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Isotope Effects in the Infrared Spectra of the Metal Carbonyl Hydride/Deuteride Anions $(H/D)M(CO)_4^-$ (M = Fe, Ru, or Os)

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Received September 14, 1981

The structures and reactivities of transition-metal carbonyl hydrides have been the subject of considerable recent interest,[1] in part owing to the potential roles of such species in various catalysis schemes.[2] In the course of investigating the acid/base properties[3] and possible catalysis roles of several metal carbonyl hydrides, we have prepared the deuteride complexes $DM(CO)_4^-$ of the iron triad (M = Fe, Ru, or Os) as the PPN^+ salts (PPN^+ = bis(triphenylphosphine)iminium). Comparison of the infrared spectra of these species to the spectra of the hydride analogues $[PPN][HM(CO)_4]$ demonstrates considerable isotope effects in the region corresponding to the carbonyl stretching frequencies (ν_{CO}), indicating significant resonance interaction between the metal–hydrogen and carbon oxygen stretching vibrations. Although similar effects have been noted previously in certain other metal carbonyl hydride complexes,[4] the present observations add emphasis to the necessity of considering such resonance interactions in force field calculations based on the vibrational spectra.[5]

Experimental Section

The salts $[PPN][HFe(CO)_4]$, $[PPN][HRu(CO)_4]$, and $[PPN][HOs(CO)_4]$ were prepared by the previously described procedures.[5b,6] The deuterio complex $[PPN][DFe(CO)_4]$ was prepared by the method described for its protio analogue[5] with the exception that NaOD, D_2O, and CH_3OD were used as reactants and solvents in place of the protio species. The deuterio complexes $[PPN][DRu(CO)_4]$ and $[PPN][DOs(CO)_4]$ were prepared from the reactions of the dianions $Ru(CO)_4^{2-}$ and $Os(CO)_4^{2-}$ with methanol as described for the protio species[6] with the exception that CH_3OD was used in place of CH_3OH. Infrared spectra were obtained as tetrahydrofuran (THF) solutions in NaCl cells with a Perkin-Elmer Model 683 infrared spectrophotometer operated in the transmittance mode and calibrated against polystyrene. The THF was freshly distilled from purple sodium/benzophenone solution.

Results and Discussion

Table I. IR Absorptions in the Carbonyl Region for the $[PPN][HM(CO)_4]$ Salts (M = Fe, Ru, Os) and Their Deuterated Analogues

complex	ν_{CO} freq,[a] cm^{-1} $A_1(2)$	$A_1(1)$	E
$HFe(CO)_4^-$	1995	1905	1876
$DFe(CO)_4^-$	1994	1888	1875
$HRu(CO)_4^-$	2003	1927	1885
$DRu(CO)_4^-$	1999	1906	1884
$HOs(CO)_4^-$	2008	1945	1881
$DOs(CO)_4^-$	2003	1904	1881

[a] Values reported are ±1 cm^{-1}, in THF solution.

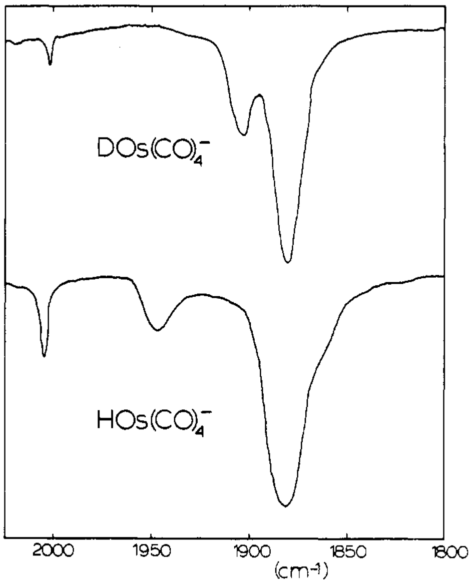

Figure 1. Infrared spectra in the carbonyl region of $[PPN][HOs(CO)_4]$ (bottom) and $[PPN][DOs(CO)_4]$ (top) in THF.

The absorption bands of the ν_{CO} region for each of the six complexes are listed in Table I, and the spectra obtained for $[PPN][HOs(CO)_4]$ and $[PPN][DOs(CO)_4]$ are illustrated in Figure 1. In Figure 1, the two higher frequency carbonyl bands are shifted to lower energy upon deuteration (−5 and −41 cm^{-1} shifts, respectively) but the band at 1881 cm^{-1} is not appreciably affected. In analogy with the assignments made for the $HFe(CO)_4^-$ ion, the three bands can be assigned to the $A_1(2)$, $A_1(1)$ and E vibrational modes (from highest to lowest frequency, respectively) expected for the ion in a C_{3v} configuration.[5] The deuterium isotope effects are consistent with these assignments since the M–H(D) stretch would also have an A_1 symmetry in this configuration and can be expected to couple to the A_1 ν_{CO} modes. The spectra of all the $HM(CO)_4^-$ and $DM(CO)_4^-$ homologues are entirely analogous with the $A_1(2)$ band shifting to slightly lower frequency in each case but the $A_1(1)$ band shifting −17, −21, and −41 cm^{-1} respectively for M = Fe, Ru, and Os (Table I). The M–D stretching vibrations were not identifiable owing to the interfering bands of the PPN^+ cation in the expected frequency region. Similarly the M–H vibrations are apparently obscured by the more intense ν_{CO} bands. In the absence of these data, a detailed vibrational analysis cannot be carried out to determine the parameters responsible for the larger effects noted with the heavier analogues. However, the isotope effects reported here suggest the failure of the procedure of energy factoring of the carbonyl and metal–hydrogen stretching modes with this series of complexes. Such an approximation could be made in analyzing the $HMn(CO)_5$ vibrational spectrum given very minor differences with the $DMn(CO)_5$ spectrum.[5a] Similarly, the IR spectra of some recently reported phosphine-substituted manganese carbonyl hydrides display very small isotope effects.[7] However, in view of the present observations, assumptions of minimal interactions between the ν_{MH} and ν_{CO}

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0020-1669/82/1321-2509$01.25/0

modes without empirical confirmation should be made very cautiously.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences (Contract No. EY-76-503-0034, PA262).

Registry No. [PPN][$HFe(CO)_4$], 56791-54-9; [PPN][$HRu(CO)_4$], 81011-81-6; [PPN][$HOs(CO)_4$], 79408-53-0; deuterium, 16873-17-9.

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Reductive Coupling of Perrhenate To Form the Octachlorodirhenate(III) Anion: A New, Convenient, and High-Yield Synthetic Procedure

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Received October 27, 1981

The octachlorodirhenate(III) anion was the first complex to be formulated as containing a metal–metal quadruple bond,[1-3] and it remains to this day the key starting material for entry into the chemistry of multiply bonded dirhenium complexes.[4] The synthetic strategies utilized for its preparation have revolved around the following methods: (1) the high-pressure (autoclave) hydrogen reduction of $KReO_4$–hydrochloric acid mixtures;[1,5] (2) the hypophosphorous acid reduction of $KReO_4$;[1,6] (3) the disruption of Re_3Cl_9 by molten diethylammonium chloride.[7] The disadvantages of these methods are the often low and variable yields (usually only 40% or so at best), the inconvenience of using an autoclave in the H_2 reduction, and the need to synthesize Re_3Cl_9 (itself best prepared from quadruply bonded $Re_2(O_2CCH_3)_4Cl_2$).[8] In exploring alternative and more convenient methods which might be employed to reduce perrhenate to low-valent rhenium chlorides, we have discovered a remarkably simple and high-yield conversion of $[ReO_4]^-$ to $[Re_2Cl_8]^{2-}$. In view of the high cost of rhenium we feel that this procedure must now constitute the preferred method of preparing $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$, the usual starting material for dirhenium chemistry.

Although $KReO_4$ is insoluble in benzoyl chloride (PhCOCl), prolonged reaction under reflux conditions affords a solution which upon addition of ethanol and tetra-*n*-butylammonium bromide produces $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ (**1**) in yields of ca. 50%. In this reaction, we find that there are two insoluble "intermediates" formed which can be readily separated and identified. When the reaction mixture which results from refluxing $KReO_4$ with PhCOCl for 5 h was filtered, a mixture of emerald green crystals (water insoluble) and yellow–green crystals (water soluble) was isolated. On the basis of microanalytical and spectroscopic data, the emerald green crystals were identified as $Re_2(O_2CPh)_2Cl_4$. This bis(carboxylate) complex is formulated as a dinuclear quadruply bonded complex similar in type to those of this stoichiometry which have been reported and characterized previously.[4,9,10] The yellow-green crystals were identified as K_2ReCl_6. This salt is completely insoluble in the reaction mixture and does not react further with PhCOCl, even after prolonged reflux, thereby explaining why the yields of **1** produced from $KReO_4$ were never greater than 60% since the K_2ReCl_6, once it is formed, does not react further due to its insolubility. On the other hand, $Re_2(O_2CPh)_2Cl_4$ is an intermediate on the way from $KReO_4$ to $[Re_2Cl_8]^{2-}$. Upon reaction with fresh PhCOCl and subsequent treatment with a HCl(g) saturated ethanol solution of $[(n\text{-}C_4H_9)_4N]Br$, it produces solutions from which **1** may be isolated in high yield. Thus the role of PhCOCl in these reactions is not only to reduce and chlorinate the metal centers but to couple them via the agency of benzoate bridges. The benzoate ligands are presumably formed from PhCOCl through oxygen transfer from the perrhenate starting material.

Although K_2ReCl_6 could not be converted into $[Re_2Cl_8]^{2-}$ by PhCOCl, this cannot be construed to mean that such rhenium(IV) species are inert to reduction by PhCOCl. We believe that it is only the extreme insolubility of K_2ReCl_6 which hinders its reaction. In accord with this interpretation we find that when the much more soluble tetra-*n*-butylammonium salt $[(n\text{-}C_4H_9)_4N]_2ReCl_6$ is reacted with PhCOCl, **1** can be produced in yields of 95%. This indicates that the solubility of the intermediates in the reaction mixture is crucial for the high-yield formation of **1**.

The preceding observation prompted us to use $[(n\text{-}C_4H_9)_4N]ReO_4$ in place of $KReO_4$ in these reactions with PhCOCl. The conversion proceeds smoothly without the obvious precipitation of any insoluble intermediates, and **1** can now be formed in yields up to 95% (a yield of 90% was typical). However, the most critical factor which we found determined the yield was the reaction temperature. With a mercury bubbler, which ensured a higher pressure in the system, we found that the boiling point of PhCOCl was close to 209 °C. With a mineral oil bubbler and a boiling point of 198 °C, the yield of **1** decreased dramatically from ca. 90% to 60%.

An alternative starting material for the synthesis of **1** with PhCOCl is the rhenium(V) complex $ReOCl_3(PPh_3)_2$, which is itself prepared (in high yield) from perrhenate. The reaction proceeds through the red *trans*-$ReCl_4(PPh_3)_2$ which can be isolated. The overall conversion of $ReOCl_3(PPh_3)_2$ to **1** can be accomplished in yields of ca. 70%.

$Na_2MoO_4{\cdot}2H_2O$, K_2MoO_4, $H_2MoO_4{\cdot}4H_2O$, $MoO_2(acac)_2$, $Na_2WO_4{\cdot}2H_2O$, WO_3, and MoO_3 were all checked for their reactivity toward PhCOCl in hopes that these systems could be used to produce dimolybdenum and ditungsten complexes. In only two cases were we able to isolate any identifiable products. $MoO_2(acac)_2$ and K_2MoO_4 both yielded $[(n\text{-}C_4H_9)_4N]MoOCl_4$ in yields of 76% and 84%, respectively. Thus, in the case of molybdenum and tungsten, the formation of high oxidation state oxo halide species predominates.

Experimental Section

Starting Materials. $KReO_4$ was purchased from ROC/RIC Chemicals. PhCOCl was obtained from Aldrich Chemical Co. and distilled under vacuum prior to use. All other chemicals were purchased from commercial sources and used as received. All solvents were thoroughly deoxygenated prior to use.

$[(n\text{-}C_4H_9)_4N]ReO_4$ was prepared in 98% yield from $KReO_4$ by the slow addition of a hot aqueous $(n\text{-}C_4H_9)_4NBr$ solution to one of $KReO_4$. The resulting white precipitate was washed with water and dried in vacuo. $[(n\text{-}C_4H_9)_4N]_2ReCl_6$ was prepared in 80% yield by

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