_3)_2Cu]PF_6 + 4MeCN \quad (1)$$

1a, L = $PMePh_2$
1b, L = PMe_2Ph

structure determination[5] of colorless crystals of **1a** grown from hot MeCN confirmed this formulation and revealed some unique features of the molecule (Figure 1A). The formally Cu(I) center is coordinated to *six* hydrides in an unprecedented *octahedral* configuration. The Cu center binds to three cisoid hydrides of the dodecahedron about Re. Thus, each $ReH_5P'_3$ unit is functioning as a tridentate ligand to the Cu center. The possibility of Re → Cu donation cannot be excluded. Compound **1a** is the first isolated molecule in which a Cu(I) center is ligated exclusively by hydrides.

The solution structure of the more soluble $[(ReH_5P_3)_2Cu]^+$ **1b** was found by low-temperature ^1H NMR[6] to be consistent with the presence of three bridging hydrides and two terminal hydrides. The ^1H NMR of **1b** at both +16 °C and +75 °C shows a quartet for the hydride resonances, indicating a bridge/terminal hydride scrambling process that maintains Re–H bonds: the hydride never migrates rapidly past the copper (via a terminal Cu–H) to the other rhenium.

To probe the interaction of the Cu(I) electrophile with a rhenium polyhydride that also contains a Re/Re multiple bond, we have characterized the purple precipitate that is isolated in 83% yield from the reaction of equimolar $Cu(MeCN)_4PF_6$ with $Re_2H_8P_4$. The absence of gas evolution (established quantitatively by Toepler pumping) and of copper metal deposition, in addition to spectral data,[7a] are indicative of a Re_2/Cu ratio of 1:1. An X-ray diffraction study[7b,8] shows this ratio of metal atoms to be correct, but reveals that the actual structural unit consists of *two* Re dimers and *two* Cu cations (Figure 1B, eq 2). This hexanuclear product displays an unprecedented planar rhomboidal metal array. While this is contrary to the closed polyhedral structures commonly seen for molecular six metal atom compounds, the raft-like aggregate represents an attractive geometric analogue of a metal surface. $Re_4Cu_2H_{16}L_8^{2+}$ is the most hydride-rich species demonstrated to date. The unique geometry of the metals about copper and the steric accessibility (Figure 1B, space-filling model) of copper suggest possible enhanced reactivity of this dication.

$$2Re_2H_8L_4 + 2Cu(MeCN)_4PF_6 \xrightarrow{THF} [Re_4Cu_2H_{16}L_6](PF_6)_2 + 8MeCN \quad (2)$$

2a, L = $PMePh_2$
2b, L = PMe_2Ph

Proton NMR of both **2a** and **2b** (hydride quintets) reveal that, as with **1**, the hydrides execute facile migration only in zones localized about one Re_2L_4 unit; even on a flat "raft" of metals, hydride migration past copper is significantly hindered.

The unpredictable stoichiometry ($(ReH_5P_3)_2Cu^+$) and aggregation ($(Re_2H_8P_4Cu)_2^{2+}$) revealed in this work is associated with the total loss of acetonitrile from Cu^+, coupled with an aversion on the part of Cu^+ to tolerate ligation from only one side. $Cu(NCMe)_4^+$, as an operational source of "naked" Cu^+, is thus an attractive reagent for considerably aggregated (i.e., not merely dimeric) mixed-metal species.

Acknowledgment. This work was supported by the National Science Foundation Grant No. CHE-80-06331, by the Bloomington Academic Computer Services, and by Cleveland Refractory Metals. The NMR spectra were obtained on an instrument funded in part by NSF Grant No. CHE-80-05004. We also thank Kevin Gilbert, David Hoffman, Edward Kober, and Mark Noble for valuable discussions and technical assistance.

Registry No. 1a, 86323-22-0; **1b**, 86323-24-2; **2a**, 86323-26-4; **2b**, 86310-24-9; $Cu(MeCN)_4PF_6$, 64443-05-6; $ReH_5(PMePh_2)_3$, 79245-21-9; $ReH_5(PMe_2Ph)_3$, 65816-70-8; $Re_2H_8(PMePh_2)_4$, 79245-22-0; $Re_2H_8(PMe_2Ph)_4$, 76317-34-5; Cu, 7440-50-8; Re, 7440-15-5.

Supplementary Material Available: Table of fractional atomic coordinates, thermal parameters, and structure factors for **1a** and **2b** (65 pages). Ordering information is given on any current masthead page.

---

(5) Crystallographic data (−168 °C): a = 25.486 (13) Å, b = 12.010 (4) Å, c = 13.340 (5) Å, β = 116.26 (2)°, V = 3661.9 Å^3, Z = 2 in space group $P2/a$; RF = 3.9%, R_wF = 3.9%. All hydrogen atoms were refined isotropically. Selected structural parameters: Re–Cu = 2.607 (2), Re–P3 = 2.375 (2), Re–P4 = 2.398 (2), Re–P5 = 2.417 (2), Re–H1 = 1.52 (12), Re–H2 = 1.35 (12), Re–H3 = 1.67 (10), Re–H4 = 1.50 (8), Re–H5 = 1.67 (8), Cu–H3 = 2.20 (8), Cu–H4 = 1.81 (7), Cu–H5 = 1.78 (8) Å. ∠Re–Cu–Re′ = 169.2 (1)°.

(6) 360-MHz ^1H NMR (acetone-d_6) (−80 °C) δ −5.17 (quartet, J_{PH} = 18 Hz, 2 H), −6.49 (br s, 3 H); the latter resonance is broad by virtue of direct (bridging) interaction with quadrupolar ^{63}Cu and ^{65}Cu (I = 5/2).

(7) (a) 220-MHz ^1H NMR (acetone-d_6) (16 °C) δ −5.86 (quintet, J_{PH} = 9 Hz, 12–14 H), +1.97 (d, J = 9 Hz, 24 H), +7.40–+7.70 (multiplets, 80 H). (b) Integration of the 220-MHz or 360-MHz proton NMR spectra of this compound gave hydride counts (12–14) consistently short of the 16 required. Toepler pump measurements, GC analysis of solvent, and ^2H NMR of $(Re_2D_8P_4Cu)_2^{2+}$ show that the "missing" hydrides are not lost as H_2, not used in reduction of the solvent, nor resonate at unusual frequencies (i.e., downfield of Me_4Si). Furthermore, subsequent derivatization reactions (to be reported later) of **2b** with phosphines show recovery of all 16 hydrides. On the basis of the structure found for **1a**, we feel certain that the hydrides not found by X-ray diffraction bridge not only the Re_2 unit but also the Re–Cu and perhaps the Cu–Cu bonds. The bridging hydrides may not be detectable in the NMR because of extreme broadening caused by quadrupolar Cu.

(8) Crystallographic data (−162 °C): a = 14.964 (8) Å, b = 12.866 (8) Å, c = 11.585 (5) Å, α = 93.11 (3)°, β = 93.37 (3)°, γ = 98.03 (3)°, V = 2200.5 Å^3, Z = 1 in space group $P\bar{1}$; RF = 5.7%; R_wF = 5.2%. All hydrogen atoms located were refined isotropically. However, only six of the metal-bound hydrogens were located. Selected structural parameters: Re1–Re2 = 2.572 (1), Re1–Cu3 = 2.627 (2), Re1–Cu3′ = 2.704 (2), Re2–Cu3′ = 2.708 (2), Cu3–Cu3′ = 2.493 (3), Re–P ranges from 2.343 (4) to 2.398 (4), Re1–H2 = 2.18 (14), Re2–H1 = 1.24 (13), Re2–H3 = 0.94 (13), Re2–H2 = 2.12 (13) Å.