Stereospecific Incorporation of Oxygen-18 into Manganese and Rhenium Pentacarbonyl Derivatives via Exchange Reactions with $H_2{}^{18}O$

Sir:

Recently we have reported the preparation of a series of monosubstituted complexes of the type $LM(CO)_5{}^+$, where L = phosphine, phosphite, acetonitrile, and pyridine, and M = Mn or Re.[1,2] This synthetic capability has allowed us to carry out a variety of rather interesting spectral and reactivity investigations on these substituted group 7B pentacarbonyl cationic species. In earlier studies on the parent hexacarbonyl cation of rhenium, Muetterties[3] has observed that this species exchanges oxygen with oxygen atoms in water, presumably through nucleophilic attack of ^-OH on the carbonyl carbon atom to give the intermediate $Re(CO)_5COOH$. There is indeed much precedent now for the carbonyl carbon atom in these cationic carbonyls to be susceptible to attack by sufficiently strong nucleophiles. For example, we have shown that these cationic carbonyl derivatives rapidly react with RLi, RMgX, and amines to yield *cis*-$RC(O)Mn(CO)_4L$ and *cis*-$R'_2NC(O)Mn(CO)_4L$ derivatives, respectively.[1,2,4]

There is much current interest in stereospecifically labeling metal carbonyl derivatives employing thermal or photochemical carbonyl ligand replacement reactions with isotopically enriched carbonyl ligands, ^{13}CO or $C^{18}O$.[5-16] In addition, studies of the electronic factors responsible for controlling the specific site of nucleophilic attack in metal carbonyl derivatives are particularly important since these processes lead to the preparation of new organometallic complexes and in the generation of reaction intermediates useful in organic synthesis.[17,18] We have therefore undertaken oxygen-18 enrichment studies on manganese and rhenium pentacarbonyl cationic complexes via reaction with $H_2{}^{18}O$ where the possibility of stereospecific labeling may exist.

Our initial investigations were carried out using samples of $M(CO)_5L^+$ (where M = Mn, Re and L = PMe_2Ph, CH_3CN, C_5H_5N) dissolved in dried CH_3CN which contained small quantities of added 95% $H_2{}^{18}O$.[19] The following procedure employed for incorporation of oxygen-18 into the $Me_2PhPMn(CO)_5{}^+$ derivative is representative. $[Me_2PhPMn(CO)_5][PF_6]$ (0.040 g, 0.084 mmol) was dissolved in 1.0 ml of acetonitrile containing 0.10 ml of $H_2{}^{18}O$ (5.0 mmol). The reaction was quenched periodically by withdrawing small amounts of solution followed by removal of the solvent-mixture under reduced pressure. Samples were then redissolved in dried CH_3CN, and the enrichment progress was monitored by ir spectroscopy in the ν(CO) region. Figure 1 illustrates the ν(CO) spectra obtained at various reaction time intervals for the incorporation of oxygen-18 into $Me_2PhPMn(CO)_5{}^+$. The high frequency portion of the spectra exhibits six ν(CO) absorptions separated by 7–14 cm^{-1}. These correspond to the all $C^{16}O$ species (a), the five equatorially $C^{18}O$ substituted species (b, c, d, and e),[20] and the all $C^{18}O$ species (f). These species are depicted in Figure 2. It was possible to assign all the observed bands to the species as listed by noting the rates of appearance and decay of bands concomitantly aided by calculations involving a restricted CO force field.[21,22]

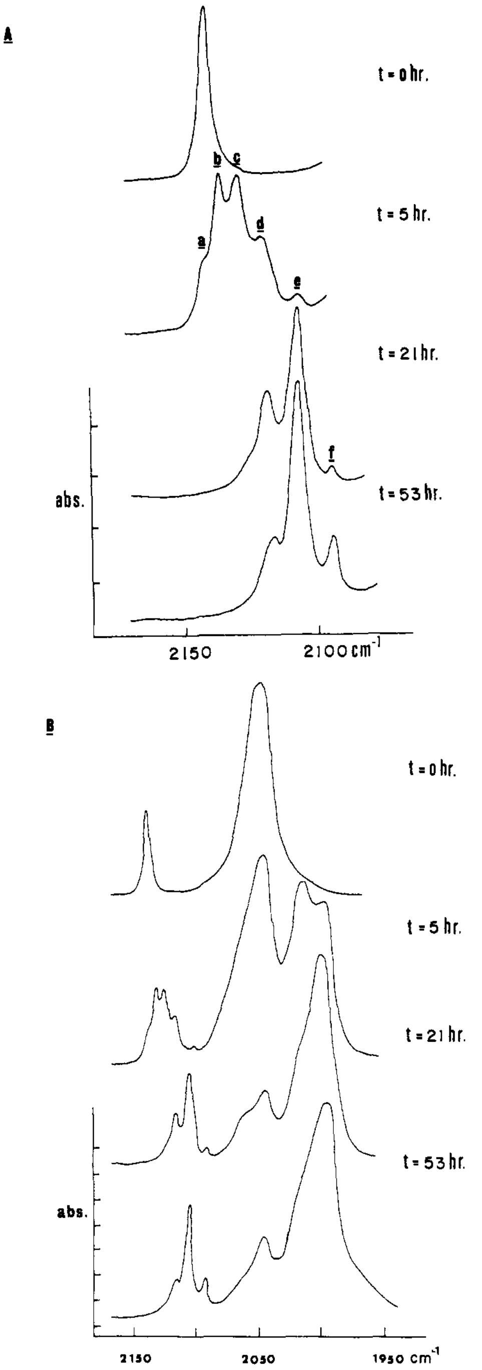

Figure 1. Infrared spectra in the ν(CO) region in acetonitrile of $Me_2PhPMn(CO)_5{}^+$ at various stages of oxygen-18 enrichment: (A) high frequency region only, (B) entire ν (CO) region.

This analysis unequivocally illustrates that oxygen exchange in the equatorial carbonyl ligands is occurring in a stepwise manner and at a rate much faster than four times (which accounts for the statistical factor) the oxygen exchange at an axial CO ligand. It is not until most of the $Me_2PhPMn(CO)_5{}^+$ species exist as the equatorial tetrasubstituted $C^{18}O$ species (band e) does the all $C^{18}O$ species begin to appear, as indicated by band f. This necessitates concluding that *there is an enhanced equatorial carbonyl oxygen labilization over that of an axial carbonyl oxygen.* A similar conclusion can be drawn from the lack of shifting to lower frequency of the vibration around 2064 cm^{-1} which corresponds primarily to an axial $C^{16}O$ motion in the various species in Figure 2 (a, b, c, and d). Results on the rhenium analogue, $Me_2PhPRe(CO)_5{}^+$, were identical with those described above for manganese except that oxygen exchange occurs more rapidly in the manganese derivative. For the derivatives, $(CH_3CN)M(CO)_5{}^+$ (M = Mn, Re) and $(C_5H_5N)Mn(CO)_5{}^+$, the enrichment reactions were only carried out until about 50% of all molecules existed as the mono-substituted $C^{18}O$ species as indicated by ir. In these derivatives the band due to the species containing one $C^{18}O$ grouping in an axial position is calculated to appear out of the region of the equatorial mono-substituted $C^{18}O$

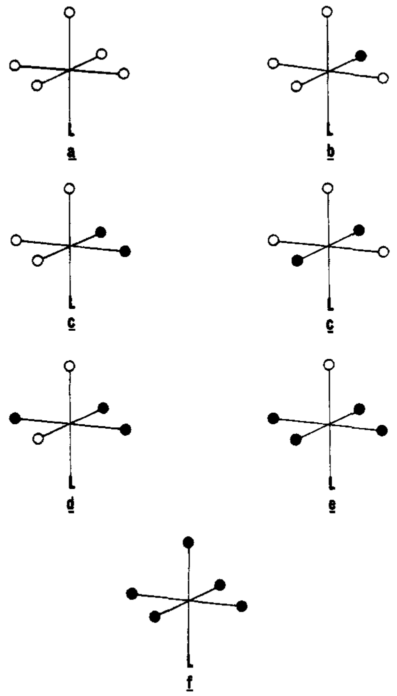

Figure 2. Illustration of the observed arrangements of $C^{18}O$ groups (represented as closed circles) in $M(CO)_5L^+$ derivatives.

species.[23] Therefore if oxygen-18 substitution did occur at the axial carbonyl ligand in these derivatives it would indeed be directly observable in the ir. For these highly enriched mono-substituted oxygen-18 derivatives, however, only bands due to the parent all $C^{16}O$ (a) species and the equatorial mono-substituted $C^{18}O$ species (b) were observed, indicating that oxygen exchange in these derivatives is as well occurring preferentially at an equatorial CO site or cis to the substituted ligand (L).

Therefore, these experimental findings demonstrate a cis oxygen labilization in $M(CO)_5L^+$ species with the manganese derivatives undergoing oxygen exchange more readily than their rhenium analogues.[24] It is important to note that since there is no carbonyl-metal bond cleavage occurring in these reactions it is not necessary to consider possible rearrangements in the intermediates as is necessary when unsaturated metal species are produced. The slow rates of these reactions as compared with other nucleophilic reactions which we have studied, e.g., reactions of $M(CO)_5L^+$ species with RMgX and amines are instantaneous, are suggestive of hydroxyl attack at carbonyl since OH^- is present at such low concentration. These slow rates will allow us to carry out a detailed kinetic study of these reactions employing conventional techniques. The ability to stereospecifically label $M(CO)_5L^+$ derivatives is an essential step in assessing the fluxional (or lack of fluxional) behavior of the intermediates produced in reactions involving thermal dissociation of CO or L.[25,26] The latter studies are in progress in our laboratories.

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(19) Obtained from Monsanto Research Corporation, Mound Laboratory, Miamisburg, Ohio 45342.
(20) In the case of the two equatorially substituted CO groups, approximately the same high frequency $\nu(CO)$ band is calculated (within 2 cm^{-1}) regardless of cis or trans geometry.
(21) The force constants computed for the $Me_2PhPMn(CO)_5^+$ derivatives were $k_1 = 17.43$, $k_2 = 17.44$, $k_c = 0.22_2$, $k_c' = 0.24_6$, and $k_t = 0.45_2$. Fourteen bands were calculated within ±1.3 cm^{-1}. Although there is still some discussion concerning the use of force constants obtained by the method of restricted $\nu(CO)$ force fields, there is widespread agreement that ^{13}CO or $C^{18}O$ frequencies calculated by these procedures are correct.[22]
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(23) This is a result of the fact that the low frequency A_1 vibration in these derivatives occurs at much lower frequency than the E mode in the $M(C^{16}O)_5L^+$ species. By contrast, in the phosphine substituted derivatives the low frequency A_1 and E modes are grossly overlapped.
(24) We have made qualitative measurements of the rates of incorporation of oxygen-18 in $M(CO)_6^+$ vs. $M(CO)_5(phosphine)^+$. The exchange was found to occur much more rapidly in the hexacarbonyl cations. This would be expected from force constant arguments.[17,18] Therefore, cis labilization is not meant to imply that L is labilizing with respect to CO in the oxygen exchange process.[12]
(25) We have observed some CO scrambling in the labeled mono-$C^{18}O$ equatorial $Mn(CO)_5(CH_3CN)^+$ species when it is allowed to stand in acetonitrile for long periods of time. This is presumably resulting from acetonitrile dissociation and scrambling occurring in the unsaturated $[Mn(CO)_5^+]$ species.
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A Long Range Deuterium Isotope Effect on a Lanthanide Induced Chemical Shift

Sir:

Electrophilic ring opening of *cis*-1,2,3-trimethylcyclopropane (I) proceeds with a mixture of retention and inversion by the electrophile (D^+) and nearly complete inversion by the nucleophile.[1] When the solvent is methanol a mixture of two diasteriomeric methyl ethers is formed (eq 1), erythro (IIE) and threo (IIT) which differ only in the relative positions of their hydrogen and deuterium atoms. We wish to report that a mixture of these two diasteriomers gives rise to two different methoxyl signals when their NMR spectra are recorded in the presence of the lanthanide shift reagent $Eu(fod)_3$.

Similarly the trans isomer III on ring opening gives rise to a mixture of four isomers (eq. 2). IIE and IIT come from deuteron attack on the carbon bearing the trans methyl group (33% of the ether product) and IVE and IVT (66%) arise from attack on the carbons bearing the cis methyls. In the presence of $Eu(fod)_3$ all four methyl ether peaks are clearly distinguished (Figure 1) and can be identified by