We are currently attempting to apply spin-trap techniques to check for the eventual formation of radical anions.[19] However, it is difficult to find a radical trap that is unreactive toward hydride donors.

Finally, we wish to underscore the synthetic utility of the reported reaction, given that many "superhydrides" are available in a laboratory. By extension, any good hydride donor will function as an apparent catalyst precursor for substitution reactions of $Ru_3(CO)_{12}$.

Acknowledgment. Special thanks are extended to Herbert D. Kaesz for helpful discussions regarding this work. Financial support from the CNRS is gratefully acknowledged. We are also grateful to Johnson-Matthey for generous loans of ruthenium trichloride.

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(20) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Pressure Tuning of Exchange Interactions in Dinuclear Chromium(III) Complexes

Sir:

Luminescence spectroscopy has proved to be a very powerful tool for probing exchange interactions in dinuclear chromium(III) complexes. This communication reports the first experiments under high pressure. They allow a study of the pressure and volume dependence of the exchange. The investigated complexes are $[LCr^{III}(OH)_3Cr^{III}L](ClO_4)_3$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane; the complex is abbreviated $\{triol\}(ClO_4)_3$ in the following) and $[(NH_3)_5Cr^{III}OHCr^{III}(NH_3)_5]Cl_5{\cdot}H_2O$ (abbreviated $\{rhodo\}Cl_5{\cdot}H_2O$). Dramatic shifts of the luminescence line positions up to several hundred wavenumbers are observed upon application of a hydrostatic pressure of 40 kbar. The effects are 1 order of magnitude larger than for the ruby R lines.[1] A detailed account of this work is given in ref 1, and the pressure cell is described in ref 2.

Figure 1 shows 14 K luminescence spectra of $\{triol\}(ClO_4)_3$ at three pressures obtained by using a 4:1 methanol/ethanol mixture as a pressure-transmitting medium.[2] The emitting dimer state in this complex is a spin triplet, and the dominant peak in the emission spectrum corresponds to the spin-allowed $S^* = 1 \rightarrow S = 1$ transition.[3,4] The energy shifts are accompanied by a broadening of the lines that is due to nonhydrostatic pressure components. In Figure 2 the observed energy differences between the dimer ground-state levels in $\{triol\}(ClO_4)_3$ are plotted as a function of the applied pressure. The dependence is linear within the pressure range examined here: $\delta(E(S = 1) - E(S = 0)) = 1.3 \pm 0.1$ cm^{-1} kbar^{-1} P^{-1} and $\delta(E(S = 2) - E(S = 0)) = 2.6 \pm 0.15$ cm^{-1} kbar^{-1} P^{-1}. The energy differences over the whole pressure range are well accounted for by the eigenvalues of the Hamiltonian

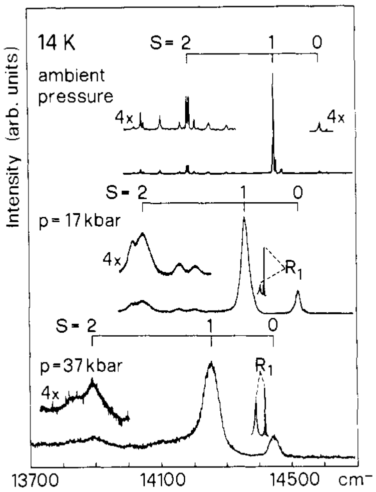

Figure 1. Luminescence spectra (14 K) of $\{triol\}(ClO_4)_3$ at three selected pressures. The lines denoted R_1 arise from the sapphire anvils (sharper line) and the ruby chips (broader line), which were added for pressure calibration. The purely electronic transitions to the ground-state dimer levels S = 0, 1, and 2 are indicated.

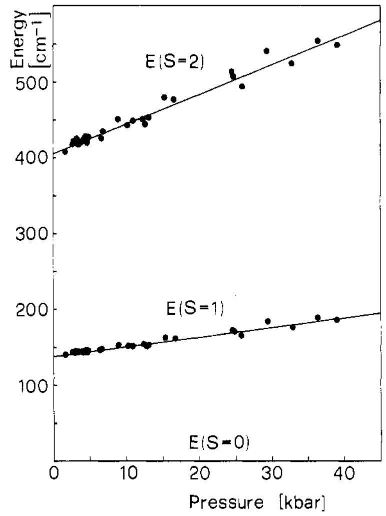

Figure 2. Ground-state exchange splitting as a function of hydrostatic pressure for $\{triol\}(ClO_4)_3$ at 14 K. The lines were obtained by a linear regression through the data points.

Table I. Exchange Parameters as a Function of Hydrostatic Pressure

$\{triol\}(ClO_4)_3$			$\{rhodo\}Cl_5{\cdot}H_2O$		
P, kbar	*J*, cm^{-1}	*j*, cm^{-1}	*P*, kbar	*J*, cm^{-1}	*j*, cm^{-1}
0	−64.0	1.6	0	−15.2	0.16
9	−72.3	1.2	9.5	−16.4	0.16
25	−82.6	0.8	25	−18.8	0.3
39	−87.8	1.6	42	−21.4	0.3

$$H_{ex} = -2J\vec{S}_1{\cdot}\vec{S}_2 - j(\vec{S}_1{\cdot}\vec{S}_2)^2 \qquad (1)$$

Table I lists parameter values for a few selected pressures.

The observed effects in $\{rhodo\}Cl_5{\cdot}H_2O$ are similar, the energy shifts being somewhat smaller because the exchange coupling is weaker. The emitting dimer state in this complex is a spin quintet, and the observed transitions are $S^* = 2 \rightarrow S = 1$, 2, and 3.[5] As for $\{triol\}^{3+}$, the exchange splittings increase linearly with pressure. Exchange parameters are listed for a few selected pressures in Table I.

We obtain the following pressure dependences of the bilinear exchange parameter J for the two complexes:

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$$\{\text{triol}\}(\text{ClO}_4)_3\text{:}\quad |J\,(P)| = |J_0| + (0.7 \pm 0.1\ \text{cm}^{-1}\ \text{kbar}^{-1}\ P)$$

$$\{\text{rhodo}\}\text{Cl}_5\cdot\text{H}_2\text{O:}\quad |J\,(P)| = |J_0| + (0.15 \pm 0.02\ \text{cm}^{-1}\ \text{kbar}^{-1}\ P)$$

The zero subscript refers to ambient pressure. The biquadratic parameter j is pressure-independent for both complexes within the experimental accuracy of our measurements. Considering that J_0 is −64 and −15.2 cm^{-1} for {triol}$(ClO_4)_3$ and {rhodo}$Cl_5\cdot H_2O$, respectively, the relative increase of $|J|$ with pressure is practically the same for the two complexes.

We can estimate the pressure dependence of the molecular structure, i.e. the local compressibility from the observed shift of the spin-allowed $^4A_2 \rightarrow {}^4T_2$ band in the crystal absorption spectrum under applied pressure. Approximating the ligands as point charges and assuming an isotropic compression, we can calculate the compressibility of the complex with volume V, which is defined as

$$\chi = -(1/V)\mathrm{d}V/\mathrm{d}P \tag{2}$$

We obtain 10×10^{-4} and 6×10^{-4} kbar^{-1} for {triol}$^{3+}$ and {rhodo}$^{5+}$, respectively. The {triol}$^{3+}$ complex appears to be significantly more compressible than the {rhodo}$^{5+}$ complex. The relative increase of the exchange parameter with decreasing volume is given by

$$-(V/J)(\mathrm{d}J/\mathrm{d}V) = (1/\chi J)(\mathrm{d}J/\mathrm{d}P) \tag{3}$$

Insertion of the experimental values of χ, J, and $\mathrm{d}J/\mathrm{d}P$ leads to the following relative volume dependences: 10.9 and 16.4 for {triol}$^{3+}$ and {rhodo}$^{5+}$, respectively.

The antiferromagnetic part of the exchange parameter J can be interpreted as "kinetic exchange",[6] and as such it is related to one-electron-transfer integrals which can be estimated by a molecular orbital calculation.[7] For a chromium(III) pair we have[8]

$$J = -\frac{1}{18U}\sum_{i=1}^{3}(e_i^- - e_i^+)^2 \tag{4}$$

where i numbers the singly occupied t_2 orbitals on a single chromium(III) center. e_i^- and e_i^+ are the energies of MO's built from the minus and plus combinations of the magnetic orbitals i. U is the electron-transfer energy, a slowly varying quantity as a function of distortions. We performed extended Hückel MO calculations[9] for both complexes in their ambient and compressed geometries and obtained the following values for the relative volume dependence $(-(V/J)(\mathrm{d}J/\mathrm{d}V))$: 3.1 and 6.3 for {triol}$^{3+}$ and {rhodo}$^{5+}$, respectively. Both these values are approximately a factor of 3 smaller than those dedudced experimentally, 10.9 and 16.4, respectively. Part of this discrepancy may be due to our assumption of an isotropic local compressibility. But it is clear that the extended Hückel technique is not able to reproduce the pressure dependence quantitatively. However, it is significant that the greater relative volume dependence of J in the {rhodo}$^{5+}$ complex is correctly obtained in the calculation.

Acknowledgment. We are indebted to P. Chaudhuri and K. Wieghardt from the University of Bochum for providing {triol}$(ClO_4)_3$. Financial support by the Swiss National Science Foundation is acknowledged.

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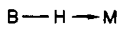
Cupracarboranes Containing a *closo*-Cu$^{I}C_2B_9$ Geometry. Synthesis and Structure of $[(PPh_3)CuC_2B_9H_{11}]^-$ and $[(PPh_3)_2Cu_2(\mu\text{-}H)_2C_2B_9H_9]$

Sir:

An additional manifestation of the versatile electron-donor ability of $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ (**1**)[1] in metallacarborane chemistry has recently appeared in the form of polynuclear metallacarboranes involving exopolyhedral boron–hydride–metal three-center, two-electron linkages.[2,3] While the bridge bonding mode I is the most usual pattern encountered in polynuclear metal complexes of **1**, the unit II has only been realized in the bimetallic aluminacarborane *commo*-3,3′-Al[(*exo*-8,9-$(\mu\text{-}H)_2Al(C_2H_5)_2$-3,1,2-$AlC_2B_9H_9$)(3′,1′,2′-$AlC_2B_9H_{11}$)] (**2**),[3c,4] in which the bridging BH units stem from the upper and lower pentagonal belts of one dicarbollide cage. As part of the investigation into the extended use of **1** in the synthesis of novel metallacarboranes containing metal–hydride–boron bridge bonds, the reaction chemistry of **1** with copper(I) has been examined.[5]



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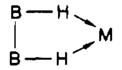

II

Routes to two novel phosphinocupracarboranes have recently been discovered. Depending on the absence or presence of $(PPN)^+Cl^-$ (PPN^+ = bis(triphenylphosphoranylidene)ammonium cation), the dithallium salt[6] of **1** reacts with triphenylphosphine-substituted copper(I) chlorides (L_nCuCl; n = 1, 2) to form either dinuclear *closo*-[*exo*-4,8-$(\mu\text{-}H)_2Cu(PPh_3)$-3-$(PPh_3)$-3,1,2-$CuC_2B_9H_9$] (**3**; white; 79%) or mononuclear (PPN)[*closo*-3-(PPh_3)-3,1,2-$CuC_2B_9H_{11}$] ((PPN)**4**; off-white; 84%). Both compounds were characterized by single-crystal X-ray analyses[7] as well as other means.[8]

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(4) The bridging unit II is not uncommon in metallaboranes or in mononuclear metallacarboranes. Examples include the following. (a) $Cu_2(PPh_3)_4(B_{10}H_{10})$: Gill, J. T.; Lippard, S. J. *Inorg. Chem.* **1975**, *14*, 751. (b) $HMn_3(CO)_{10}(BH_3)_2$: Kaesz, H. D.; Fellman, W.; Wilkes, G. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1965**, *87*, 2753. (c) *exo*-*nido*-(Phosphine)rhodacarboranes: Knobler, C. B.; Marder, T. B.; Mizusawa, E. A.; Teller, R. G.; Long, J. A.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2990.

(5) The derivative chemistry of **1** with Cu(I) has remained virtually unexplored. The only compound reported to date is $[(PPh_3)CuC_2B_9H_{10}(NC_5H_5)]$, for which X-ray structural data are not available: Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1979**, 619.

(6) Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1178.

(7) (a) Suitable crystals of **3** and (PPN)**4** were grown from dichloromethane/ether. Diffraction data on both compounds were collected at 25 °C on a locally built automated diffractometer, using Mo Kα radiation, to a maximum 2θ value of 50°. The structures were solved by a combination of conventional Patterson, Fourier, and least-squares techniques. (b) Crystallographic data for **3** [(PPN)**4**]: a = 10.005 (2) [11.507 (1)] Å; b = 20.693 (4) [14.772 (1)] Å; c = 18.998 (3) [30.751 (2)] Å; β = 92.664 (6) [90.284 (2)]°; V = 3924 [5227] Å^3; space group $P2_1/n$ [$P2_1/n$]; unique data ($I > 3\sigma(I)$ 5071 [4831]; R (R_w) = 4.5 (6.1) [6.4 (7.5)] %. All calculations were performed on the DEC VAX 750 computer of the J. D. McCullough Crystallography Laboratory using the UCLA Crystallography Package.

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