Ion pairing in solutions of Na[HIr$_4$(CO)$_{11}$]: evidence for Na$^+$ interaction with one of the bridging carbonyls

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Abstract

The infrared and ^{13}C nuclear magnetic resonance spectra of Na[HIr$_4$(CO)$_{11}$] demonstrate that in diethyl ether this salt is largely present as a contact ion pair, the principal site of interaction being one of the bridging carbonyls. In tetrahydrofuran this salt exists as a mixture of free and ion-paired clusters as appears to be the case in diethyl ether when 18-crown-6 ether or kryptofix-222 are added to complex the Na$^+$ in solution.

Introduction

Cation pairing to transition metal carbonyl compounds in solution has been shown to affect the reactivity of these complexes in such processes as alkyl migration [1], CO$_2$ insertion into metal–methyl bonds [2] and catalytic CO hydrogenation [3]. Although ion-pairing studies have been performed on a number of mononuclear metal carbonyl compounds [4], reports of ion pairing effects on polynuclear carbonyl complexes as studied by IR and NMR spectroscopies are limited [5]. A number of factors have been proposed [4] to influence the type and degree of ion pairing to carbonyl clusters: cation size and electrostatic potential, solvent donor and acceptor properties, solvent polarity and the structure of the cluster in question. Reported here is a study of the ion-pairing properties of the hydride cluster anion HIr$_4$(CO)$_{11}$$^-$ (Fig. 1) [6], an important component in the homogeneous catalysis of the water gas shift reaction when employing Ir$_4$(CO)$_{12}$ as the catalyst precursor in alkaline solution [7].

Experimental

Materials and instrumentation. Tetrairidium dodecacarbonyl was used as received from Strem Chemicals, Inc. The iridium compound [NEt$_4$] [HIr$_4$(CO)$_{11}$] was synthesized according to its literature preparation [8]. Sodium tetraphenylborate,
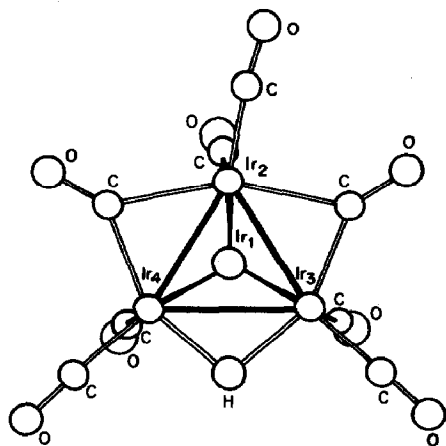
Fig. 1. Molecular structure of the $HIr_4(CO)_{11}^-$ anion as determined by Bau et al. [6] (the three terminal carbonyl ligands on Ir(1) omitted for clarity).

lithium bromide, 18-crown-6 ether (1,4,7,10,13,16-hexaoxacyclooctadecane) and kryptofix-222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) were obtained from Aldrich and used as received except for drying under vacuum prior to use. Carbon monoxide was purchased from the Linde Division of Union Carbide, while ^{13}CO was purchased from Icon Services, Inc. and used as received.

Tetrahydrofuran and diethyl ether were dried by distillation under nitrogen from sodium benzophenone ketyl. Methanol, acetonitrile and chlorobenzene were dried from calcium hydride. THF-d_8 and diethyl ether-d_{10} were purchased from Aldrich and Merck respectively and were dried with CaH_2 prior to use as NMR solvents.

All solvents and compounds were handled under anaerobic conditions in standard Schlenk glassware. The solvents were degassed by several freeze-pump-thaw cycles. Solutions were transferred by plastic or glass syringes equipped with stainless steel needles.

Infrared spectra were recorded on a Digilab FTS-60 Fourier transform spectrometer or Perkin–Elmer 683 IR spectrophotometer. Samples were run in NaCl plates separated by a 1.0 mm Teflon spacer with a solvent sample as reference. NMR spectra were obtained on a GE model GN 500 spectrometer. Spectra (^{13}C) were referenced relative to the natural abundance ^{13}C of the solvent.

Solution preparations. A solution of the sodium salt of $HIr_4(CO)_{11}^-$ was prepared from a sample of $[NEt_4][HIr_4(CO)_{11}]$ dissolved in CO saturated THF. The solution was syringed into another flask containing 1.1 equiv. of sodium tetraphenylborate and stirred. Formation of a white precipitate of $[NEt_4][BPh_4]$ occurred within one minute and was separated from the yellow supernatant solution by filtration. Solutions of $Na[HIr_4(CO)_{11}]$ were obtained in diethyl ether by performing the cation exchange as above, removing the THF solvent in vacuo, and redissolving the resulting oil in diethyl ether under CO. Solutions of 18-crown-6 ether or kryptofix-222 in THF or ether were prepared separately for addition to solutions of the hydride.

NMR experiments. Samples for NMR analysis were prepared by allowing $[NEt_4][HIr_4(CO)_{11}]$ to stir under a ^{13}CO atmosphere in THF for a miniumum of 24 h. An infrared spectrum of this solution showed down-frequency shifts of ca. 30

cm^{-1} in the ν(CO) bands indicating nearly complete exchange had occurred. Cation exchange to the sodium salt was then effected as above. The THF was then removed in vacuo and the sample redissolved in THF-d_8 or diethyl ether-d_{10} and syringed into an NMR tube containing a ^{13}CO atmosphere.

Results

IR studies. Solutions of the salt [NEt$_4$][HIr$_4$(CO)$_{11}$] were used as the starting material for all cation exchanges and as the reference spectrum (Table 1 and Fig. 2a). Virtually the same spectrum was obtained for a THF solution of [PPN][HIr$_4$(CO)$_{11}$] (PPN$^+$ = bis(triphenylphosphoranylidene)ammonium). In both cases, the bridging carbonyl region displayed two bands at 1832(mw) and 1805(m) cm^{-1}. The spectrum of [NEt$_4$][HIr$_4$(CO)$_{11}$] in methanol was similar but all terminal CO bands were shifted to somewhat higher frequency.

Solutions of Na[HIr$_4$(CO)$_{11}$] prepared from [NEt$_4$][HIr$_4$(CO)$_{11}$] in THF as described in the Experimental section were examined by IR spectroscopy in the carbonyl region (Fig. 2b). Exchange of Na$^+$ for NEt$_4^+$ resulted in relatively minor changes in the IR spectrum. The terminal bands were shifted only 1–2 cm^{-1} to higher frequency but new weak bands appeared at 1767 and 1815(sh) cm^{-1}.

For a fresh sample of [NEt$_4$][HIr$_4$(CO)$_{11}$], the NEt$_4^+$ cation was exchanged for Na$^+$ in THF as above, and the solvent was removed in vacuo. The residue was redissolved in diethyl ether under CO and the IR spectrum recorded (Fig. 2c). In comparison to Fig. 2b, the most significant differences lie in the bridging carbonyl region where the bands at 1805 and 1832 cm^{-1} are no longer present but are replaced by two independent, symmetrical bands, one at much lower frequency (1730 cm^{-1}) than in THF. For the terminal carbonyls there is a modest shift (< 10 cm^{-1}) to higher frequency.

These changes in the IR spectra, especially in the bridging CO region, suggest the following: (a) the NEt$_4^+$ and PPN$^+$ salts of HIr$_4$(CO)$_{11}^-$ are free of contact ion pairing between the cation and the bridging carbonyl; (b) the Na$^+$ salt in THF is present both as "free" or solvent separated ions and as the contact ion pairs Na$^+$Ir$_4$(CO)$_{11}^-$, evidenced by the weak IR bands at 1815 and 1768 cm^{-1}; (c) the

Table 1

Effects of cation, solvent, and additives on ν(CO) values of HIr$_4$(CO)$_{11}^-$

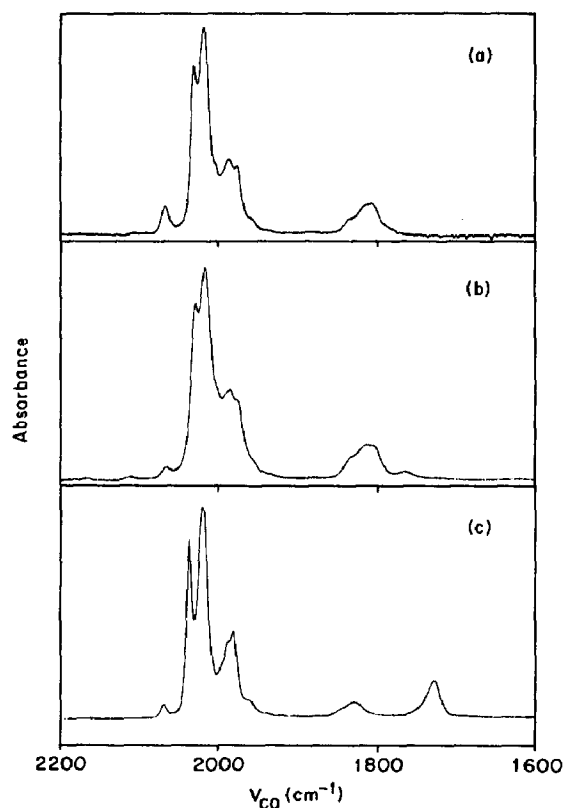| Cation	Solvent	Added reagent	ν(CO) (cm^{-1})
NEt$_4^+$	THF	–	2067w, 2030s, 2017vs, 1985m, 1975m sh, 1832m, 1805m
NEt$_4^+$	(C$_2$H$_5$)$_2$O	LiBr (9 equiv.)	2070w, 2031s, 2018vs, 1989m, 1832m, 1820m, 1805m, 1740m
NEt$_4^+$	MeOH	–	2070w, 2036s, 2022vs, 1993m, 1984m sh, 1815m, br
Na$^+$	THF	–	2068m, 2030s, 2017vs, 1986m, 1978m, 1832m, 1815m, 1805m,sh 1768w
Na$^+$	(C$_2$H$_5$)$_2$O	–	2072w, 2039s, 2021vs, 1990m, 1984m, 1829m, 1730m
Na$^+$	(C$_2$H$_5$)$_2$O	CE ^{a} (2 equiv.)	2070w, 2031s, 2017vs, 1987m, 1979m, 1835sh, 1817m, 1805sh, 1774w
Na$^+$	(C$_2$H$_5$)$_2$O	KF ^{b} (2 equiv.)	2068w, 2031s, 2017vs, 1988m, 1977m, 1835sh, 1813m, 1795sh
PPN$^+$	THF	–	2068w, 2030s, 2018s, 1987m, 1975m, 1830m, 1815m

^{a} CE = 18-crown-6. ^{b} KF = kryptofix-222.

Fig. 2. IR spectra (ν(CO) region) for (a) [NEt$_4$][HIr$_4$(CO)$_{11}$] in THF, (b) Na[HIr$_4$(CO)$_{11}$] in THF, (c) Na[HIr$_4$(CO)$_{11}$] in diethyl ether.

Na$^+$ salt in diethyl ether is nearly exclusively a contact ion pair. Given that, for the ion paired species, one of the bridging carbonyls occurs at a dramatically lower frequency (1730 cm^{-1}) while the other (1829 cm^{-1}) is close to those of the free HIr$_4$(CO)$_{11}$$^-$, one may conclude that the ion pairing site involves but one of the bridging carbonyl oxygens. That the two bridging ν(CO) bands in diethyl ether represent spectral properties of a single species (rather than an equilibrium mixture of free and associated ions) was tested by examining the IR spectrum of Na[HIr$_4$(CO)$_{11}$] in diethyl ether as a function of concentration. Over a fifty-fold range (5.4 × 10^{-4} to 2.7 × 10^{-2} M) the intensity ratio of the 1730 and 1832 cm^{-1} bands remained constant at 2.2, consistent with the view that these bands are characteristic of a single species. In contrast, the intensity ratio of the ν(CO) band at 1767 cm^{-1} relative to that at 1832 cm^{-1} for Na[HIr$_4$(CO)$_{11}$] in THF decreased ~ 25% upon a twenty-fold dilution (1.35 × 10^{-4} to 2.7 × 10^{-2}) consistent with the view that these solutions represented a mixture of species in equilibrium. In addition, dilutions led to some sharpening of the terminal ν(CO) bands in THF.

Addition of the alkali ion encapsulating agents 18-crown-6 ether and kryptofix-222 (2 equiv.) to Na[HIr$_4$(CO)$_{11}$] in diethyl ether (Table 1) resulted in key changes in the IR spectra. The most significant were the disappearance of the band at 1730 cm^{-1} with the appearance of new weak bands at 1817 and 1774 cm^{-1} for addition of 18-crown-6 ether and at 1813 and 1795 cm^{-1} for addition of kryptofix-222. In

addition there were shifts of the terminal $\nu(CO)$ bands to frequencies resembling those for the tetraethylammonium salt in THF and shift of the other bridging $\nu(CO)$ to lower frequency (Table 1). These changes are consistent with the formation of free ions upon the encapsulation of the sodium ions, although the appearance of two new weak signals below 1800 cm^{-1} may indicate some formation of species in which the encapsulated cations have some electrostatic interaction with a carbonyl site (vide infra). Similar changes were observed upon addition of sequestering agent to the Na$^+$ salt in THF rather than diethyl ether, although the changes were less dramatic due to the smaller population of ion pairs in this solvent.

NMR studies. The room temperature ^{13}C NMR spectra of ^{13}CO enriched samples of the Na$^+$ and NEt$_4$$^+$ salts of HIr$_4$(CO)$_{11}$$^-$ in THF-d_8 and of the Na$^+$ salt in diethyl ether-d_{10} show singlets at δ 172.4, 171.5 and 172.5 ppm, respectively. These spectra are consistent with complete exchange of the coordinated carbonyls at this temperature. The resonance for the sodium salt in ether is considerably broader (ca. 3 × at half-height) relative to the other spectra. Notably, the addition of excess 18-crown-6 ether to this solution resulted in the narrowing of this singlet.

The ^{13}C NMR spectra at $-95°C$ for [NEt$_4$][HIr$_4$(CO)$_{11}$] in THF-d_8 and Na[HIr$_4$(CO)$_{11}$] in diethyl ether-d_{10} are compared in Fig. 3. In the terminal
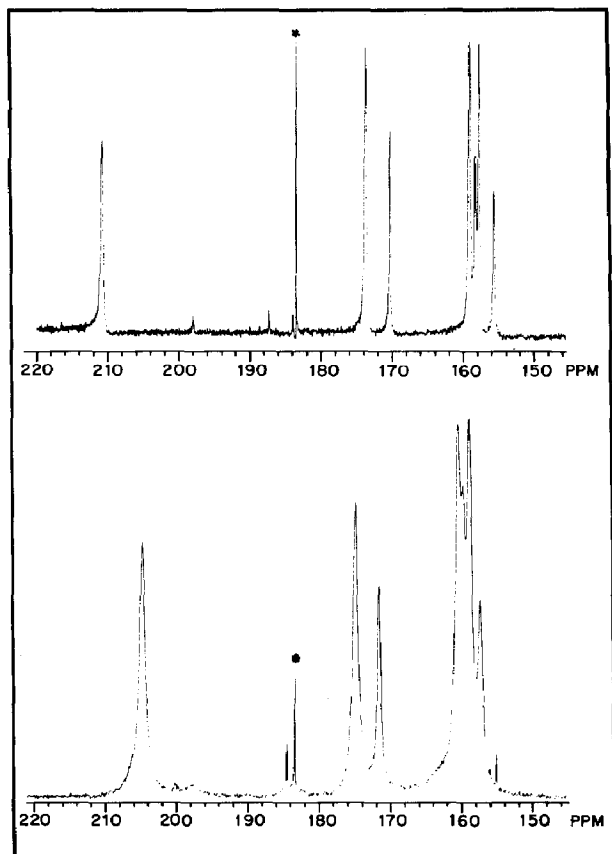
Fig. 3. ^{13}C NMR spectra at $-95°C$ for Na[HIr$_4$(CO)$_{11}$] in diethyl ether-d_{10} (upper) and for [NEt$_4$][HIr$_4$(CO)$_{11}$] in THF-d_8 (lower). Free CO indicated by *.

carbonyl region, the two spectra are quite similar in pattern and chemical shift. The most significant difference lies in the bridging carbonyl region where the Na$^+$ salt gives a singlet at δ 211.0 ppm, shifted downfield from that of the tetraethyl ammonium salt at 204.8 ppm [9*]. This behavior is consistent with the increased deshielding of the bridging carbonyl carbons as the result of Na$^+$ ion-pairing at a bridging carbonyl oxygen site. Similar shifts of ^{13}C NMR resonances as the result of ion-pairing have been reported by other workers [5c,10].

The observation of a singlet in the bridging carbonyl region at low temperature suggests that the two bridging sites are equivalent on the NMR time scale, observation of a unique ion-paired carbonyl site being precluded by rapid Na$^+$ exchange.

The ^{13}C NMR spectrum of Na[HIr$_4$(CO)$_{11}$] in diethyl ether-d_{10} at an intermediate temperature of $-72°$C shows only two broad terminal carbonyl resonances at δ 172 and 161 ppm plus a broadened bridging carbonyl resonance at 211 ppm which indicates the onset of CO fluxional exchange processes. These sharpen at $-95°$C (Fig. 3) to the approximate integrated intensity patterns 2/1 and 2/1/2/1, respectively, for the terminal carbonyl multiplets and 2 for the bridging carbonyls consistent with assignment of the resonances at δ 174.0 and 170.6 ppm to the three carbonyls on Ir(1), and the remaining terminal resonances to the carbonyl ligands on the front face of the cluster. Notably, the calculated weighted-average of all the bands in the $-95°$C spectrum gives the same chemical shift value as seen for the singlet in the room temperature spectrum.

Discussion

The data described above are consistent with the formation of contact ion-pairs between HIr$_4$(CO)$_{11}$$^-$ and Na$^+$ in solvents of low polarity. The relatively large down-frequency shift (80 cm^{-1}) for one of the bridging CO bands suggest that only one CO is participating in ion pairing at any one instant, i.e., that neither triple ions or some sort of chelating of a cation by two carbonyl oxygens is indicated. A higher equilibrium constant for ion pairing in ether than in THF is consistent with the lower dielectric constant for ether (4.3) vs. THF (7.6). However, the difference might lie in solvation of the anion, since there is a larger difference in the Gutmann acceptor numbers than in the donor numbers, (THF: DN = 20.0, AN = 8.0, diethyl ether: (DN = 19.2, AN = 3.9) [11].

The shifts to higher frequency of the terminal carbonyl bands are also consistent with the formation of ion pairs [4,5]. The Na$^+$ interaction should result in net electron-withdrawal from the cluster thereby decreasing the back-bonding to the terminal carbonyls.

The addition of 18-crown-6 ether or kryptofix-222 to the Na$^+$/HIr$_4$(CO)$_{11}$$^-$ ion pair in diethyl ether caused the shifting of the ν(CO) bands to those resembling free HIr$_4$(CO)$_{11}$$^-$ plus the appearance of two new weak bridging ν(CO) bands characteristic of each sequestering agent. These observations suggest an equilibrium mixture of free ions and those paired with encapsulated Na$^+$. Such a result would be in agreement with previous observations that 18-crown-6 ether complexed Na$^+$ can

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* Reference numbers with asterisks indicate notes in the list of references.

interact via an accessible open face of the cation. For example, Cooper and co-workers [12] have determined that the solid [Na-18-crown-6] [W(CO)$_5$SH] is chain polymeric in nature with sodium-carbonyl linkages between alternating cations and anions. Similarly, Edgell and Chanjamsri [13] have reported IR evidence for [Na-crypt-221]$^+$ interaction with the carbonyl ligands of Co(CO)$_4$$^-$.

It is of some interest to compare these results with those obtained for other transition metal carbonyl clusters. The clusters HRu$_3$(CO)$_{11}$$^-$ and HFe$_3$(CO)$_{11}$$^-$, which each have one bridging CO, also form contact ion pairs in oxygen donor solvents [3,5a,b]. However, each of these show evidence of ion pairing even with NEt$_4$$^+$ in THF. Furthermore, a hydrogen bonding interaction has been observed between the μ-CO of HFe$_3$(CO)$_{11}$$^-$ and alcohols. Lack of evidence for these two types of interaction under similar conditions for HIr$_4$(CO)$_{11}$$^-$ may reflect the different structure of this cluster.

The presence of two bridging CO's in this larger cluster may act to delocalize the electron density more effectively and therefore disfavor electrostatic interactions. In summary, the iridium hydride cluster anion HIr$_4$(CO)$_{11}$$^-$ has been shown by IR spectroscopy to form contact ion pairs with Na$^+$ in THF and diethyl ether solutions. The site of this interaction is proposed to be at the oxygen of one of the bridging carbonyls.

Acknowledgement

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