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Relative Affinities of Carbonylbis(triphenylphosphine)rhodium(I) and Related Cations for Anionic Ligands in CH_2Cl_2

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Infrared spectroscopy has been used to determine the relative anion affinities in CH_2Cl_2 of $Rh(PPh_3)_2(CO)^+$ and $Rh(AsPh_3)_2(CO)^+$ via measurement of equilibrium constants for the metatheses $RhL_2(CO)Y + PPN^+Z^- = RhL_2(CO)Z + PPN^+Y^-$. Observed for L = PPh_3 was the anion affinity trend $NCO^- \gg O_2CMe^- \sim O_2CPh^- \gg F^- \sim NCS^- > Cl^- > Br^- > I^- \gg ONO_2^- \sim O_2CCF_3^- \gg OTf^- \sim OClO_3^-$. A smaller series for L = $AsPh_3$ displayed a similar trend, but with positions of NCS^- and Cl^- reversed. For most anion pairs studied, the equilibrium lies so far to the left or right that only limits could be calculated, given the inherent experimental limitations. For L = PPh_3, the equilibrium constant for replacement of the least preferred anion by the most can be inferred as $>10^{19}$. $Rh(PCy_3)_2(CO)Cl$ and $Rh(PCy_3)_2(CO)Z$ (Z = NCS, NCSe, O_2CMe; but not F, O_2CPh, and NCO) interact strongly in solution and thus limit study of that series.

Introduction

Numerous studies have investigated the reactivity of soluble metal species in stoichiometric and catalytic processes as a function of the nature of both neutral and anionic ligands.[1] Although bonding between metal moieties and ligands has been addressed qualitatively by the hard and soft acids and bases concept[2] and quantitatively by the E and C approach,[3] few quantitative experimental data have been reported for anion affinities of electron-rich metal species in solution.[4] We report herein an expanded[5] set of anion affinities of $Rh(PPh_3)_2(CO)^+$ and related species in dichloromethane determined by infrared spectroscopic studies of the metathesis equilibria $RhL_2(CO)Y + PPN^+Z^- = RhL_2(CO)Z + PPN^+Y^-$.

Experimental Section

Syntheses. *trans*-$Rh(PPh_3)_2(CO)Cl$ was prepared as in the literature.[6] Its perchlorate analogue (vide infra) was synthesized according to Vaska's method.[7] Its trifluoromethanesulfonate (triflate, OTf) analogue was prepared by a similar Ag^+-assisted metathesis in benzene, although a 10% excess of AgOTf was required to give complete conversion of the chloride to the triflate.[8] *Safety note*: Although we experienced no mishaps in this series of experiments, a related synthesis of $CpW(CO)_3OClO_3$ in benzene using only 190 mg of $AgClO_4$ resulted in a powerful explosion that seriously injured one of us. This accident occurred in spite of our having pounded numerous small samples with a hammer without prior incident! We recommend using either silver tetrafluoroborate or triflate for abstraction of halide ligands in this type of complex.[9] The *trans*-$Rh(PPh_3)_2(CO)Y$ species (Y = NCO, NCS, O_2CMe, O_2CPh, ONO_2, O_2CCF_3) were prepared via modification of the Vaska general synthetic route.[10] The perchlorate or triflate complex (rather than the fluoride used by Vaska) was treated with excess sodium or potassium salt in methanol or acetone; the reaction mixtures were processed by (i) Vaska's method of aqueous precipitation or (ii) removal of all solvent followed by extraction of the Rh(I) product from the resulting solid with dichloromethane or chloroform and subsequent crystallization via concentration and addition of ether/heptane. Attempts to prepare the hydroxide complex, using both exact stoichiometric amounts and large excesses of NaOH, afforded mixtures containing several species (detected as multiple carbonyl bands in the IR spectrum) that we were unable to separate.

trans-$Rh(AsPh_3)_2(CO)Cl$ was prepared via the method of Goswami and Singh.[11] Its perchlorate and triflate[8] analogues were generated in high yield in the manner described above for the PPh_3 complexes. The *trans*-$Rh(AsPh_3)_2(CO)Y$ species[11] (Y = NCO, NCS, O_2CMe, O_2CPh, ONO_2) were prepared via the metathesis of a weakly coordinating anion as described above for the PPh_3 complexes.

trans-$Rh(PCy_3)_2(CO)Cl$ was prepared via addition of a 2% excess of PCy_3 (used as received from Organometallics, Inc.) to $[Rh(CO)_2Cl]_2$ (used as received from Strem Chemicals or Pressure Chemical) in benzene under nitrogen, followed by aerobic processing (concentration, precipitation with absolute ethanol, filtration, and washing with 1:1 ethanol/ether) in 97% yield. Its properties matched those reported in the literature.[12] The *trans*-$Rh(PCy_3)_2(CO)Y$ species[12] (Y = NCO, NCS, NCSe, O_2CMe, O_2CPh, ONO_2) were prepared via the metathesis of a weakly coordinating anion as described above for the PPh_3 complexes. $Rh(PCy_3)_2(CO)F$[12] was synthesized[8,13] by addition of excess "$(PPN)F{\cdot}CH_2Cl_2$" to the triflate or perchlorate[14] in CH_2Cl_2, followed by solvent removal, extraction of the fluoro complex from the PPN^+ salt mixture, and subsequent crystallization with ether/heptane.

All the above Rh(I) complexes were dried at reduced pressure and checked for purity by using thin-layer chromatography (silica gel) and IR and visible spectroscopy.

Equilibrium Studies. Dichloromethane (Fisher or Sargent-Welch ACS grade) was dried over freshly activated Mol Sieve 4A or via distillation under nitrogen from CaH_2 (indistinguishable results). The bis(triphenylphosphine)nitrogen(1+) salts, (PPN)Z (Z = Cl, O_2CMe, ONO_2),[15,16] were used as purchased from Strem, Alfa, or Aldrich after drying at reduced pressure. (PPN)SCN was prepared by Songstad's

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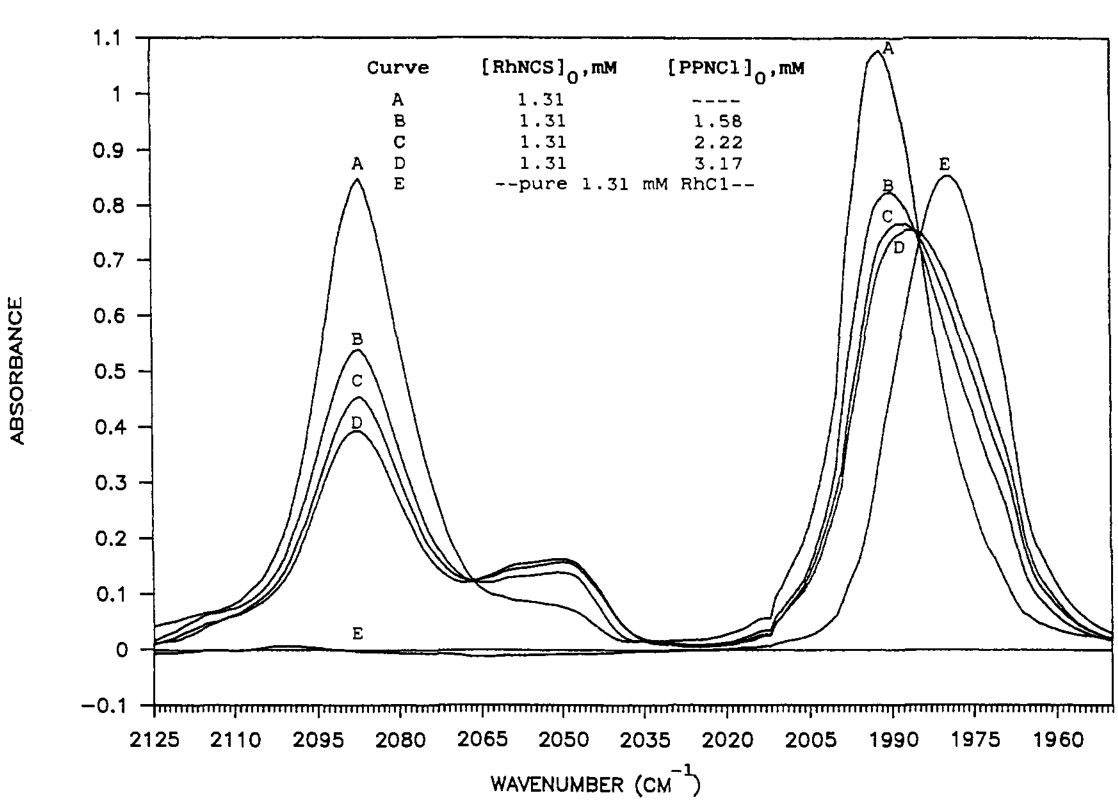

Figure 1. $Rh(PPh_3)_2(CO)NCS/(PPN)Cl$ mixtures.

method.[15] Solution preparations (in standard volumetric glassware) and manipulations were performed by using standard techniques in a Vacuum Atmospheres recirculating glovebox.

The procedure for measuring equilibrium constants in these metathesis systems has been described previously.[5a] The principal equilibrium studied was that starting with RhL_2COY and (PPN)Cl (Z = Cl). In many cases the Cl/Y equilibrium lay too far to the left or the right to afford a reasonable number for the equilibrium constant (i.e., at least one significant figure). Constraints imposed by solubility/molar absorptivity of the rhodium(I) species and solubility of the PPN^+ salts allowed a range of $[(PPN)Z]_0/[RhL_2COY]_0$ ratios[17] from 1 to 5. In such cases where carbonyl stretching frequencies for the respective Rh(I) species differed by at least 4 cm^{-1} or where the C–N stretching frequency might be utilized (respective ν(C–N) for coordinated and ion-paired NCO^- and NCS^- are well resolved), quantitative data or orderings for anion affinity were also obtained from other $RhL_2COY/(PPN)Z$ experimental formats (Y = OTf, Z = NO_3; Y = $OClO_3$, Z = NO_3; Y = NCO, Z = O_2CMe; Y = F, Z = NCS).

The validity of the instrumental/computer-analysis combination was confirmed by (i) obtaining satisfactory Beer's law plots over the pertinent concentration ranges for pure RhL_2COY and RhL_2COZ solutions and (ii) obtaining RhL_2COY and RhL_2COZ concentrations within experimental error for mixtures of known concentrations of RhL_2COY and RhL_2COZ. Spectra for the sets of such mixtures at constant total Rh concentration but different $[RhL_2COY]/[RhL_2COZ]$ ratios displayed clear isobestic points,[18] as expected. Sets of solutions of identical initial RhL_2COY concentrations having different $[(PPN)Z]_0/[RhL_2COY]_0$ ratios[17] also displayed the expected clear isobestic points (after subtraction of the small PPN^+ absorptions), consistent with the presence of only the two rhodium species RhL_2COY and RhL_2COZ (Figure 1).[18] Spectra of CH_2Cl_2 solutions of $RhL_2COY/(PPN)Y$ and $RhL_2COZ/(PPN)Z$ mixtures revealed no interactions that would cause deviation from Beer's law behavior.

Solutions of mixtures of $Rh(PCy_3)_2(CO)Cl$ and $Rh(PCy_3)_2(CO)Y$ for Y = NCS, NCSe, and O_2CMe afforded IR spectra that did not display the expected additive pattern of two considerably overlapping bands (Figure 2).

Results and Discussion

Table I. Metathesis Equilibrium Constants ($Rh(PPh_3)_2(CO)Y/PPN^+Z^-$)

Y	Z	$K_{Z/Y}$	method
F	Cl	0.34 (±0.17)	M
F	Br	0.013 (±0.004)	M
F	I	0.00035 (±0.00027)	M
F	NCS	0.39 (±0.15)	M
F	NCS	0.87 (±0.51)	C
NCS	Cl	0.39 (±0.12)	M
O_2CPh	Cl	$<10^{-4}$	M
O_2CMe	Cl	$<10^{-4}$	M
NCO	O_2CMe	$<10^{-4}$	M
OTf	Cl	$>10^4$	M
$OClO_3$	Cl	$>10^4$	M
ONO_2	Cl	$>10^4$	M
O_2CCF_3	Cl	$>10^4$	M
OTf	ONO_2	$>10^4$	M
OTf	O_2CCF_3	$>10^4$	M
$OClO_3$	ONO_2	$>10^4$	M
$OClO_3$	O_2CCF_3	$>10^4$	M
I	Cl	972 (±894)	C
I	Br	37 (±31)	C
Br	Cl	26 (±15)	C
$OClO_3$	NCO	$>10^{19}$	C

[a] M = measured experimentally; C = calculated by Hess' law.

The technique chosen to study the anion affinity in an aprotic solvent of $Rh(PPh_3)_2(CO)^+$ and its $AsPh_3$ analogue entailed analysis by infrared spectroscopy of solutions made by dissolving the appropriate rhodium Vaska halide or pseudohalide and the bis(triphenylphosphine)nitrogen(1+) salt, (PPN)Z,[15,16] in $[(PPN)Z]_0/[RhL_2COY]_0$ ratios[17] in the range 1–5 in CH_2Cl_2 to afford equilibrium 1. Data for L = PPh_3, including those from

$$RhL_2(CO)Y + PPN^+Z^- \overset{K_{Z/Y}}{\rightleftharpoons} RhL_2(CO)Z + PPN^+Y^- \qquad (1)$$

our earlier study[5] on halide preference, are listed in Table I. Also included are several values computed by using Hess' law for $K_{Z/Y}$ of equilibria not directly examined. The value for $K_{NCS/F}$ so calculated from $K_{Cl/F}/K_{Cl/NCS}$ agreed within experimental error with that measured directly for $K_{NCS/F}$. When the equilibrium lay so far to the left or right that we were unable to detect the presence of one of the Rh(I) species, a limit of $K_{Z/Y} < 10^{-4}$ or $>10^4$, respectively (based on a 99/1 or 1/99 ratio of the two), was used. No complications due to side reactions of PPN^+ salts

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(17) $[RhL_2COY]_0$ and $[(PPN)Z]_0$ denote initial respective concentrations.

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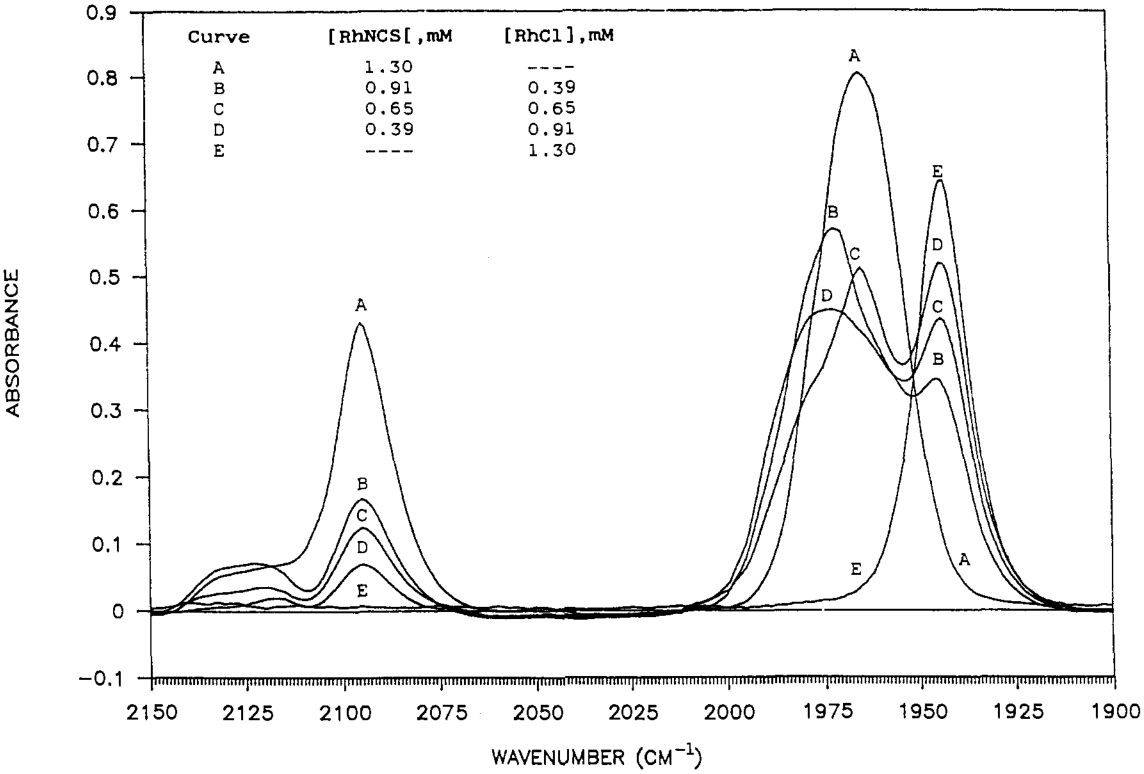

Figure 2. $Rh(PCy_3)_2(CO)NCS/Rh(PCy_3)_2(CO)Cl$ mixtures.

with CH_2Cl_2 were observed, although we purposely excluded the azide[16] and nitrite[19] for that reason.

The more complete series available (L = PPh_3) displays the order of anion affinity $NCO^- \gg O_2CMe^- \sim O_2CPh^- \gg F^- > NCS^- > Cl^- > Br^- > I^- \gg ONO_2^- \sim O_2CCF_3^- \gg OTf^- \sim OClO_3^-$. Using Hess' law, one can estimate the metathesis equilibrium constant for replacement of the least preferred, $OClO_3^-$, by the most preferred, NCO^-, as $>10^{19}$. As expected, the "weakly coordinating" anions OTf^-, $OClO_3^-$, ONO_2^-, and $O_2CCF_3^-$ have the lowest affinities for $Rh(PPh_3)_2(CO)^+$. Somewhat surprising is the degree of preference of the Rh(I) species for ONO_2^- and $O_2CCF_3^-$ over OTf^- and $OClO_3^-$.

The much less complete series available for L = $AsPh_3$ displays an order of anion affinity qualitatively similar to that observed for its PPh_3 analogue above: $NCO^- \gg O_2CMe^- \sim O_2CPh^- \gg Cl^- > NCS^- \gg ONO_2^- \gg OTf^- \sim OClO_3^-$. The major inconsistency observed between the two trends is the relative NCS^-/Cl^- affinity (a value here of 2.8 ± 0.6 versus 0.39 ± 0.15 for L = PPh_3).

Within the halide subset, a rough, nonlinear correlation exists between ν(C–O) and $K_{Cl/Y}$. ν(C–O) decreases for the halide complex (attributed to π-back-bonding competition with the trans carbonyl ligand[20] in the order $F^- \ll Cl^- < Br^- < I^-$), as the strength of the Rh(I) cation/halide interaction increases. [A similar correlation exists between λ_{max}(LMCT) and $K_{Cl/Y}$; as λ_{max} decreases from RhI (372 nm) to RhF (358 nm), respective anion affinities increase significantly.] The correlations break down completely outside the halide subset; there the above-cited IR and electronic spectroscopic parameters fail even to respond to anion nature in a concerted fashion. Comparison of our data with anion affinities of $Co(NH_3)_5^{3+}$ (in aqueous solution, where solvation of uncomplexed ions is a major factor)[21] shows only moderate agreement (once again principally in the halide subset); the isocyanate ion was, unfortunately, not included in the pertinent studies. Our anion affinity data also correlate poorly with Vaska's electronegativity scale for anionic ligands[22] (generated in the same type of Rh(I) and Ir(I) carbonyl systems for which our data are reported) and the half-wave reduction potenials for $Rh(PPh_3)_2(CO)Y$ reported by Schiavon and co-workers.[23] The failure of the electronic parameters listed above to satisfactorily rationalize relative anion affinities for $Rh(PPh_3)_2(CO)^+$ and the reversal of relative NCS^-/Cl^- affinity upon going to the $AsPh_3$ analogue imply that both steric and electronic factors are important determinants in anion affinity.[1a,24]

The isothiocyanate ion is present as a relatively strongly bound ligand in many transition-metal complexes.[21,25] Much less studied is the isocyanate ligand.[26] We were unable to find data in the literature that would predict or rationalize its marked preference by the three rhodium(I) Vaska moieties in our studies, and all of the parameters described above placed the isocyanate ligand in unexceptional positions. We[5a] have previously suggested that fluoride ion is the preferred anion within the halide subset because fluoride has no 2d orbitals with which to compete in π-back-bonding with the trans carbonyl ligand. In principle, one might be able to estimate the extent to which the isocyanate ligand engages in π-back-bonding in a given complex from its C–N stretching frequency, i.e., lower ν(C–N) when more electron density from metal d orbitals moves into the C–N antibonding orbitals. In practice, the data of Norbury and Sinha[26] for palladium(II) and platinum(II) isocyanate complexes demonstrate the difficulty of using ν(C–N) to judge the extent of such a phenomenon. A possible rationalization for the strong bonding observed between the rhodium(I) carbonyl cations and NCO^- is the relatively high negative atomic charge[26] located on the isocyanate nitrogen (−0.7712; compare with that on N in NCS^-, which is much less tightly held by $Rh(PPh_3)_2(CO)^+$, of −0.4826). We can exclude π-donation from the bonding π orbitals of the isocyanate ligand into the rhodium d orbitals to push more electron

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density toward the carbonyl π^* orbitals as a major stabilizing factor,[27] for inductive effects should make NCS^- a stronger π-donor than the very tightly held NCO^-.

Only equilibria containing the fluoro ligand are highly sensitive to the presence of water or other polar molecules. Values of $K_{X/F}$ (X = Cl, Br, I) obtained carefully in benchtop experiments were higher by factors of 3–5 than those measured under rigorously anhydrous (glovebox) conditions.[5a] Addition of methanol (ca. 200-fold molar excess relative to Rh) to the 1/1 $Rh(PPh_3)_2(CO)NCO/(PPN)Cl$ mixture afforded a weak new carbonyl band at 2026 cm^{-1} (where a band was observed upon treating $RhL_2(CO)OClO_3$ in CH_2Cl_2 with 500-fold excess of methanol, characteristic of $RhL_2(CO)S^+$ species[28]); however, only the slightest decrease in absorbance of the coordinated isocyanate C–N stretching band was noted, and the shape and wavenumber maximum of the carbonyl band of the original mixture remained essentially unchanged. Similar results were noted for the 1/1 $Rh(PPh_3)_2(CO)O_2CMe/(PPN)Cl$ and $Rh(PPh_3)_2(CO)O_2CPh/(PPN)Cl$ mixtures. All experiments other than those containing the fluoro ligand afforded no differences within experimental error for those values of $K_{Z/Y}$ determined anhydrously and those determined aerobically.

Studies by Songstad and co-workers[16] have shown that PPN^+ salts are strongly associated in CH_2Cl_2 as ion pairs, with association constants of 1.5 (±0.3) × 10^3 independent of anion nature. Their results suggest little thermodynamic preference in formation of PPN^+Y^- relative to PPN^+Z^-; if so, then our $K_{Z/Y}$ values (where we were able to measure them using our limited range of $[(PPN)Z]_0/[RhY]_0$ ratios) and limits may be taken as estimates of relative stabilities of RhZ and RhY in solution.

Solution mixtures of $Rh(PCy_3)_2(CO)Cl$ and $Rh(PCy_3)_2(CO)Y$ for Y = NCS, NCSe, and O_2CMe afforded IR spectra from 2300 to 1900 cm^{-1} inconsistent with the presence of only the two Rh(I) Vaska species. Pertinent spectra for the Y = NCS case are displayed in Figure 2; a very similar pattern was observed for the Y = NCSe case. In the former set of spectra, the intensities of the anionic ligand C–N stretching band were observed to be much lower than expected for simply (unchanged) more dilute Rh–NCS, and the carbonyl band patterns were strongly dependent upon the [Rh–NCS]/[Rh–Cl] ratio. For Y = O_2CMe, a similar terminal carbonyl band pattern shift was noted. A possible rationalization for such a phenomenon is ligand bridge formation;[29] that it occurs for the very bulky PCy_3 complexes but not the somewhat less hindered PPh_3 and $AsPh_3$ analogues suggests loss of one or more ligands before bridge formation occurs. $[Rh(CO)_2Cl]_2$ reacts with 2 equiv of the very bulky ligand $P(Bu^t)_3$ followed by metathesis of a bridging chloride with an organothiolate ligand to form the mixed-bridge dimer *cis*-$RhL(CO)(\mu\text{-}SR)(\mu\text{-}Cl)RhL(CO)$.[30] Work is in progress to further define the nature of interaction between the respective Vaska species. No such interactions (i.e., no deviations from Beer's law behavior noted) were seen for Y = NCO, O_2CPh, ONO_2, OTf, and F. As for the analogous PPh_3 and $AsPh_3$ systems, the infrared spectra of the $Rh(PCy_3)_2(CO)NCO/(PPN)Cl$ mixtures showed no measurable quantities of $Rh(PCy_3)_2(CO)Cl$.

Our results show a very wide range of anion affinities for the $RhL_2(CO)^+$ species; particularly striking is preference of the rhodium(I) carbonyl cations for the isocyanate anion. We are currently studying the generality of such bonding patterns in low-valent transition-metal complexes, especially to learn whether the marked preference for the isocyanate anion is general or limited to cases in which the anionic ligand is trans to CO or other strongly π-back-bonding ligands. We are also expanding our technique to include UV–visible spectroscopy to be able to measure equilibrium constants for some Z/Y pairs whose IR spectra do not present sufficient resolution of respective analytical bands.[31]

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(31) In the $RhL_2(CO)^+$ series, it appears that slightly more than half of our IR-unfavorable Y/Z combinations are amenable to study by UV–visible spectroscopy.[21]

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Photochemistry of Aqueous *trans*-Cyanochlorotetraamminechromium(III). Evidence for an Excited-State Trans Effect

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The *trans*-$Cr(NH_3)_4(CN)Cl^+$ complex has been prepared and photolyzed in acidic aqueous solution (10^{-3} M $HClO_4$). Ligand-field (LF) irradiation causes release of CN^- ($\Phi = 0.31$) and NH_3 ($\Phi = 0.09$), with essentially wavelength-independent quantum yields. The main photoreaction, CN^- aquation, and its stereochemistry (>90% cis product) contrast with stereoretentive loss of Cl^- in the ground state. The photobehavior is in disagreement with the LF additive angular overlap model, predicting preferential photolabilization of Cl^-. The proposed explanation is a kind of excited-state trans effect, arising from mutual interaction of CN^- and Cl^-, respectively π-acceptor and π-donor ligands. Charge-transfer (CT) excitation leads to photoaquation of CN^- ($\Phi = 0.14$), Cl^- ($\Phi = 0.06$), and NH_3 ($\Phi = 0.16$). The results suggest a photoactive CT($Cl \rightarrow Cr$) state and a photoinert CT($Cr \rightarrow CN$) one. Comparison between the LF and CT photochemistries allows evaluation of the intrinsic CT reactivity ($\Phi \sim 0.2$) and of the efficiency ($\eta \sim 0.4$) of conversion of CT to LF states. The latter is confirmed by the relative phosphorescence yields as a function of the excitation wavelength.

Introduction

By now, some 20 *trans*-$Cr(NH_3)_4XY^{z+}$ and *trans*-$Cr(en)_2XY^{z+}$ ions have been studied photochemically,[1–4] playing a major role in the development and testing of the models for the preferential photosolvation[4–9] and the photostereochemistry[10] of chromium(III).

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