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 $Rh_2(O_2CCF_3)_4\cdot$(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	$10^6 k_{osbd}$, 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.

can be attributed to the low solubility of CO in hydrocarbon solvents (for example, 5.8×10^{-3} M in bicyclohexyl at 127 °C)[14] and the low nucleophilic strength of CO vs. $P(C_6H_5)_3$.[15]

Product distributions are sensitive to the added carbon monoxide. Under an atmosphere of N_2, both mono- and bissubstituted products form initially. The complex $Re_2(CO)_8[P(C_6H_5)_3]_2$, evident in the initial IR spectra, was the major species present upon completion of the reaction. Under an atmosphere of CO, only the monosubstituted complex forms initially and the bissubstituted complex slowly reaches an equilibrium concentration.

So that the presence of $Re(CO)_5$ radicals could be tested, $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ were added in equal amounts to rigorously dry and deoxygenated decalin and maintained at 130° C under an atmosphere of N_2.

$$Mn_2(CO)_{10} + Re_2(CO)_{10} \nrightarrow 2MnRe(CO)_{10} \qquad (1)$$

After 92 h (5.7 substitution half-lives of $Re_2(CO)_{10}$), there was no detectable IR absorption (at 2056 cm^{-1}) corresponding to $MnRe(CO)_{10}$. If the Re–Re and Mn–Mn bonds break at this temperature, the $MnRe(CO)_{10}$ absorption should appear. This contrasts with the photochemical cross-coupling reaction between $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, which produces bond homolysis and generates, $MnRe(CO)_{10}$ in high yield.[16] We cannot comment as to whether the Mn–Mn bond ruptures but assume it would cleave more readily than the Re–Re bond if conditions were severe enough to lead to Re–Re bond breaking. It seems well established that the order of metal–metal bond strengths is Mn–Mn << Mn–Re ≈ Re–Re.[17–21]

The mixed-metal dimer was examined to be sure that the lack of formation of $MnRe(CO)_{10}$ according to eq 1 was not due to an unfavorable equilibrium. Again, the rate of substitution[22] with $P(C_6H_5)_3$ at 130 °C yielded a k_{obsd} (of 6.4×10^{-5} s^{-1}) in excellent agreement with published results.[5,11] At no point during the reaction were homodimetallic species observed, in concord with Sonnenberger and Atwood's[11] report. So that contribution of bond homolysis could be studied, another crossover test was applied.

$$2MnRe(CO)_{10} \rightarrow Mn_2(CO)_{10} + Re_2(CO)_{10} \qquad (2)$$

A 2.6×10^{-3} M solution of $MnRe(CO)_{10}$ in decalin was kept at 130 °C under N_2. Absorptions for $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ appeared very slowly. Following the loss of $MnRe(CO)_{10}$ by monitoring the band at 2056 cm^{-1}, we measure an approximate first-order rate constant of 6.8×10^{-7} s^{-1}. These rate data might suggest a minor contribution due to metal–metal bond scission; however, reaction 2 can be completely quenched with added CO. After 146 h (48 half-lives of the substitution reaction), there was no loss of $MnRe(CO)_{10}$ when the CO pressure above the solution was maintained at 1 atm. We do not fully understand this result. It suggests that the slow process that yields products apparently attributable to metal–metal bond homolysis results from a minor pathway that requires CO loss at some point. If simple $Re(CO)_5$ and $Mn(CO)_5$ radicals were the only intermediates, then inhibition by CO would not be expected. In this context we examined reaction 1 at 140 °C in decalin solvent and did find slow conversion ($t_{1/2} \approx 97$ h) to the heterometal product. Once again, 1 atm of carbon monoxide completely inhibited the cross-coupling reaction.

These crossover experiments support initial dissociation of CO in substitution reactions of $MnRe(CO)_{10}$ and $Re_2(CO)_{10}$ at 130 °C and the absence of significant concentrations of metal radical intermediates. Further experiments will be necessary to solve the dilemma for $Mn_2(CO)_{10}$. Because of the weaker metal–metal bond in this species, we do not think it wise to extend our conclusions for $Re_2(CO)_{10}$ and $MnRe(CO)_{10}$ to $Mn_2(CO)_{10}$. It is also possible that metal–metal bond cleavage may become an important mechanistic pathway for reactions of $MnRe(CO)_{10}$ and $Re_2(CO)_{10}$ at temperatures above 140 °C.[9b]

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Demonstration of the Existence of Single Cubane-Type $MoFe_3S_4$ Clusters with $S = {}^3/_2$ Ground States: Preparation, Structure, and Properties

Sir:

In recent reports describing our development of the chemistry of cubane-type $MoFe_3S_4$ clusters[1–4] we have detailed one of our interests in these species, viz., as preliminary structural models of the Mo atom coordination site in FeMo proteins and the FeMo cofactor of nitrogenase. The most readily accessible clusters are those assembled from simple reactants in methanol reaction mixtures. These clusters are invariably isolated as bridged double-cubanes and include the types $[Mo_2Fe_6S_8(\mu\text{-}SR)_3(SR)_6]^{3-}$,[3,5,6] $[Mo_2Fe_6S_8(\mu\text{-}OMe)_3(SR)_6]^{3-}$,[3,6] and $[Mo_2Fe_7S_8(\mu\text{-}SR)_6(SR)_6]^{3-,4-}$.[7,8] Because of coordination saturation by tightly bound bridge ligands, these clusters offer little promise as effective species for testing the reactivity properties of molybdenum, in a Mo–Fe–sulfide environment, toward enzymatic and other potential substrates. However, a route to more promising clusters has recently been found. Treatment of $[Mo_2Fe_7S_8(SR)_{12}]^{3-}$ with certain 3,6-disubstituted catechols (3,6-R'_2catH_2; R′ = *n*-Pr, $CH_2CH{=}CH_2$)

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