

tivation energies for desorption must be small,<sup>11</sup> it is highly unlikely that any of the present reactions could be desorption controlled. Rate constants for transport-limited reduction ( $k_1$ ) can be calculated from  $k_1 = DR_0/\delta$ , where  $DR_0$  is the diffusion coefficient for the RoL ion and  $\delta$  is the diffusion layer thickness. Taking as reasonable values for the latter parameters,  $DR_0 \approx 7 \times 10^{-6}$  cm<sup>2</sup>/sec and  $\delta \approx 10^{-3}$  cm,<sup>1d</sup> we estimate  $k_1 \approx 7 \times 10^{-3}$  cm/sec, which is the same order of magnitude as that measured for the halogen-containing RoL ions, excepting the fluoro complex (Table I). Transport-limiting reduction is also suggested by the comparable reaction rates of other RoL ions; e.g., the  $\text{RoOH}_2^{3+}$  ion is only threefold less reactive toward  $\text{Cu}^0$ , despite being as much as  $10^8$ -fold less reactive toward cuprous ion in homogeneous solution (Table I). Transport of the  $\text{RoOH}_2^{3+}$  ion is probably also partially rate limiting; i.e., a significant diffusion layer develops during reaction. Similar arguments have been advanced in support of transport-limited reduction of  $\text{RoBr}^{2+}$  and  $\text{RoCl}^{2+}$  ions by silver metal.<sup>1d</sup>

With RoL ions containing alkenoic acid or aminoalkene ligands, measured rate constants are too low to be accounted for by variations in transport rates; cf.  $\text{RoO}_2\text{CCH}_3^{2+}$  and  $\text{RoO}_2\text{CCH}=\text{CH}_2^{2+}$ . Preferential adsorption to copper by  $\pi$  coordination to the olefin bond might account for the low reactivity as electron transfer does not occur by this pathway in cobalt(III)-copper(I) binuclear ions (Table I). From this perspective, the marked enhancement of reduction by copper metal over cuprous ion might be attributed to increased probabilities for electron transfer through the  $\pi$ -bridging system resulting from geometrical distortions of adsorbed RoL ions, to relaxation of spin restrictions<sup>10</sup> through spin-orbit interactions involving the copper lattice, or to the availability of other pathways. Facile reaction by "outer-sphere"-type pathways is evident from the relatively rapid reduction of the hexaamminecobalt(III) complex ion by copper metal.

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**Registry No.**  $\text{RoF}^{2+}$ , 15392-06-0;  $\text{RoCl}^{2+}$ , 14970-14-0;  $\text{RoBr}^{2+}$ , 14970-15-1;  $\text{RoI}^{2+}$ , 15392-08-2;  $\text{RoN}_3^{2+}$ , 14403-83-9;  $\text{RoOH}_2^{3+}$ , 14403-82-8;  $\text{RoO}_2\text{CCH}_3^{2+}$ , 16632-78-3;  $\text{RoO}_2\text{CCH}=\text{CH}_2^{2+}$ , 44982-34-5;  $\text{RoO}_2\text{CCH}=\text{CHCO}_2\text{H}^{2+}$  (trans), 17712-85-5;  $\text{RoO}_2\text{CCH}_2\text{CH}=\text{CH}_2^{2+}$ , 45017-98-9;  $\text{RoO}_2\text{C}(\text{CH}_2)_2\text{CH}=\text{CH}_2^{2+}$ , 45095-56-5;  $\text{RoNH}_2\text{CH}_2\text{CH}=\text{CH}_2^{3+}$ , 55012-62-9;  $\text{RoNH}_3^{3+}$ , 14695-95-5;  $\text{RoNH}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2^{3+}$ , 55012-63-0; Cu, 7440-50-8.

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## Dinuclear Rhenium Carbonyl Diketonate Complexes

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The preparation of a number of group 6 metal tetracarbonyl diketonate anions has been previously described.<sup>1</sup> The study of these materials is often complicated by the presence of the bulky cations. The isoelectronic group 7 metal complexes, being neutral, avoid this problem and could provide interesting comparisons with the anionic derivatives of the group 6 metals. The manganese complex  $\text{Mn}(\text{CO})_4(\text{hfacac})^2$  and several rhenium pentacarbonyl carboxylate complexes<sup>3</sup> had previously been prepared by methods similar to that used for the group 6 metal anionic derivatives. It therefore seemed likely that under these mild conditions, complexes of the type  $\text{Re}(\text{CO})_4(\text{diket})$  (where diket = a  $\beta$ -diketonate anion) could also be easily prepared. Barrick and coworkers<sup>4</sup> were able to prepare dimeric complexes of the type  $\text{Re}_2(\text{CO})_6(\text{diket})_2$ ; however rather forcing conditions were used. Nevertheless under identical conditions an analogous manganese compound yielded  $\text{Mn}(\text{CO})_4(\text{hfacac})$  indicating a distinct difference in behavior between the two metals.

## Results and Discussion

The reaction between various thallium diketonates and rhenium pentacarbonyl chloride in the usual solvents, chloroform and tetrahydrofuran, proved to be very sluggish. After refluxing for several days only partial conversion of the reactants had occurred and the resultant products were very difficult to separate from the starting materials. In order to facilitate the reaction, the higher boiling solvent 1,2-dimethoxyethane was chosen. Using this solvent, complete reaction was observed after refluxing for 72 hr as evidenced by the weight of  $\text{TlCl}$  formed. The products isolated from the reaction mixtures were not the expected  $\text{Re}(\text{CO})_4(\text{diket})$  complexes but rather complexes which analyzed for  $[\text{Re}(\text{CO})_3(\text{diket})]_2\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ . The dimethoxyethane appears to be strongly held since it could not be removed by warming to  $40^\circ$  under a reasonably good vacuum ( $<10^{-3}$  mm). The products are yellow to red crystalline solids (the color depending on the specific ligand) which are stable indefinitely at room temperature under a nitrogen atmosphere. Other solvents such as acetonitrile, dimethyl sulfoxide, and diglyme were tried but in each case decomposition seemed to take place and no identifiable products could be isolated.

Infrared and NMR data have proven helpful in establishing the geometry of the complexes, but the exact configuration of all the groups cannot be determined from the available data. A bridged structure similar to that determined for  $\text{Re}_2(\text{CO})_6(\text{dbzm})_2^4$  with dimethoxyethane solvent molecules held in the crystal lattice appears to be quite likely. Alternately a structure with dimethoxyethane bridging two octahedral  $\text{Re}(\text{CO})_3(\text{diket})$  groups also seems possible and satisfies the 18-electron rule as does the structure with bridged diketonate groups.

When prepared as Nujol mulls, all the  $[\text{Re}(\text{CO})_3(\text{diket})]_2(\text{dme})$  complexes give infrared spectra which consist of a relatively sharp, strong band at around  $2030\text{--}2040\text{ cm}^{-1}$  and a very intense broad band centered around  $1900\text{ cm}^{-1}$ . In  $\text{CH}_2\text{Cl}_2$  solution this broad band is often resolved (although poorly) to two bands of approximately equal intensity. (See Table I.) The position of the two lower frequency bands is very uncertain since the bands are still very broad and poorly resolved. Although these complexes deviate somewhat in local symmetry, their infrared patterns are reminiscent of M-

Table I. Analytical, Infrared, and NMR Data for Some Rhenium Carbonyl Diketonate Complexes<sup>a</sup>

|  | % calcd |      |      | % found |      |      | $\tau_{\text{CO}}$ , cm <sup>-1</sup><br>(in CH <sub>2</sub> Cl <sub>2</sub> ) | $\tau$ , ppm (in acetone- <i>d</i> <sub>6</sub> )  |
|--|---------|------|------|---------|------|------|--|--|
|  | C       | H    | P    | C       | H    | P    |  |  |
| [Re(CO) <sub>3</sub> (acac)] <sub>2</sub> (C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> )   | 28.98   | 2.92 |      | 28.77   | 2.80 |      | 2040, 1925, 1890   | acac: 8.04, 8.05; CH <sub>3</sub> : 4.42, CH<br>dme: 6.71, CH <sub>3</sub> ; 6.53, CH <sub>2</sub>               |
| [Re(CO) <sub>3</sub> (hfacac)] <sub>2</sub> (C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> ) | 22.99   | 1.16 |      | 22.28   | 1.35 |      | 2047, 1942, 1934   | hfacac: 3.53, CH<br>dme: 6.71, CH <sub>3</sub> ; 6.52, CH <sub>2</sub>   |
| [Re(CO) <sub>3</sub> (dpm)] <sub>2</sub> (C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> )    | 38.54   | 4.85 |      | 38.89   | 4.55 |      | 2041, 1908   | dpm: 8.86, CH <sub>3</sub> ; 4.09, CH<br>dme: 6.71, CH <sub>3</sub> ; 6.53, CH <sub>2</sub>                      |
| [Re(CO) <sub>3</sub> (dbzm)] <sub>2</sub> (C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> )   | 44.60   | 3.00 |      | 43.97   | 2.94 |      | 2033, 1920, 1885   | dbzm: 1.93, 2.50, C <sub>6</sub> H <sub>5</sub> ; 2.92, CH<br>dme: 6.73, CH <sub>3</sub> ; 6.55, CH <sub>2</sub> |
| [Re(CO) <sub>3</sub> (trop)] <sub>2</sub> (C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> )   | 33.03   | 2.31 |      | 32.55   | 2.24 |      | 2031, 1910, 1882   | trop: ~2.5, CH<br>dme: 6.72, CH <sub>3</sub> ; 6.54, CH <sub>2</sub>   |
| Re(CO) <sub>3</sub> (acac)[CH <sub>3</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ]  | 44.28   | 3.54 | 5.44 | 44.95   | 3.31 | 5.33 | 2041, 1933, 1885   | acac: 8.31, CH <sub>3</sub> ; 4.75, CH<br>Phosphine: 7.93, CH <sub>3</sub> ; 2.52, C <sub>6</sub> H <sub>5</sub> |

<sup>a</sup> Abbreviations: Hacac, 2,4-pentanedione; Hhfacac, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; Hdpm, 2,2,6,6 tetramethyl-3,5-heptanedione; Hdbzm, 1,3-diphenyl-1,3-propanedione; Htrop, tropolone; dme, 1,2-dimethoxyethane.

(CO)<sub>3</sub>L<sub>3</sub> complexes with a *cis* configuration and are not at all similar to the rarer *trans* derivatives.<sup>5</sup> Several Mn-(CO)<sub>3</sub>(hfacac)L complexes also have similar infrared spectra in the CO stretching region.<sup>2</sup> The positions of the C—C and C—O stretching bands of the acetylacetonate ligand (1580 and 1528 cm<sup>-1</sup>, respectively) are consistent only with the usual symmetrical coordination of the diketonate group through the two oxygen atoms.

The NMR spectra observed for these complexes are consistent with either bridged structure. The resonance signals for the protons on the diketonate ligands (Table I) have shifts typical of that observed for most carbonyl diketonate complexes. The protons on the 1,2-dimethoxyethane ligands have shifts very similar to the free molecule. The only unusual feature observed in the NMR spectra was seen in that of the acetylacetonate complex, where the methyl protons on the acetylacetonate ligand give rise to two closely spaced signals of nearly equal intensity while the  $\gamma$  proton is observed as a sharp singlet. Thus either one of the methyl groups on each of the two acetylacetonate ligands on the dinuclear complex is not equivalent to the other (as would be the case with the structure containing bridging diketonate groups) or both methyl groups on each ligand are equivalent but then the acetylacetonate ligands themselves are not. The latter possibility would require that the resonances for the  $\gamma$  protons would also have nearly the same chemical shifts which would not be too unexpected. Since the dimethoxyethane ligand is quite flexible and can exist in several conformations, either (or both) of the possibilities could exist in a structure containing a bridging dme ligand and cannot be distinguished with the present data.

When [Re(CO)<sub>3</sub>(acac)]<sub>2</sub>(dme) reacts with an excess of methylidiphenylphosphine, the dimethoxyethane ligand is displaced and the mononuclear complex Re(CO)<sub>3</sub>(acac)-[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>3</sub>] is formed. The reaction proceeds at room temperature and under these conditions no CO evolution takes place. Even with a large excess of phosphine ligand, no diphosphine complexes such as those formed from Mn(CO)<sub>4</sub>(hfacac)<sub>2</sub> were observed. Infrared and NMR data (Table I) suggest a *cis* structure for this complex also.

### Experimental Section

**Analyses.** Elemental analyses were carried out by the Analytical and Information Division of Exxon Research and Engineering Company. The results are given in Table I.

**Spectra.** Infrared spectra were obtained either on a Perkin-Elmer Model 521 infrared spectrometer or on a Beckman Model 20 infrared spectrometer. Spectra were obtained either as solutions in CH<sub>2</sub>Cl<sub>2</sub> or as Nujol mulls between KBr plates. NMR spectra were obtained on a Varian Model A-60 NMR spectrometer usually as solutions in CD<sub>3</sub>COCD<sub>3</sub>.

**Reagents.** The preparation of the thallium(I) diketonate complexes was carried out by allowing exactly equivalent amounts of thallium(I) ethoxide to react with the  $\beta$ -diketonates in benzene. Rhenium pen-

tacarbonyl chloride was obtained by the method of Abel and Wilkinson.<sup>6</sup> All other reagents were purchased from commercial sources.

**Preparation of Re(CO)<sub>3</sub>(diket)<sub>2</sub>(dme) Complexes.** A mixture of 3.61 g (0.01 mol) of Re(CO)<sub>5</sub>Cl, an exactly equivalent amount of the thallium(I) diketonate salt, and 30 ml of dimethoxyethane was refluxed under N<sub>2</sub> for 72 hr. The solutions were filtered through a fine glass frit and the filtrate was evaporated to dryness on a rotary evaporator. The residue was washed several times with cold pentane and then redissolved in dimethoxyethane. The solution was again filtered and the filtrate was added to 150 ml of pentane precipitating the yellow solid complex. This was collected on a filter then dried by heating under vacuum (0.001 mm) at 50° for several hours. Yields were approximately 75%.

**Preparation of Re(CO)<sub>3</sub>PCH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(acac).** Two grams each of [Re(CO)<sub>3</sub>(acac)]<sub>2</sub>(dme) and CH<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> were added to a flask containing 30 ml of acetone and were allowed to stand overnight in a N<sub>2</sub>-filled drybox. The solution evaporated to a heavy oil during this period and the oil was washed several times with pentane. The residue was redissolved in acetone, the resulting solution was filtered, and the filtrate was added to 100 ml of pentane precipitating a yellow solid. This was collected on a filter and dried. The yield was 80%.

**Registry No.** [Re(CO)<sub>3</sub>(acac)]<sub>2</sub>(C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>), 55222-36-1; [Re(CO)<sub>3</sub>(hfacac)]<sub>2</sub>(C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>), 55222-35-0; [Re(CO)<sub>3</sub>(dpm)]<sub>2</sub>(C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>), 55222-38-3; [Re(CO)<sub>3</sub>(dbzm)]<sub>2</sub>(C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>), 55222-39-4; [Re(CO)<sub>3</sub>(trop)]<sub>2</sub>(C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>), 55222-37-2; Re(CO)<sub>3</sub>(acac)-[(CH<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>), 55124-59-9; Re(CO)<sub>5</sub>Cl, 14099-01-5; 1,2-dimethoxyethane, 110-71-4.

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### Metal Isotope Shifts and Normal-Coordinate Analysis of the [<sup>58</sup>Ni(<sup>92</sup>MoS<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> Ion and Its <sup>62</sup>Ni and <sup>100</sup>Mo Analogs

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Recently, we reported the preparation of novel coordination  
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