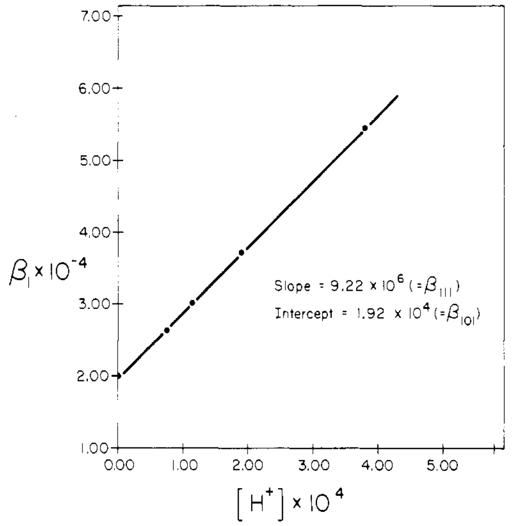

Figure 1. Variation of β_1 with $[H^+]$ for the Eu-malonate system at $\mu = 0.10$ M ($NaClO_4$) at 25.0 °C.

10^3 and $\beta_{111} = 3.0 \times 10^6$. Paramonova et al.[7] measured the complexation in 0.5 M $NaNO_3$ medium and calculated $\beta_{101} = 4.0 \times 10^3$ and $\beta_{111} = 3.3 \times 10^6$ while an earlier study from our laboratory[8] used potentiometry to obtain $\beta_{101} = 4.17 \times 10^4$ at $\mu = 0.10$ M ($NaClO_4$) and pH 3.5–3.7. No analysis was made for β_{111}. Powell et al.[9] measured β_{101} at pH >4.8 where formation of [EuHL] is negligible and reported a value of 2.03×10^4 in 0.1 M KNO_3. This would correspond to $\beta_{101} = 2.9 \times 10^4$ at $\mu = 0.10$ ($NaClO_4$). The agreement between these values (with allowance for differences in ionic strength, etc.) is not completely satisfactory and probably reflects differences (and difficulties) in calculational procedures for obtaining β_{101} and β_{111} from potentiometric techniques. The method we have described reduces that problem considerably.

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Registry No. Eu, 7440-53-1; malonic acid, 141-82-2.

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Correspondence

The Question of a Synergystic Metal-Metal Interaction Leading to π-Back-Bond Stabilization in Dirhodium Tetrabutyrate Adducts

Sir:

We have recently[1] claimed that the large radial projection in the d orbitals in rhodium(II) leading to a metal–metal interaction in Rh_2^{4+} systems gives rise to a π-antibonding orbital that projects toward the axial donors in such a way as to make π*-back-bonding system (see Figure 1). Apparently our position was not made clear because this conclusion was challenged[2] recently with a very distorted view of the basis for our conclusion about π stabilization. It is the purpose of this paper to rectify these problems and, in so doing, demonstrate the very strong case that can be made for π stabilization. The observations involved are (1) thermodynamic data, (2) redox potentials for 1:1 adducts, and (3) electronic transitions. It is stated[2] that (1) and (2) above "do not provide positive evidence for π bonding, and the correctness of Drago's conclusion depends critically on the spectral data and his interpretation thereof, namely, that the lowest energy, strong, electron transition in all the bis adducts is the $\pi^* \rightarrow \sigma^*$ transition...." Drago, Tanner, Richman, and Long[1] in no way wish to imply that they support such an indefensible position and regret that our publication could have been interpreted in this way. The argument for π-back-bond stabilization receives its strongest support from our thermodynamic analysis, and it was our intent to show[1] that the electonic absorption spectra and redox potentials show *general trends* that are consistent with this assessment. The least convincing and most difficult observation to interpret of those mentioned above is the electonic absorption spectrum. The problems involved in interpreting this data, even when the assigment is obvious, have been clearly stated.[3] We would never base a bonding argument primarily on an observation as complex as an electronic transition even for the 1:1 adducts where the assignment is clear. Thus, the fact that the 2:1 adducts may undergo a different electron transition is irrelevant to the essential conclusion.

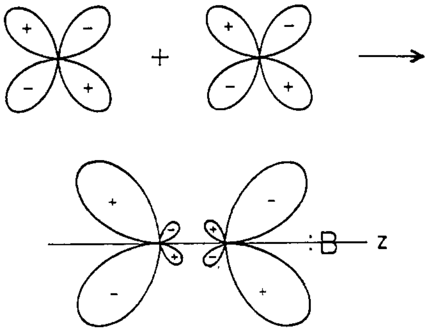

Figure 1. Metal-metal π interactions leading to π*.

The thermodynamic analysis provides by far the best data to utilize to infer relative coordinating tendencies and to understand how bonding considerations influence these tendencies. In terms of sensitivity and the direct bearing this data has on the bond strength contribution to chemical reactivity, no other information is as valuable. Confusion may have arisen in our report[1] as a result of our presentation of these data in terms of the *E* and *C* model. The *E* and *C* parameters are 3.21 and 1.32, respectively, for $Rh_2(But)_4$ (But = butyrate), and, for example, those for BF_3 are 9.9 and 1.6. This means that it is impossible to have a normal σ-donor interaction that will lead to stronger binding to $Rh_2(But)_4$ than to BF_3 since both *E* and *C* are greater for the latter. It is to be emphasized that the empirical nature of the *E* and *C* parameters means that all known thermodynamic data support this point. There

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(3) See, for example: Drago, R. S. "Physical Methods in Chemistry"; W. B. Saunders: Philadelphia, PA, 1977; p 105.

simply are no σ donors whose enthalpy of adduct formation is greater for $Rh_2(But)_4$ than BF_3. With this fact in mind, note the contrasting behavior whereby CO and PF_3 form adducts with $Rh_2(But)_4$ but interact weakly or not at all[4] with BF_3.

It should be emphasized that $Rh_2(But)_4$ is a weak acid, and when the claim is made that it is an effective π*-back-donating system, this is in terms of the percentage of the interaction that can be attributed to this effect. Since this[1] is the first time a quantitative assessment of the π and σ contributions have been made and reported, there should be no misinterpretation of our position on this point.

The second most significant observations on this system are the electrochemical results on the 1:1 adducts. In general, these measurements are complicated by ion pairing and solvation effects. In a structurally analogous series one might expect the differences in solvation and ion pairing to be slight. As a result of this uncertainty, the results of these experiments are not as definitive but provide support for our interpretation of the thermodynamic data.

The recent results[2] of the Xα calculations on $Rh_2(O_2CH)_4(PH_3)_2$ that show no π-bonding are surprising[7] to us and may suggest a reexamination of the approximations involved. Our EPR analysis[6] of the $Rh_2(O_2CCF_3)_4$·(nitroxide) showed measurable mixing of the rhodium π* orbitals with the nitroxide unpaired electron. Of course, the metal–ligand π*-back-bonding interaction will be *very* sensitive to the real or assumed orbital energy match, making this a difficult effect to predict. We have no data on PH_3 as a ligand, and thus there is no direct basis for comparing our experimental results on phosphites with the reported calculations on $Rh_2(O_2CH)_4(PH_3)_2$.

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Registry No. $Rh_2(But)_4$, 56281-34-6.

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Communications

Crossover Experiments and the Mechanism of Substitution of Metal-Metal-Bonded Carbonyls

Sir:

Although substitution reactions of the dinuclear metal carbonyls, $M_2(CO)_{10}$, M = Mn, Tc, Re and M_2 = MnRe, have been studied by several groups, whether the metal–metal bond ruptures during this process remains a controversial question. Wawersik and Basolo[1] favored a mechanism involving reversible formation of $Mn_2(CO)_9$ + CO by a dissociative pathway in substitution reactions of $Mn_2(CO)_{10}$. Extensive studies by Poë and co-workers[2-9] ultimately led them to propose[10] homolytic cleavage of the metal–metal bond as the first step in the substitution mechanisms for $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $MnRe(CO)_{10}$, and their derivatives. Sonnenberger and Atwood[11,12] recently examined the mechanism of substitution of manganese rhenium decacarbonyl and suggest CO dissociation as the rate-determining step. We now report the results of crossover experiments that show for the case of substitution processes of $Re_2(CO)_{10}$ at 130° C the metal–metal bond is not broken and that for $MnRe(CO)_{10}$ homolytic cleavage is, at best, a secondary pathway.

Table I. Rate Constants[a] for the Reaction of $Re_2(CO)_{10}$ with $P(C_6H_5)_3$ in Decalin at 130 °C

$[Re_2(CO)_{10}]$, M	$[P(C_6H_5)_3]$, M	10^6k_{osbd}, s^{-1}
2.55×10^{-3}	1.00×10^{-1}	11.6[b]
2.55×10^{-3}	1.00×10^{-1}	12.5[b]
1.63×10^{-3}	1.00×10^{-1}	11.3[c]
1.91×10^{-3}	1.97×10^{-2}	8.07[c]
3.40×10^{-4}	6.65×10^{-3}	7.00[c]
4.45×10^{-4}	4.84×10^{-3}	9.14[b]
4.45×10^{-4}	4.84×10^{-3}	10.3[b]

[a] Rate of disappearance of 2074-cm^{-1} peak of $Re_2(CO)_{10}$. [b] Under an N_2 atmosphere. [c] Under a CO atmosphere.

Reactions of $Re_2(CO)_{10}$ with a large excess of $P(C_6H_5)_3$ (Table I)[13] yield rate constants in good agreement with those reported by Haines and Poë.[3] In the presence of a large excess of ligand an atmosphere of CO does not appreciably suppress the rate of reaction; however, when the concentration of $P(C_6H_5)_3$ is lower, CO does lead to inhibition. This behavior

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(13) Purified, deoxygenated decalin was used as a solvent in all experiments. Kinetics measurements were performed at a constant temperature of 130 °C, and reaction flasks were foil wrapped to exclude light. Substitution reactions were maintained under pseudo-first-order conditions, with at least a tenfold excess of reagent. Rates of reaction were determined by observing changes in the C–O stretching region of the infrared spectrum to observe the disappearance of the decacarbonyl. During the reactions, especially with $Mn_2(CO)_{10}$, any oxygen in the system results in decomposition to metallic oxides. Oxygen was rigorously excluded with conventional syringe and Schlenkware techniques. The substitution of CO by $P(C_6H_5)_3$ in $Re_2(CO)_{10}$ was examined under a variety of conditions, and pseudo-first-order rate constants are listed in Table I. These reactions were followed by monitoring the decrease in absorbance of the 2074-cm^{-1} peak due to $Re_2(CO)_{10}$ over a period of at least 3 half-lives. Rate constants were reproducible to within 10% or better.

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