

of **6** and **7** are very similar (Table I). The chemical shifts of **6** and **7** are a result of two transverse factors: an upfield shift due to shielding of the negative charges and a downfield shift due to the formation of a diamagnetic ring current in the expected aromatic dianion. The expected average upfield shift due to π -electron shielding is 1.4 ppm.⁹ However, the transformation of neutral hydrocarbons into the dianionic species **6** and **7** does not displace the center of gravity of the chemical shifts despite the negative charges. Noteworthy are the signals of the fused benzene protons which appear at lower field relative to the neutral hydrocarbon **3**. These results clearly indicate the formation of a diamagnetic ring current in the aromatic dianions **6** and **7**, and they may be considered as perturbed peripheral [16]annulene dianions. Quenching of **7** with D₂O yielded **5b**: deuteration at positions 1 and 9, the most deshielded positions as emphasized by the ¹H NMR.

From all of the above, it may be concluded that 1,9-dimethylidibenzo[*b,f*]pentalene (**3**) can either be oxidized or reduced to the respective dicationic and dianionic species. The dication **4** and dianions **6** and **7** are delocalized diatropic aromatic systems. From the ¹H NMR shifts of the benzene rings fused to the pentalene moiety, we deduce that these charged species behave like peripheral [16]annulene dication and dianion, respectively. To our knowledge, this is the first example of a fused $4n\pi$ polycyclic system including a pentalene nucleus, to show aromatic character as both dication and dianion. We are extending our investigations by examining the possibility of generating the charged species, prepared chemically in the present work, by electrochemical methods.

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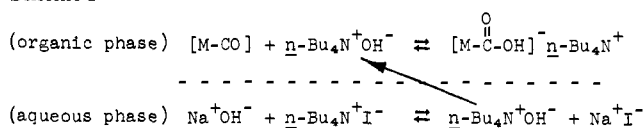
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Phase-Transfer Catalyzed Oxygen-18 Labeling Studies of Carbonyl Ligands in Neutral Metal Carbonyl Derivatives

Sir:

Recently we have reported on the incorporation of oxygen-18 into cationic metal carbonyl derivatives of manganese and rhenium.¹⁻⁴ This process was proposed to proceed via neutral

Scheme I



metal carbonyl intermediates containing the hydroxycarbonyl ligand, i.e., $L_n(\text{CO})_{5-n}\text{M}(\text{COOH})$ ($n = 0-2$) species. Furthermore, it was shown that in substituted metal carbonyl derivatives, where there are two electronically different CO groups, the oxygen atoms on the more electron-poor carbonyl ligands (i.e., carbonyl groups with the larger CO stretching force constant⁵) were exchanged at a faster rate. Thus, it was possible to afford stereospecifically labeled metal carbonyl derivatives employing the H₂¹⁸O exchange reaction. In addition the corollary observation that the relative rates of oxygen exchange decrease with increasing substitution at the metal center with electron donating ligands was noted, $\text{M}(\text{CO})_6^+ > \text{M}(\text{CO})_5\text{L}^+ \gg \text{M}(\text{CO})_4\text{L}_2^+$. The $L_n(\text{CO})_{5-n}\text{M}(\text{COOH})$ intermediates were also found to undergo CO₂ elimination with metal hydride formation, a process common to the energy-important metal-catalyzed water-gas shift reaction.⁶⁻⁸

To understand these processes more fully we have begun studies to investigate the conditions for oxygen exchange in neutral metal carbonyl derivatives. In this communication we wish to report on phase-transfer catalyzed oxygen-18 labeling studies of the carbon monoxide ligands bound to neutral group 6b and iron metals.

Although the cationic hexacarbonyl derivatives of the group 7b metals readily undergo oxygen-exchange reactions with H₂¹⁸O, the neutral isoelectronic group 6b analogues were found to be totally inert under similar reaction conditions.^{2,9} On the other hand, we have shown that the rate of oxygen exchange between metal bound CO and H₂O is greatly accelerated in the electron-rich $[\text{Mn}(\text{CO})_4(\text{diphos})]^+$ derivative if trace quantities of triethylamine are added to the reaction solution.³ Therefore, it should be possible to enhance the rate of reaction of the less electrophilic carbonyl groups in the group 6b metal derivatives by raising the pH of the solution. This was accomplished using a biphasic reaction system with the organic phase consisting of the neutral carbonyl derivative in benzene and an aqueous phase consisting of sodium hydroxide with a small quantity of tetra-*n*-butylammonium iodide as the phase-transfer catalyst (Scheme I). The complexes we have initially examined include $\text{M}(\text{CO})_5\text{L}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$, and $\text{L} = \text{CO}, \text{PPh}_3$, and $\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$; and $\text{M} = \text{Cr}$ and $\text{L} = n\text{-Bu}_3\text{P}$) and $\text{Fe}(\text{CO})_4\text{PPh}_3$ derivatives.

In a typical experiment, a 0.05-mL sample of 11.3 M Na¹⁸OH solution (prepared by equilibrating 0.090 g (2.24 mmol) of NaOH in 0.20 mL of 99% enriched H₂¹⁸O) was added to a mixture of 0.0420 g (0.119 mmol) of $\text{W}(\text{CO})_6$ and 0.010 g (0.027 mmol) of *n*-Bu₄NI dissolved in 5.0 mL of dry benzene under a nitrogen atmosphere. The resulting two-phase system was heated at 75 °C with vigorous stirring. Samples (0.50 mL) were withdrawn at various time intervals and the solvent mixture removed in vacuo. The samples were redissolved in 0.60 mL of hexane and their ν_{CO} infrared spectra were recorded in 1.0-mm NaCl sealed solution cells.

Figure 1 illustrates representative ν_{CO} spectral traces obtained during the course of oxygen-18 incorporation into a group 6b metal carbonyl derivative, $\text{W}(\text{CO})_6$. It was possible to assign all the observed bands in all the complexes studied to the various C¹⁸O substituted species by noting the rates of appearance and decay of bands concomitantly aided by calculations involving a restricted CO force field.¹⁰

We have been able to discern from a detailed analysis of these ν_{CO} spectral results in the $\text{M}(\text{CO})_5\text{L}$ species studied, where L is a poorer electron-withdrawing ligand than CO, that

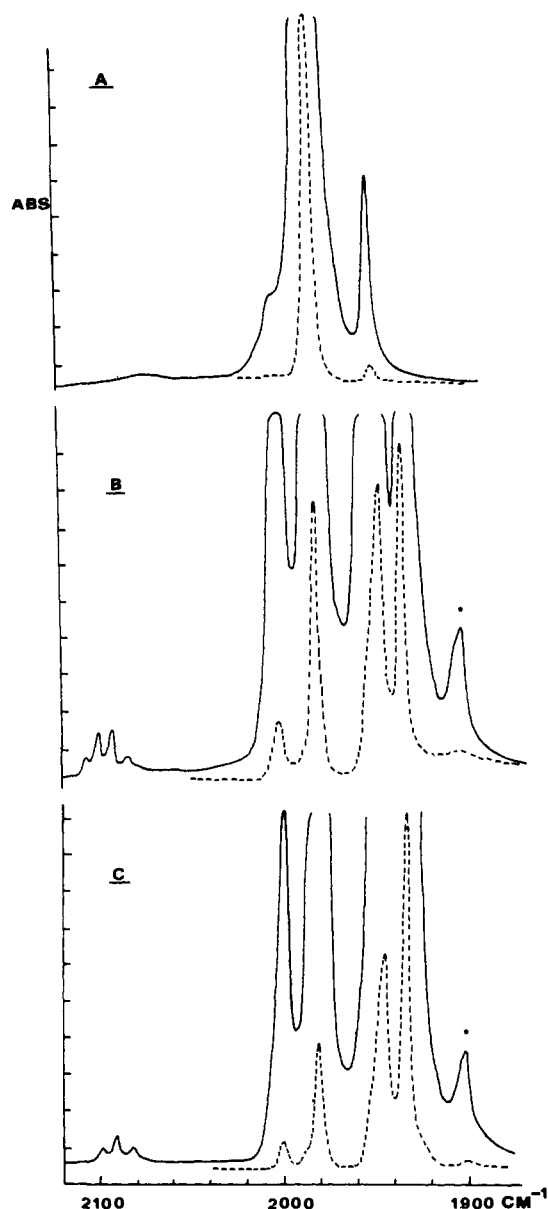


Figure 1. Time-dependent ν_{CO} spectra in hexane solution for the oxygen-exchange reaction of $\text{W}(\text{CO})_6$ with hydroxide ion: A, initial spectrum; B, 1 h; C, 3 h. The peak marked with an asterisk is assigned to the natural abundance mixed labeled $^{13}\text{C} \text{ } ^{18}\text{O}$ species.

the equatorial carbonyl oxygen atoms undergo exchange with oxygen atoms in OH^- at a much faster rate than the axial carbonyl oxygen atom.¹¹ Moreover, as electron-donating ligands were added to the metal center the rate of oxygen exchange was retarded; e.g., the order of exchange (after proper consideration was given to statistical factors) was $\text{Cr}(\text{CO})_6 > \text{Cr}(\text{CO})_5\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5 > \text{Cr}(\text{CO})_5\text{PPh}_3 > \text{Cr}(\text{CO})_5\text{P}(n\text{-C}_4\text{H}_9)_3 \gg \text{Cr}(\text{CO})_4(\text{diphos})$.¹² It should be pointed out that, although reaction rates in these biphasic systems are influenced in part by the same chemical factors normally encountered in homogeneous media (modified by ion-association and ion-solvation interactions), they are also affected by the heterogeneity of the system and the distribution of the ions between the two phases.¹³ We have assumed in our discussion of relative rates that these various physical factors remain constant in the reactions investigated with differences in rate being determined principally by the chemical factors involved in the oxygen-exchange process.¹⁴

The reaction of $\text{Cr}(\text{CO})_6$ with OH^- to afford the dinuclear bridging hydride species, $\mu\text{-H}[\text{Cr}(\text{CO})_5]_2^-$, has been known for sometime.¹⁵ We have found under the reaction conditions

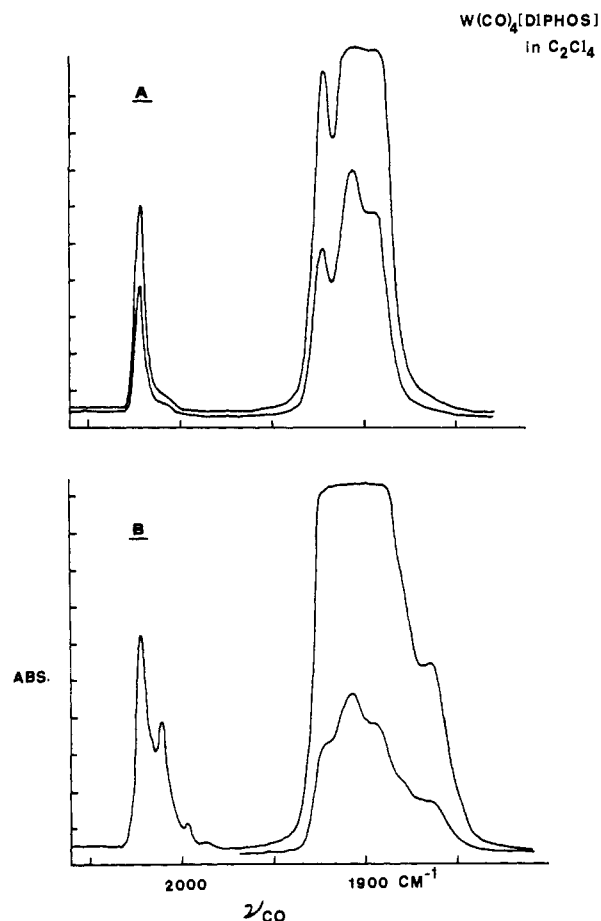
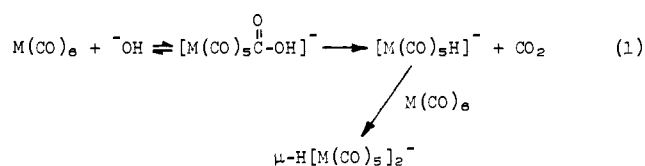


Figure 2. ν_{CO} spectra of $\text{W}(\text{CO})_4(\text{diphos})$ in C_2Cl_4 : A, $\text{W}(\text{CO})_4(\text{diphos})$ prepared in normal water; B, $\text{W}(\text{CO})_4(\text{diphos})$ prepared in ^{18}O -enriched water.

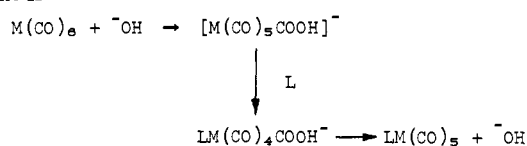
of our oxygen-exchange reactions that $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ derivatives are indeed formed, albeit rather slowly and in poor yields. However, oxygen-exchange occurs much more rapidly than does CO_2 elimination from the $[\text{M}(\text{CO})_5\text{COOH}]^-$ intermediate (eq 1).¹⁶ On the other hand, we have not isolated



substituted bridging hydrides, resulting from CO_2 elimination, in reactions of the substituted group 6b metal carbonyl derivatives with hydroxide ion.^{17,18} The lack of a *significant* secondary reaction involving CO_2 elimination coupled with metal hydride formation in the group 6b metal derivatives is therefore consistent with our previous studies with the group 7b metal carbonyls. In those cases it was demonstrated that this secondary reaction was retarded as the metal becomes more electron rich by the addition of donor ligands.

In a closely related study Hui and Shaw¹⁹ have proposed the intermediacy of the anionic hydroxycarbonyl species, $[\text{M}(\text{CO})_5\text{COOH}]^-$, in substitution reactions of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) with phosphines. Although at least some portion of these substitution reactions undoubtedly proceeds via the $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ species,¹⁸ these researchers¹⁹ have involved the hydroxycarbonyl ligand as a labilizing group. That is, Scheme II was suggested. As our results have indicated, the first step in this process is reversible; therefore this procedure, whether proceeding through the $\mu\text{-H}[\text{M}(\text{CO})_5]_2^-$ or $\text{LM}(\text{CO})_4\text{COOH}^-$ intermediates, should afford oxygen-la-

Scheme II



beled species when carried out in the presence of isotopically enriched hydroxide ion. Figure 2 illustrates the ν_{CO} infrared spectra obtained employing the Hui and Shaw¹⁹ preparation in $^{18}\text{OH}^-$ when L = diphos (1,2-bis(diphenylphosphino)ethane). These spectra indicate the oxygen label to be equally distributed between the axial and equatorial carbonyl positions. The oxygen label was indeed confirmed to be statistically distributed in the $\text{W}(\text{CO})_4(\text{diphos})$ derivative by the ^{17}O NMR spectrum of a sample prepared in the presence of H_2^{17}O .²⁰

In conclusion, since the oxygen-exchange reaction of the group 6b metal hexacarbonyls is so facile, to prepare specifically labeled derivatives of substituted metal carbonyls, it is necessary to carry out the enrichment on the substituted metal carbonyl species themselves.

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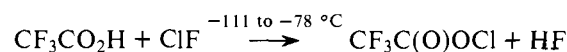
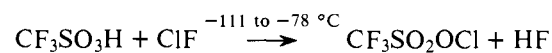
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Chlorine(I) Derivatives of Trifluoromethanesulfonic Acid and Trifluoroacetic Acid

Sir:

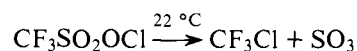
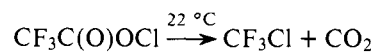
Halogen (Cl, Br, I) derivatives of strong oxy acids are exceedingly powerful electrophilic halogen sources. Their

properties and utility as synthetic reagents are exemplified by the halogen fluorosulfates $\text{XOSO}_2\text{F}^{1-4}$ and pentafluororhotoselenates XOSeF_5 .^{4,5} The chlorine(I) and bromine(I) derivatives are the most useful for synthesis. Two strong acids, whose halogen derivatives ($\text{X} = \text{Cl}, \text{Br}$) have not been previously reported, are $\text{CF}_3\text{SO}_3\text{H}$ ⁶ and $\text{CF}_3\text{CO}_2\text{H}$.^{7,8} Derivatives of both acids are of course well known and large in number.⁹⁻¹⁰ However, the lack of a suitable strong oxidizing agent containing these groups limits the scope of their chemistry. We have prepared both $\text{CF}_3\text{SO}_2\text{OCl}$ and $\text{CF}_3\text{C}(\text{O})\text{OCl}$ by the low temperature reaction of the acids with chlorine monofluoride.



The reactions are carried out in Kel-F reactors by condensing the ClF onto the acid at -196°C and warming slowly from -111 to -78°C , followed by several hours at -78°C . On a 10-mmol scale the reactions are quantitative yielding a pale yellow liquid and a colorless layer of HF. The HF is removed from $\text{CF}_3\text{SO}_2\text{OCl}$ by pumping at -78°C . For $\text{CF}_3\text{C}(\text{O})\text{OCl}$, the mixture is transferred onto NaF at -196°C through a short connection as the reactor warms slowly from -78°C . Pure $\text{CF}_3\text{C}(\text{O})\text{OCl}$ is then collected at -111°C by pumping through traps at -60 , -111 and -196°C as the NaF container warms slowly from -78°C .

Both compounds are somewhat unstable at 22°C and $\text{CF}_3\text{C}(\text{O})\text{OCl}$ will explode if the pressure of the gas exceeds ~ 50 Torr.



The compounds have been characterized by their reaction stoichiometry, by quantitative decomposition, and by their NMR and Raman spectra. Their ^{19}F NMR shows a singlet at δ 73.52 ($\text{CF}_3\text{SO}_2\text{OCl}$) and 70.94 ($\text{CF}_3\text{C}(\text{O})\text{OCl}$) relative to CFCl_3 as an external and internal standard, respectively. The identification of $\nu(\text{OCl})$ is easily made by comparing the liquid Raman spectra of the acid and chlorine derivative under identical conditions. It is an intense polarized band at 688 ($\text{CF}_3\text{SO}_2\text{OCl}$) and 716 cm^{-1} ($\text{CF}_3\text{C}(\text{O})\text{OCl}$). The complete spectra are consistent with that of other covalent compounds containing these groups.

In spite of their instability, these new chlorine derivatives can be readily prepared and used as reagents. The main difficulty in carrying out reactions of the compounds is to estimate the amount of hypochlorite. For $\text{CF}_3\text{SO}_2\text{OCl}$, reactions are normally carried out in the same vessel used for preparation, assuming quantitative formation from the acid. Alternatively, the compound can be vacuum transferred from a vessel at -40 to one at -196°C via a short connection. In the case of $\text{CF}_3\text{C}(\text{O})\text{OCl}$, the total, combined $\text{CO}_2/\text{CF}_3\text{Cl}$ pressure from purification and manipulation can be used to estimate the amount of the hypochlorite. The compound can be readily vacuum transferred from a vessel at -60 to one at -196°C via a short path. After transfer, the $\text{CF}_3\text{CO}_2\text{Cl}$ can be warmed to -111°C and the CO_2 and CF_3Cl removed and measured. Clearly, both compounds must be stored at low temperature ($\leq -78^\circ \text{C}$) and all reactions and manipulations conducted with proper shielding.

We are currently investigating their chemistry and find they add readily to unsaturated organic and inorganic substrates. In addition, $\text{CF}_3\text{SO}_2\text{OCl}$ is so powerful a Cl^+ source that it readily undergoes reaction with covalent chlorides to form Cl_2