

corresponding quantities for cutting the end atom off a semi-infinite chain and a joining atom out of an infinite chain, shown in Figure 3 only for $VEC = 4$ because the values for other VECs are distorted by (or have to be adjusted for) differences in E_F . The similarity is in accordance with the localization of the bond energy already noted. However, Figure 3 shows clearly that ΔH_2 is not in general double the ΔH_1 value: the ΔH is seen to be nearly proportional to coordination number (CN) for low VEC but vary roughly as $(CN)^{1/2}$ for a half-filled band, in accordance with the principles⁶ of metallic bonding.

Finally we comment on the relation to experiment. Given that one has the chain structure, our calculations do show that the existence of band gaps causes the structure to become rapidly less stable at the observed VEC. However, no compounds with the chain structure are known for VEC around 2 (Figure 1) or $VEC \approx 1.4-2$ (Figure 2), where the structure would appear to be most stable. Presumably other structures have an even lower energy: if it is favorable to condense clusters into a chain, it is presumably even better to condense them into layers or three-dimensional arrays. We believe the latter argument is valid for low VEC, but not near a half-filled band (which would be consistent with the experimental facts stated) from the following analogy. Two hydrogen molecules with bonding states completely full have little interaction when approaching each other sideways, whereas two H_2^+ ions would experience strong bonding effects (ignoring the Coulomb repulsion) in a simple LCAO model, in accordance with the principles of metallic (very unsaturated) bonding.⁶ More research is planned into the relative stability of different one-, two-, and three-dimensional condensation structures.

Acknowledgment. We have benefited greatly from discussions with Professors A. Simon and O. K. Andersen and from financial support by the Science and Engineering Research Council, U.K.

Registry No. Nb_5Te_4 , 12035-11-9.

(6) Reference 4, pp 81-84.

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Received October 28, 1983

^{103}Rh NMR Spectrum of $[(\text{Rh}_2(\text{mhp})_4)_2]$: First Measurement of $^1J(^{103}\text{Rh}, ^{103}\text{Rh})$ for a Rh_2^{4+} Core

Sir:

The synthesis and study of complexes containing the Rh_2^{4+} core has attracted considerable and sustained attention,¹⁻¹⁴

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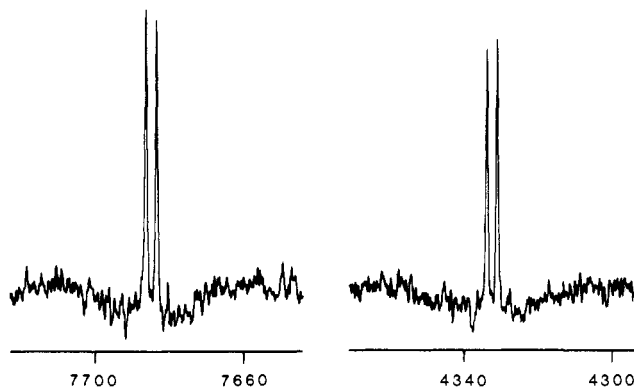


Figure 1. ^{103}Rh NMR spectrum of $[(\text{Rh}_2(\text{mhp})_4)_2]$ in $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ at ca. 300 K.

especially with respect to the nature of the metal-metal bonding. A general consensus has now been established⁸⁻¹³ that, for $\text{Rh}^{\text{II}}\text{L}_4$ (where L is a bridging ligand, especially a carboxylate or oxypyridine) and related complexes, a $\sigma^2\pi^4\delta^2\delta^*\pi^*4$, Rh-Rh (net) single bonding interaction occurs over the metal-metal separation of 2.359¹³-2.486 Å.⁷ We considered that it would be of interest to record the ^{103}Rh NMR spectra of such complexes, especially for systems in which the two rhodium atoms are inequivalent, whence a direct measure of the $^1J(^{103}\text{Rh}, ^{103}\text{Rh})$ coupling constant should be obtained.

We chose for our initial ^{103}Rh NMR studies $[\text{Rh}_2(\text{mhp})_4]$ ¹³ and $[(\text{Rh}_2(\text{mhp})_4)_2]$.¹⁴ $[\text{Rh}_2(\text{mhp})_4]$ ¹³ is a member of the family of $[\text{M}_2(\text{mhp})_4]$ molecules, known at present for $\text{M} = \text{Cr}, \text{Mo}, \text{W}, ^{15}\text{Rh}, ^{13}\text{Ru}, ^{16}\text{and Pd}.¹⁷ In each case, the molecules possess approximate D_{2d} symmetry, with each metal atom being coordinated to two nitrogen and two oxygen atoms. In contrast, $[(\text{Rh}_2(\text{mhp})_4)_2]$ involves¹⁴ an asymmetric arrangement of the four mhp ligands spanning the dimetal centers; one oxygen and three nitrogen atoms are coordinated to one rhodium(II) and one nitrogen and three oxygen atoms to the other. This arrangement of the ligands has the consequence that three methyl groups are located at one end of the molecule and one at the other: thus additional coordination is possible at the latter, open end of the molecule. In $[(\text{Rh}_2(\text{mhp})_4)_2](\text{c})$ this occurs via two $[\text{Rh}_2(\text{mhp})_4]$ moieties each binding an oxygen atom of the other to form a central Rh-O-Rh-O ring and ^1H NMR studies are consistent with this structure being retained in solution.$

The 12.65-MHz ^{103}Rh NMR spectra of saturated solutions of $[\text{Rh}_2(\text{mhp})_4]$ and $[(\text{Rh}_2(\text{mhp})_4)_2]$ in $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ solution at ~ 300 K have been recorded on a Bruker WH-400 spectrometer, and the data are consistent with the molecular structures. Thus, the spectrum of the former compound consists of a single resonance at $\delta = 5745$ (reference used $\Xi(^{103}\text{Rh}) = 3.16$ MHz).¹⁸ The ^{103}Rh NMR spectrum of the

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latter compound (Figure 1) shows clearly that the rhodium atoms of this molecule are inequivalent; the resonances are manifested as a pair of doublets centered at $\delta = \text{ca. } 7644$ and 4322 ($14.3 \times 10^{22} \text{ cm}^{-3}$) splitting of each doublet is ca. 35 Hz.

The large differences between these ^{103}Rh resonance positions is quite remarkable and is a dramatic illustration of the sensitivity of this measurement to changes in the immediate environment of this nucleus. In this case, this environment consists of $\text{Rh}(\text{N}_2\text{O}_2\text{Rh})$ (in $[\text{Rh}_2(\text{mhp})_4]$) and $\text{Rh}(\text{N}_3\text{ORh})$ and $\text{Rh}(\text{NO}_3\text{Rh})$ (in $[(\text{Rh}_2(\text{mhp})_4)_2]$) and it is notable that the average of the chemical shifts of these last two nuclei (5984 ppm) is close to the chemical shift of the first (5745 ppm).

The splitting of the ^{103}Rh resonances of $[(\text{Rh}_2(\text{mhp})_4)_2]$ into doublets is attributed to $^1J(^{103}\text{Rh}, ^{103}\text{Rh})$ coupling, primarily as a result of a direct interaction via a metal-metal single bond. The value of $^1J(^{103}\text{Rh}, ^{103}\text{Rh})$ ($K_{XY}(2\pi/\hbar\gamma_X\gamma_Y)J_{XY}$)¹⁹ of 35 Hz ($29.4 \times 10^{22} \text{ cm}^{-3}$) is the largest so far observed directly. Lawson and Shapley²⁰ have reported $^1J(^{103}\text{Rh}, ^{103}\text{Rh})$ values of 4.2 Hz ($3.5 \times 10^{22} \text{ cm}^{-3}$) and 4.4 Hz ($3.7 \times 10^{22} \text{ cm}^{-3}$) for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3]$ and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{NO})_2]$, respectively, and Caddy et al.²¹ have indicated that $^1J(^{103}\text{Rh}, ^{103}\text{Rh})$ (K) is 17 Hz alone or for $[\text{Rh}_2(\text{C}_2\text{H}_5)(\text{C}_2\text{HMe}_2)(\eta^5\text{-C}_9\text{H}_7)_2]$. However, Mague and Sanger have claimed²² $^1J(^{103}\text{Rh}, ^{103}\text{Rh})$ (K) values of 128 (± 25) Hz ($107.6 (\pm 21.0) \times 10^{22} \text{ cm}^{-3}$) and 167 (± 15) Hz ($140.3 (\pm 12.6) \times 10^{22} \text{ cm}^{-3}$) from the ^{31}P NMR spectra of the "A-frame" complexes $[\text{Rh}_2(\text{CO})_3\text{Cl}(\text{dpm})_2]-[\text{BPh}_4]$ ($\text{dpm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) and $[\text{Rh}_2\text{Cl}_2(\text{SO}_2)(\text{dpm})_2]-[\text{BPh}_4]$, respectively. The magnitudes of these latter two coupling constants seem surprisingly large, in view of those observed directly, especially for $[(\text{Rh}_2(\text{mhp})_4)_2]$.

Previous discussions^{19,20,23} have suggested that the dominant contribution to a $^1K_{XY}$ value is the Fermi contact term, which is predicted to be fairly large and positive for an appreciable s-orbital involvement in the X-Y bond. This view, with respect to the $^1K_{\text{RhRh}}$ value for $[(\text{Rh}_2(\text{mhp})_4)_2]$, appears to be reasonably consistent with the current theoretical interpretations⁹⁻¹¹ of $\text{Rh}^{\text{II}}-\text{Rh}^{\text{II}}$ interactions. There is now general agreement that the 14 electrons of a Rh_2^{4+} center fill the σ , π , δ , δ^* , and π^* orbitals of the metal-metal framework; the latest calculations¹¹ favor the orbital sequence $\pi^4\delta^2\pi^4\delta^2\sigma^2$, for a $[\text{Rh}_2(\text{O}_2\text{CR})_4]$ complex alone or with axially coordinated H_2O molecules, with a 5s contribution to the Rh-Rh σ orbital of ca. 0.25.

The results of the study clearly demonstrate that ^{103}Rh NMR spectroscopy is potentially a very useful technique for the study of complexes based on the Rh_2^{4+} center, and further studies are in progress.

Acknowledgment. We thank the SERC and The Cancer Research Campaign for financial support.

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Synthesis and Characterization of a Technetium Phosphite Complex: Hexakis(trimethyl phosphite)technetium(I) Tetraphenylborate

Sir:

Binary zerovalent or low-valent transition-metal phosphite complexes are interesting because of their analogy to transition-metal carbonyls and their applications in catalysis. Well-characterized zerovalent complexes include $\text{M}[\text{P}(\text{OCH}_3)_3]_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$),¹⁻⁵ $\text{Re}_2[\text{P}(\text{OR}_3)_{10}]$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$),^{2,6,7} $\text{M}[\text{P}(\text{OR}_3)_5]$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}, \text{R} = \text{CH}_3$; $\text{M} = \text{Fe}, \text{R} = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{R}_3 = (\text{CH}_2)_3\text{CC}_2\text{H}_5$),⁸⁻¹³ $\text{M}_2[\text{P}(\text{OR}_3)_8]$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}, \text{R} = \text{aryl}$; $\text{M} = \text{Co}, \text{R} = \text{CH}_3, \text{C}_2\text{H}_5$),¹⁴⁻¹⁸ $\text{M}[\text{P}(\text{OR}_3)_4]$ ($\text{M} = \text{Co}, \text{Ni}, \text{Pd}, \text{Pt}, \text{R} = \text{CH}_3$; $\text{M} = \text{Co}, \text{R} = i\text{-C}_3\text{H}_7$; $\text{M} = \text{Ni}, \text{Pt}, \text{R} = \text{aryl}$; and numerous others where $\text{M} = \text{Ni}$),^{14,16,19-27} and $\text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_3$.²⁸ Among the low-valent complexes are $\text{Fe}[\text{P}(\text{OCH}_3)_3]_{5,6}^{2+}$,^{9,11} $\text{M}[\text{P}(\text{OR}_3)_5]^+$ ($\text{M} = \text{Co}, \text{Rh}, \text{R} = \text{CH}_3$; $\text{M} = \text{Co}, \text{R} = \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7, \text{R}_3 = (\text{CH}_2)_3\text{CC}_2\text{H}_5$),^{8,10,14,16,29-32} $\text{Co}[\text{P}(\text{OR}_3)_6]^{3+}$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7$),^{29,32} $\text{M}[\text{P}(\text{OR}_3)_5]^{2+}$ ($\text{M} = \text{Ni}, \text{Pd}, \text{R} = \text{CH}_3$; $\text{M} = \text{Ni}, \text{R}_3 = (\text{CH}_2)_3\text{CC}_2\text{H}_5$),^{8,10,31,32} and $\text{M}[\text{P}(\text{OR}_3)_4]^+$ ($\text{M} = \text{Cu}, \text{Ag}, \text{R} = \text{CH}_3, \text{C}_2\text{H}_5$; $\text{M} = \text{Ag}, \text{R}_3 = (\text{CH}_2)_3\text{CC}_2\text{H}_5, (\text{CH}_3)_3(\text{CH}_2)_3$),³¹⁻³⁴ and the unusual anions $\text{Co}[\text{P}(\text{OR}_3)_3]_4^-$ ($\text{R} =$

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Received December 9, 1983