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Comparison of the Stability of Iridium–(η^2-Carbon Disulfide) and Iridium–(η^2-Carbonyl Sulfide) Complexes

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New complexes of the type $IrCl(CO)(\eta^2\text{-}SCY)(L)_2$ (Y = O, L = PMe_2Ph, PMe_3; Y = S, L = PMe_3) have been prepared. Formation constants and values of ΔH and ΔS have been measured. The stability of a given complex toward dissociation of SCY is greater when L is a small, basic phosphine ligand, and the stability has also been correlated with the electron affinity of SCY.

Introduction

Complexes of the type $IrX(CO)(L)_2$ (X = halide, L = tertiary phosphine) react with carbon disulfide to afford CS_2 complexes, $IrX(CO)(\eta^2\text{-}CS_2)(L)_2$.[1,2] In serveral instances the reaction is readily reversible[1] (X = Cl, I; L = PPh_3), but the presence of a smaller, more basic phosphine ligand (L = PMe_2Ph) increases the stability of the product toward dissociation of CS_2.[2] In our attempts to synthesize metal–carbonyl sulfide complexes we have found that increasing the basicity of the metal center favors formation of metal–(η^2-COS) compounds.[3] Here we report the syntheses of two metal–(η^2-COS) complexes. We also present thermodynamic data on the relative stabilities of analogous COS and CS_2 complexes.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer. Proton and $^{31}P\{^1H\}$ NMR spectra were obtained on a JEOL FX 90Q spectrometer at 89.59 and 36.2 MHz, respectively. Peak positions are relative to tetramethylsilane and 85% phosphoric acid with downfield values reported as positive. Analyses were performed by H. Beck, Analytical Services Laboratory, Northwestern University. All reactions were performed in dried deoxygenated solvents under an atmosphere of N_2. The complexes $IrCl(CO)(PPh_3)_2$,[4] $IrCl(CO)(PMePh_2)_2$,[5] $IrCl(CO)(PMe_2Ph)_2$,[6] and $IrCl(CO)(PMe_3)_2$[7] were prepared by published methods. The complex $IrCl(CO)(PMe_3)_2$ was sublimed three times and further purified by drawing a toluene solution of the complex through a fritted funnel (fine), which removed small amounts of $[Ir(CO)(PMe_3)_4]Cl$ that remained after the sublimations. This purification is essential to the success of the synthesis of $IrCl(CO)(\eta^2\text{-}COS)(PMe_3)_2$.

Thermodynamic Measurements. Carbonyl sulfide gas or CS_2 solution (ca. 4.0×10^{-3} mol of CS_2/mL of toluene) was added with a gas-tight syringe to a serum-capped NMR tube that contained 2.00 mL of a $(1\text{–}4) \times 10^{-2}$ M solution of metal complex in toluene-d_8. The reactions of $IrCl(CO)(L)_2$ (L = PMe_2Ph, PMe_3) with COS and with CS_2 were monitored at six to seven temperatures by $^{31}P\{^1H\}$ spectroscopy with a JEOL NM VTS temperature controller that was calibrated vs. an Omega Engineering thermocouple. Spectra were recorded with pulsed decoupling to suppress nuclear Overhauser enhancement. The equilibrium constant K was evaluated at each temperature from the expression $K = [IrCl(CO)(SCY)(L)_2]/[IrCl(CO)(L)_2][SCY]$, where the ratio $[IrCl(CO)(SCY)(L)_2]/[IrCl(CO)(L)_2]$ was determined from the integrated peak areas in the $^{31}P\{^1H\}$ NMR spectrum obtained at that temperature. The value of [SCY] was determined from the difference between initial [SCY] and $[IrCl(CO)(SCY)(L)_2]$ formed. For reactions with COS, the fraction of free carbonyl sulfide in the liquid phase, *f*, was determined at each temperature[8] and this liquid–vapor distribution was taken into account in the evaluation of [COS]. Since the boiling point of CS_2 was not exceeded, we assumed that all of the CS_2 was in the liquid phase ($f = 1$). (If we assume ideal solution behavior, at the boiling point of CS_2 more than 98.5% of the CS_2 remains in the liquid phase.) Plots of ln K against $10^3/T$ were linear to within experimental error. Values of ΔH and ΔS were determined from the slope and intercept of the best least-squares line through the data. Figures 1 and 2 and Table I illustrate the observed spectral changes, a ln K vs. $10^3/T$ plot, and a sample calculation.

Syntheses. $IrCl(CO)(\eta^2\text{-}CS_2)(PMePh_2)_2$. A sample of $IrCl(CO)(PMePh_2)_2$ was dissolved in CS_2 to give a yellow solution. The infrared spectrum of this solution is consistent with coordination of CS_2 to give $IrCl(CO)(\eta^2\text{-}CS_2)(PMePh_2)_2$ (see Table II), but the coodinated CS_2 is easily removed under vacuum and no attempt was made to isolate the product.

$IrCl(CO)(\eta^2\text{-}CS_2)(PMe_2Ph)_2$. The complex was prepared by a modification of the method of Deeming and Shaw.[2] A sample of $IrCl(CO)(PMe_2Ph)_2$ was dissolved in CS_2, and the solution was blown to dryness in a stream of N_2. The yellow product was dried under vacuum. Its infrared and NMR spectra were identical with published spectral data.[2] ^{31}P NMR (toluene-d_8, 30 °C): δ −28.8 (s).

$IrCl(CO)(\eta^2\text{-}COS)(PMe_2Ph)_2$. A sample of $IrCl(CO)(PMe_2Ph)_2$ was dissolved in a minimum amount of diethyl ether, and 10 equiv of COS were added. When the solution was cooled to −78 °C, a pale yellow solid precipitated (a mixture of $IrCl(CO)(PMe_2Ph)_2$ and product). Successive warming/cooling of the sample produced a white solid after approximately three cycles. The cold suspension was centrifuged, and the ether was decanted off under N_2. The remaining ether was removed under vacuum at −78 °C. The complex $IrCl(CO)(\eta^2\text{-}COS)(PMe_2Ph)_2$ is a white solid that may be stored at −78 °C but rapidly loses COS upon warming. Infrared spectra were obtained of samples that were mulled in Nujol at −78 °C. ^{31}P NMR (toluene-d_8, −50 °C): δ −27.5 (s). ^1H NMR (toluene-d_8, −50 °C): δ 1.69 (t, J = 4.5 Hz), 1.43 (t, J = 4.5 Hz).

$IrCl(CO)(\eta^2\text{-}CS_2)(PMe_3)_2$. This complex was prepared by the procedure used to prepare $IrCl(CO)(\eta^2\text{-}CS_2)(PMe_2Ph)_2$. The yellow solid is stable toward dissociation under vacuum. Anal. Calcd for $C_8H_{18}ClIrOP_2S_2$: C, 19.85; H, 3.75. Found: C, 20.00; H, 4.11. ^{31}P NMR (toluene-d_8, 30 °C): δ −33.2 (s).

$IrCl(CO)(\eta^2\text{-}COS)(PMe_3)_2$. A sample of $IrCl(CO)(PMe_3)_2$ was dissolved in a minimum amount of ether, and 4 equiv of COS were added. When the yellow solution was cooled to −78 °C, it turned colorless and a white solid precipitated. The product was isolated by the method described for $IrCl(CO)(\eta^2\text{-}COS)(PMe_2Ph)_2$. It may be stored at −78 °C but readily dissociates COS upon warming. ^{31}P NMR (toluene-d_8, 5 °C): δ −32.1 (s). ^1H NMR (toluene-d_8, −50 °C): δ 1.16 (t, J = 3.5 Hz).

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(8) The solubility of COS in toluene was determined at several temperatures between −25 and +25 °C and is nearly linear over this temperature range. The values of *f* in Table I were calculated from these data and are specific for the cell volume and solution volume used in this experiment.

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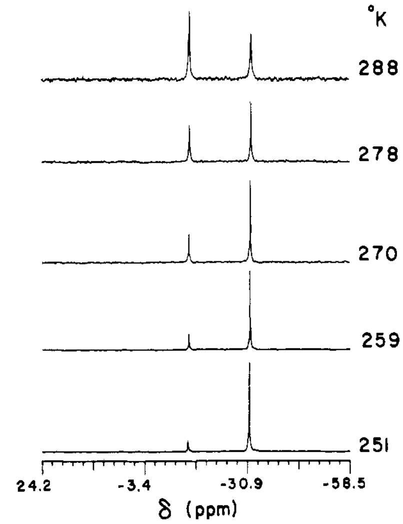


Figure 1. $^{31}P\{^1H\}$ NMR spectra of a 1:1 mixture of $IrCl(CO)(PMe_3)_2$ and COS as a function of temperature: $IrCl(CO)(PMe_3)_2$, δ −15.5; $IrCl(CO)(\eta^2\text{-}COS)(PMe_3)_2$, δ −32.1.

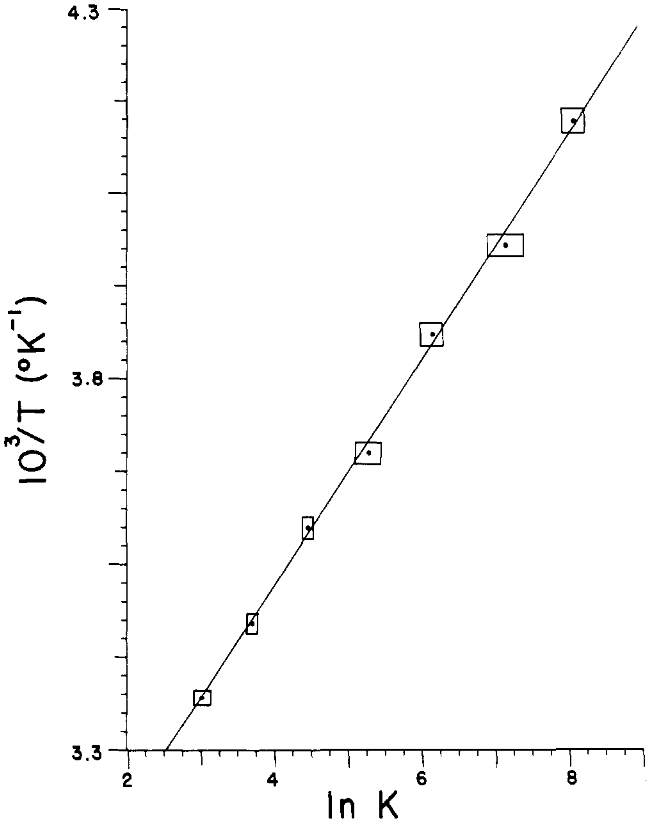


Figure 2. Plot of ln K vs. $10^3/T$ for the equilibrium $IrCl(CO)(PMe_3)_2 + COS \rightleftharpoons IrCl(CO)(\eta^2\text{-}COS)(PMe_3)_2$.

Table I. Determination of K for the Equilibrium (in Toluene)

$IrCl(CO)(PMe_3)_2 + COS \rightleftharpoons IrCl(CO)(COS)(PMe_3)_2$

T, K[a]	A[Ir(COS)][b]	A[Ir][c]	f[d]	10^3[COS],[e] M	K, M^{-1}	ln K
241.1	199	19	0.933	3.17	3.3 10^2	8.10
251.0	177	28	0.913	4.86	1.30 10^2	7.17
259.0	123	34	0.895	7.56	478	6.17
270.0	125	58	0.870	10.8	200	5.30
278.0	90	71	0.848	14.6	86.9	4.46
288.0	68	90	0.823	18.3	41.3	3.72
296.5	63	141	0.797	21.5	20.8	3.04

[a] To ±1 K. [b] A[Ir(COS)] = integrated $^{31}P\{^1H\}$ NMR peak area of $IrCl(CO)(COS)(L)_2$. [c] A[Ir] = integrated $^{31}P\{^1H\}$ NMR peak area of $IrCl(CO)(L)_2$. [d] f = (mol of COS(l))/(mol of COS(l) + mol of COS(v)). See ref 8. [e] $[COS] = f\{[COS]_0 - [IrCl(CO)(PMe_3)_2]_0(A[Ir(COS)]/(A[Ir] + A[Ir(COS)]))\}$, where for this experiment $[COS]_0 = [IrCl(CO)(PMe_3)_2]_0 = 0.039$ M.

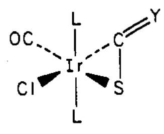
Table II. Infrared Data for the Complexes[a]

	ν(CO)	ν(C=O/C=S)	ν(IrCS)	ν(IrCl)
$IrCl(CO)(\eta^2\text{-}CS_2)(PPh_3)_2$[b]	2013	1161 1154		
$IrCl(CO)(\eta^2\text{-}CS_2)(PMePh_2)_2$[c]	2015	1156	660	
$IrCl(CO)(\eta^2\text{-}COS)(PMe_2Ph)_2$	2036	1748	662	
$IrCl(CO)(\eta^2\text{-}CS_2)(PMe_2Ph)_2$	2010	1149	650	252
$IrCl(CO)(\eta^2\text{-}COS)(PMe_3)_2$	2017	1730	660	241
$IrCl(CO)(\eta^2\text{-}CS_2)(PMe_3)_2$	2010	1152 1148	659	244

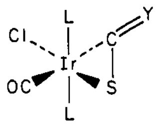
[a] In Nujol mull, except where noted; all values in cm^{-1}. [b] Reference 1. [c] In CS$_2$.

Results and Discussion

The complexes $IrCl(CO)(L)_2$ (L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3) react with CS_2 to afford complexes in which the CS_2 molecule is bound to the metal through a C=S bond.[1,2,9] The CS_2 complexes with L = PPh_3 and $PMePh_2$ dissociate CS_2, even in the solid state, but for L = PMe_2Ph and PMe_3 the solids are stable under vacuum. The complexes with smaller, more basic phosphine ligands (L = PMe_2Ph, PMe_3) also react with COS to afford similar products, which dissociate COS in the solid state and in solution at room temperature. The presence of only one terminal carbonyl and one metal–chloro stretching vibration in the infrared spectrum and of a singlet in the $^{31}P\{^1H\}$ NMR spectrum is consistent with the formation of a single isomer, either I or II. For Ir(III) complexes that have a sulfur-bound ligand trans to a chloro ligand, the metal–chloro stretching frequencies fall between 287 and 257 cm^{-1}.[10,11] The low values of ν(IrCl) in these $IrCl(CO)(\eta^2\text{-}SCY)(L)_2$ complexes, which are in the range reported for chloro ligands trans to acyl ligands,[2] suggest that isomer I is formed.



I



II

Y = O, S; L = PMe_2Ph, PMe_3

These structurally similar complexes dissociate SCY (Y = O, S). We have investigated the relative stabilities of these Ir(CS$_2$) and Ir(COS) complexes toward dissociation as no comparable data are available in the literature. Thermochemical constants for the reactions of $IrCl(CO)(L)_2$ with CS_2 and COS are listed in Table III (eq 1–4). The large equilibrium constant favoring the reaction of $IrCl(CO)(PMe_3)_2$ with CS_2 precluded the determination of values of ΔH and ΔS for this reaction.

The energy required to rearrange the square-planar complex to the pseudooctahedral complex should be very similar upon addition of COS or CS_2 since both ligands are bound through a C–S bond and hence the resultant complexes have similar steric requirements. Therefore, if we assume solvation effects are unimportant, the values of ΔH for eq 1 and 2 are a measure of the relative Ir(COS) and Ir(CS$_2$) bond energies.

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Table III. Thermodynamic Constants for the Equilibria (in Toluene)

$IrCl(CO)(L)_2 + SCY \rightleftharpoons IrCl(CO)(\eta^2\text{-}SCY)(L)_2$

L	Y	K_{eq}(30 °C), M^{-1}	ΔH, kcal/mol	ΔS, eu	eq no.
PMe_2Ph	O	1.7 ± 0.4[a]	-11.8 ± 1.1	-38 ± 5	1
PMe_2Ph	S	108 ± 20	-17.1 ± 2.5	-47 ± 9	2
PMe_3	O	12.9 ± 3	-13.1 ± 1.2	-38 ± 5	3
PMe_3	S	>1400			4

[a] Limit of error, determined graphically.

From these data we estimate that the $Ir(CS_2)$ bond is 1.4 times as strong as the $Ir(COS)$ bond. The principal bonding interaction in similar iridium complexes is thought to result from donation of electron density from the highest occupied molecular orbital (HOMO) of the $IrCl(CO)(L)_2$ complex to the lowest unoccupied molecular orbital (LUMO) of the ligand, as the stability of such complexes toward dissociation of the ligand increases with increasing electron affinity of the ligand.[12] Consistent with this, the electron affinities of CS_2 and COS are 1.0 and 0.46 eV, respectively.[13] The values of K for eq 5 and 6

$$IrCl(CO)(\eta^2\text{-}COS)(PMe_2Ph)_2 + CS_2 \rightleftharpoons IrCl(CO)(\eta^2\text{-}CS_2)(PMe_2Ph)_2 + COS$$

$$K = 64 \tag{5}$$

$$IrCl(CO)(\eta^2\text{-}COS)(PMe_3)_2 + CS_2 \rightleftharpoons IrCl(CO)(\eta^2\text{-}CS_2)(PMe_3)_2 + COS$$

$$K > 100 \tag{6}$$

reflect this increase in stability that results from substitution of CS_2 for COS, and the values of ΔH and ΔS for eq 5 ($\Delta H = -5.3 \pm 2.7$ kcal/mol, $\Delta S = -9 \pm 10$ eu)[14] suggest that it is the increase in enthalpy, and not entropy, that favors formation of the CS_2 complexes. Since the steric requirements of the COS and CS_2 complexes should be similar (for the same L), we believe this increased stability is primarily electronic in nature.

Equations 7 and 8 illustrate that formation of the CS_2 and COS complexes is favored by smaller, more basic phosphine ligands. Surely, steric as well as electronic factors are important here.

$$IrCl(CO)(\eta^2\text{-}COS)(PMe_2Ph)_2 + IrCl(CO)(PMe_3)_2 \rightleftharpoons IrCl(CO)(\eta^2\text{-}COS)(PMe_3)_2 + IrCl(CO)(PMe_2Ph)_2$$

$$K = 7.6 \tag{7}$$

$$IrCl(CO)(\eta^2\text{-}CS_2)(PMe_2Ph)_2 + IrCl(CO)(PMe_3)_2 \rightleftharpoons IrCl(CO)(\eta^2\text{-}CS_2)(PMe_3)_2 + IrCl(CO)(PMe_2Ph)_2$$

$$K > 13 \tag{8}$$

The chemistry of metal–(COS) complexes is dominated by reactions that involve cleavage of the C=S bond,[1,3,15-17] whereas analogous reactions of metal–(CS_2) complexes[18] represent only a small fraction of the observed chemistry.[18-23] The reactions discussed in this work illustrate that the bonding interaction between $IrCl(CO)(L)_2$ complexes and COS is weaker than for CS_2 and that a more basic metal complex is needed to stabilize a metal–(COS) complex than a metal–(CS_2) complex. Transfer of electron density from the basic metal center to the π^* orbital of COS should weaken the C=S bond. This need for a basic metal center to stabilize metal–(COS) bond formation and the destabilization of the weak C=S bond[24] that results account for the paucity of metal–(COS) complexes and the instability of those that have been prepared.

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Registry No. $IrCl(CO)(\eta^2\text{-}CS_2)(PMePh_2)_2$, 81178-13-4; $IrCl(CO)(\eta^2\text{-}CS_2)(PMe_2Ph)_2$, 81178-14-5; $IrCl(CO)(\eta^2\text{-}COS)(PMe_2Ph)_2$, 81178-15-6; $IrCl(CO)(\eta^2\text{-}CS_2)(PMe_3)_2$, 81178-16-7; $IrCl(CO)(\eta^2\text{-}COS)(PMe_3)_2$, 81178-17-8; $IrCl(CO)(PMePh_2)_2$, 15318-32-8; $IrCl(CO)(PMe_2Ph)_2$, 21209-82-5; $IrCl(CO)(PMe_3)_2$, 21209-86-9.

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