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Infrared and Kinetic Studies of Group VI Metal Pentacarbonyl Amine Compounds

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Compounds of the type $M(CO)_5$amine, where M = Cr, Mo, and W, undergo thermal decomposition reactions to form $M(CO)_6$ reaction products. The rate of reaction follows the first-order rate law: rate = $k_1[M(CO)_5\text{amine}]$. The rate constant k_1, for a particular metal, was found to decrease as the pK_a of the amine increased. This is consistent with the proposed dissociative mechanism which involves a cleavage of the metal–nitrogen bond in the rate-determining step. Compounds containing unsaturated amine ligands, such as pyridines, were observed to be much more stable than their pK_a values would indicate. This is interpreted as resulting from a small amount of metal–nitrogen "back-bonding." No correlation was observed between the nature of the metal–nitrogen bond, as indicated by the rate constant (k_1) or pK_a for the amine group, and the calculated CO stretching force constants.

Introduction

Kinetic studies of $Mo(CO)_5$amine complexes in solution have shown these complexes to decompose readily yielding $Mo(CO)_6$.[1] The decomposition is suggested to proceed by a rate-determining dissociation of the amine, resulting in the production of $[Mo(CO)_5]$ as the reactive intermediate (eq 1 and 2).[2]

$$Mo(CO)_5\text{amine} \xrightarrow{\text{slow}} [Mo(CO)_5] + \text{amine} \qquad (1)$$

$$[Mo(CO)_5] + Mo(CO)_5\text{amine} \xrightarrow{\text{fast}} Mo(CO)_6 + Mo(CO)_4\text{amine}(?) \qquad (2)$$

In the presence of Lewis bases (L), such as phosphines or arsines, the $[Mo(CO)_5]$ intermediate is trapped in the form of $Mo(CO)_5L$ complexes. This substitution process can also occur *via* an SN2 process (eq 3). A similar mechanism has been proposed by Ingemanson and Angelici[3] for the tungsten pentacarbonyl amine analogs.

$$\begin{tikzcd} Mo(CO)_5\text{amine} \arrow[r, shift left, "k_1"] \arrow[dr, "L"', "k_2"] & {[Mo(CO)_5]} \arrow[l, shift left, "k_{-1}"] \arrow[d, "\text{fast}"', "L"] & + \text{amine} \quad (k_1 \gg k_{-1}) \\ & Mo(CO)_5L & \end{tikzcd} \qquad (3)$$

In this study, we have measured rates of decomposition in an extensive series of $M(CO)_5$amine complexes, where M = Cr, Mo, and W. It was found that, for a given metal, the rate of decomposition (k_1) increases as the basicity of the bound amine decreases as measured by the pK_a of the free amine ligand. Complexes containing unsaturated amines, such as pyridines, which are theoretically capable of π bonding with transition metals, were found to be much more stable than those containing saturated amines with comparable pK_a's. This increased stability may be attributed to some metal–nitrogen π bonding involving the empty π^* orbitals of the aromatic ring system and the filled d orbitals on the metal.

In addition to the kinetic studies, ^{12}CO and ^{13}CO stretching frequencies were measured for a large series of amine complexes. These were employed in the calculation of the CO stretching force constants. σ and π parameters were calculated employing the method of Graham.[4] These parameters were designed to separate σ-donor and π-acceptor properties of substituent ligands in substituted metal carbonyls. It was found that these parameters did not change except within the limits of experimental error.

Experimental Section

Preparation of Metal Carbonyl Amine Compounds.—$Mo(CO)_6$ and $W(CO)_6$ were generously donated by Climax Molybdenum Co. and $Cr(CO)_6$ was purchased from Strem Chemical Co.; all were used without further purification. Amines were distilled under vacuum before use. The general preparation and procedure is outlined below.

Approximately 2 g of metal hexacarbonyl and 5–7 ml of amine in 50 ml of THF were irradiated with a Hanovia 550-W ultraviolet lamp from 2 to 4 hr. The quartz reaction vessel was maintained under a positive atmosphere of dry nitrogen. After irradiation, the bright yellow solution was evaporated to dryness under vacuum at room temperature. Excess $M(CO)_6$ was removed from the remaining solid by vacuum sublimation at 35–50° and the $M(CO)_5$amine extracted from the residue with *n*-hexane. Recrystallization at −80° from hexane resulted in bright yellow products.

The carbon–hydrogen analyses as obtained for the pyridine series are given here. *Anal.* Calcd for $Cr(CO)_5NC_5H_5$: C, 44.3; H, 1.84. Found: C, 44.27; H, 1.83 (mp 96–97°). Calcd for $Mo(CO)_5NC_5H_5$: C, 38.15; H, 1.59. Found: C, 38.40; H, 1.60 (mp 85–86°). Calcd for $W(CO)_5NC_5H_5$: C, 29.8; H, 1.24. Found: C, 30.03; H, 1.34 (mp 108–109°). All other compounds were characterized by their infrared spectra in the CO stretching region. Their respective melting points are reported: $Cr(CO)_5$piperidine, 70–71°; $Mo(CO)_5$piperidine, 75–76°; $W(CO)_5$piperidine, 99–100°; $Cr(CO)_5$pyrrolidine, 58–60°; $Mo(CO)_5$pyrrolidine, 56–57°; $W(CO)_5$pyrrolidine, 76–77°; $Cr(CO)_5$cyclohexylamine, 103–105°; $Mo(CO)_5$cyclohexylamine, 93°; $W(CO)_5$cyclohexylamine, 120–122°; $Cr(CO)_5$morpholine, 110° dec; $Mo(CO)_5$morpholine, 104–105°; $W(CO)_5$morpholine, 140–141°; $Cr(CO)_5$(3-picoline), 66–67°; $Mo(CO)_5$(3-picoline), 54–57°; $W(CO)_5$(3-picoline), 69–72°; $Cr(CO)_5$aniline, 100° dec; $W(CO)_5$aniline, 118° dec; $Cr(CO)_5$pyrrole, 95–100°; $Cr(CO)_5$-amphetamine-*d*, <22°; $Cr(CO)_5$DABCO,[5] 127° dec; $Cr(CO)_5$-(DABCO)$Cr(CO)_5$, 157–162°; $Cr(CO)_5$(1,1-dimethylhydrazine), 110° dec.

$Cr(CO)_5$aniline.—After the solvent was removed as above, the residue was transferred to a sublimator where excess aniline (mp −6.2°) was distilled onto a cold finger maintained at −80°. Excess $Cr(CO)_6$ was removed by sublimation at room temperature. No further purification of the complex was attempted because of its instability in solution.

$[W(CO)_5]_2$DABCO.—$W(CO)_6$ and DABCO in a 2:1 ratio were irradiated in 50 ml of THF for 3 hr. After removal of solvent under vacuum, excess $W(CO)_6$ was recovered by vacuum sublimation at 25°. Any $W(CO)_5$DABCO formed was extracted in hexane and recrystallized at −80°, mp 154°. $[W(CO)_5]_2$-DABCO was extracted from the residue with chloroform and

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[1] D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 1679 (1968).

[2] D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Amer. Chem. Soc.*, **93**, 2807 (1971).

[3] C. M. Ingemanson and R. J. Angelici, *Inorg. Chem.*, **7**, 2646 (1968).

[4] W. A. G. Graham, *ibid.*, **7**, 315 (1968).

[5] DABCO is 1,4-diazobicyclo[2.2.2]octane.

recrystallized at −80° (mp 180° dec). The infrared spectra in the carbonyl stretching region of both $W(CO)_5DABCO$ and $[W(CO)_5]_2DABCO$ in $CHCl_3$ were very similar with respect to band positions and relative intensities. The frequencies in chloroform are 2073.5 and 2074.5 ($A_1^{(2)}$), 1915.0 and 1919.5 ($A_1^{(1)}$), and 1922.0 and 1930.5 cm^{-1} (E) for $W(CO)_5DABCO$ and $[W(CO)_5]_2DABCO$, respectively. The $[W(CO)_5]_2DABCO$ moiety therefore has a spectrum in the CO stretching region indicative of a localized C_{4v} environment for the carbonyl groups as expected. *Anal.* Calcd for $[W(CO)_5]_2DABCO$: mol wt 760; C, 25.30; H, 1.58. Found: mol wt 772 (osmometric in $CHCl_3$); C, 25.57; H, 1.68. Chemical analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Kinetic Measurements.—The rates of decomposition of the $M(CO)_5$amine complexes were followed by observing the decrease in the most intense CO stretching vibration (E mode) with time. Kinetic studies were carried out on a Perkin-Elmer 521 spectrophotometer equipped with a linear-absorbance potentiometer and an automatic-scan recycle. Samples were run in Spectrograde hexane in a 1-mm NaCl cell which was fitted with a Beckman water jacket. The temperature of the jacket was maintained with a constant-temperature water-circulating bath to ±0.1°. Temperatures were recorded by carefully calibrating the cell's internal temperature with the temperature of the water bath. A copper–constantan thermocouple was used for this purpose.

Rate constants were calculated using a linear-least-squares computer program for the first-order rate plots of ln $(A_t - A_\infty)$ *vs.* time, where A_t is the absorbance at time t and A_∞ is the absorbance at infinite time. All plots were found to be linear to approximately 80% of the completed reaction.

Metal hexacarbonyls were formed in 35–50% yields. An attempt was made to identify the other product(s) of the reactions. The insoluble, red-brown solid present upon completion of the reaction was found to contain, in the case of $Cr(CO)_5$-piperidine, 40.7% Cr, 27.7% C, 6.2% H, and 7.8% N. This is probably a mixture of 73% $Cr(CO)_3(piperidine)_3$ and the remainder Cr metal or oxide. Two broad bands in the infrared spectrum (Nujol mull) of this material existed at 1920 and 1780 cm^{-1} which further supports this suggestion. Free amines and carbon monoxide at the concentrations involved (10^{-4} M) have no effect on the reaction kinetics. The rate of production of $M(CO)_5L$ complexes in 100% yields from $M(CO)_5$amine complexes is the same at low L concentrations as the decomposition rates of the $M(CO)_5$amines.[2] Therefore, we are truly observing the same first-order process as in the substitution reactions (see eq 3).

Infrared Spectral Measurements and Calculations.—Infrared frequency data were obtained employing a Perkin-Elmer 521 grating spectrophotometer calibrated in the CO stretching region with CO vapor above 2000 cm^{-1} and H_2O vapor below 2000 cm^{-1}. Spectrograde *n*-hexane was used without further treatment. Samples were run at various concentrations to ensure observation of natural abundance ^{13}CO stretching frequencies.

Force constants were calculated using ^{13}CO frequency data with an iterative computer program. In general, the three observed vibrations for the all-^{12}CO species and the two observed vibrations for the monosubstituted ^{13}CO equatorial species were used as input in these calculations. The program, based on the work of Schachtschneider and Snyder,[6] adjusts a set of force constants common to a group of related molecules. Calculations were performed by using an energy-factored block matrix for the carbonyl stretching modes but without any other predetermined constraints on the force field.

Results and Discussion

Kinetic Studies.—The rate of decomposition of $M(CO)_5$amine complexes obeys the first-order rate law

$$\text{rate} = k_1[M(CO)_5\text{amine}]$$

The mechanism is proposed to involve a simple dissociative rate-determining step and has been discussed elsewhere.[1-3] The values of the rate constant k_1 which were calculated from the first-order rate expression are given in Tables I–III at several temperatures between 23 and 68°. Reproducibility was generally within 5% for all of the species studied with the exceptions $Cr(CO)_5$pyrrole and $Cr(CO)_5$aniline, where differences of 20–40% were observed. The average values are reported for k_1 in these cases.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE DISSOCIATION OF $Cr(CO)_5$amine COMPOUNDS IN HEXANE

Amine	pK_a[a]	Temp, °C	10^4k_1, sec^{-1}
Piperidine	11.12	45.4	1.03
		51.4	2.05
		57.2	4.19
		62.0	7.69
Cyclohexylamine	10.68	45.4	3.17
		51.4	8.06
		57.2	15.9
		62.0	28.1
Morpholine	8.36	45.4	6.67
		51.4	13.9
		57.2	30.0
		62.0	49.1
1,1-Dimethylhydrazine	7.21	45.4	40.7
3-Picoline	5.52	45.4	0.747
		51.4	1.68
		57.2	3.14
		62.0	6.37
Pyridine	5.20	45.4	1.16
		51.4	2.52
		57.2	4.53
		62.0	8.81
Aniline	4.61	23.8	34.9
		34.7	165
		45.4	705[b]
Pyrrole	−3.80	23.8	0.593
		34.7	4.63
		45.4	22.5

[a] Values as reported at 25° by D. D. Perrin, "Dissociation Constants in Aqueous Solution," Butterworths, London, 1965. [b] This rate constant was obtained by extrapolation of the rate data to 45.4°.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE DISSOCIATION OF $Mo(CO)_5$amine COMPOUNDS IN HEXANE

Amine	pK_a	Temp, °C	10^4k_1, sec^{-1}
Piperidine	11.12	45.4	1.40
		51.4	3.25
		57.2	6.56
		62.0	8.13
Cyclohexylamine	10.68	45.4	5.10
		51.4	9.83
		57.2	17.9
		62.0	32.1
Pyridine	5.20	45.4	1.78
		51.4	4.56
		57.2	8.56
		62.0	15.1

TABLE III

FIRST-ORDER RATE CONSTANTS FOR THE DISSOCIATION OF $W(CO)_5$amine COMPOUNDS IN HEXANE

Amine	pK_a	Temp, °C	10^5k_1, sec^{-1}
Cyclohexylamine	10.68	62.0	3.97
Pyridine	5.20	62.0	1.66
Aniline	4.61	45.4	140

The activation parameters for this first-order, dissociative process are reported in Table IV. For comparative purposes the analogous parameters for CO dissociation from the parent hexacarbonyls are also listed. In all cases the enthalpy of activation for the metal–nitrogen bond cleavage is 10–15 kcal lower than

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(6) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 85, 117 (1963).

TABLE IV

ACTIVATION PARAMETERS FOR THE $M(CO)_5$amine DISSOCIATIVE PROCESS IN HEXANE

Compound	$\Delta H_1{}^*$,[d] kcal/mol	$\Delta S_1{}^*$,[d] eu
$Cr(CO)_6$[a]	40.2	22.6
$Cr(CO)_5$piperidine	25.7 ± 1.2	3.8 ± 3.8
$Cr(CO)_5$cyclohexylamine	27.7 ± 1.2	12.1 ± 3.8
$Cr(CO)_5$morpholine	25.8 ± 1.2	7.9 ± 3.8
$Cr(CO)_5$(3-picoline)	26.9 ± 1.2	6.8 ± 3.7
$Cr(CO)_5$pyridine	25.4 ± 1.1	3.1 ± 3.5
$Cr(CO)_5$aniline	26.4 ± 1.0	19.0 ± 3.2
$Cr(CO)_5$pyrrole[b]	27.1 ± 4.5	14.3 ± 14.0
$Mo(CO)_6$[a]	31.7 ± 1.4	6.7 ± 3.7
$Mo(CO)_5$piperidine	23.1 ± 1.1	−3.9 ± 3.5
$Mo(CO)_5$cyclohexylamine	23.1 ± 1.1	−1.2 ± 3.4
$Mo(CO)_5$pyridine	27.0 ± 1.2	8.9 ± 3.7
$W(CO)_6$[a]	39.9	13.8
$W(CO)_5$morpholine[c]	22.5	−13

[a] Values taken from R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968). [b] Rate constant reproducibility was poor for this species, thereby leading to large errors in the calculated values of $\Delta H_1{}^*$ and $\Delta S_1{}^*$. [c] Values taken from ref 3. [d] These errors represent standard deviations—95% confidence level.

that of the corresponding metal–carbon bond in the hexacarbonyl species. This difference in stability is primarily due to the fact that in the M–CO bond there is a substantial π-bonding interaction. This interaction is not possible in metal-saturated amine bonds and is not present to an appreciable extent in metal-unsaturated amine bonds as activation parameters indicate. In addition, there will also be expected some differences in the σ bonds formed between transition metals and carbonyl or amine ligands.

As the basicity of the amine in the $M(CO)_5$amine complexes is increased, the first-order rate constants, k_1, were observed to decrease in a predictable manner. Within the chromium series where a large quantity of data was collected, there is a fairly linear correlation between the log k_1 and the pK_a of the amine (Figure 1). This trend is also observed for the limited data presented in the Mo and W series of complexes. The slope of the least-squares line obtained from plotting ($-$log k_1) *vs.* pK_a is positive (+0.43). This is consistent with the proposed reaction mechanism of a simple S$_N$1 dissociative process which involves a cleavage of the metal–nitrogen bond in the rate-determining step. Similar linear free energy relationships have been observed for the dissociation of CO in (substituted *o*-phenanthroline)$M(CO)_4$ complexes.[7]

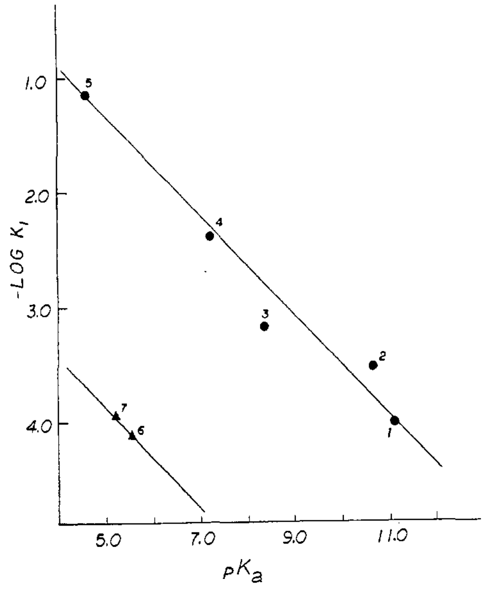

Figure 1.—Free energy plots of $-$log k_1 *vs.* pK_a for the decomposition reactions of $Cr(CO)_5$amine. The numbers represent the following amine bases: 1, piperidine; 2, cyclohexylamine; 3, morpholine; 4, 1,1-dimethylhydrazine; 5, aniline; 6, 3-picoline; 7, pyridine.

The correlation of log k_1 with the pK_a of the amine ligand is good within the saturated amine series. The unsaturated amines (pyridines and pyrrole) show a similar correlation of stability with pK_a but are substantially more stable than saturated amine complexes with the same amine pK_a value. This strengthening of the metal–amine bond may be attributed to some degree of metal–nitrogen π bonding.

MO calculations[8] on pyrrole and pyridine indicate the π^* orbitals are the lowest lying empty orbitals. The energies of these orbitals are much higher than the corresponding orbitals of carbon monoxide. However, it is possible for some small extent of "back-bonding" to occur between unsaturated amines and transition metals. The π-acceptor capability of the aromatic nitrogen would in turn increase the nitrogen's σ-donor ability. This would account for the trend between log k_1 and the pK_a of the unsaturated amine ligands. However, the correlation would be expected to be much less defined in this case, where both σ and π bonding is possible, than in the saturated amine case which involves only a donor bond.

The activation energies for the first-order process (Table IV) are remarkably similar for the amine compounds of chromium. They do not reflect expected trends in the Cr–N bond strengths in $Cr(CO)_5$amine compounds. The differences in the rates of these reactions appear to depend largely on differences in the entropies of activation.

The enthalpies of activation of the $M(CO)_5$amine compounds decrease for a given saturated amine ligand in the order Cr > Mo $\sim$ W. This order is in agreement with the expected strengths of the metal–nitrogen bonds since chromium and nitrogen orbitals are more closely matched in both size and energy than the corresponding sets in either Mo or W. The thermal stability of the $W(CO)_5$amine complexes appears to be mainly due to the entropies of activation. A trend toward more negative entropies as one proceeds down the group VI metals has also been observed in $M(CO)_4$-(*o*-phen) complexes.[7] However, this trend does not appear to be general.

Infrared Studies.—$M(CO)_5$amine compounds are ideally of C_{4v} symmetry resulting in three infrared-allowed CO stretching vibrations, two of symmetry A_1 and one of E symmetry. These are observed at approximately 2075 (w), 1935 (vs), and 1920 (s) cm^{-1} for the $A_1{}^{(2)}$, E, and $A_1{}^{(1)}$ symmetry modes, respectively. In addition bands of very low intensity are observed at $\sim$2066 and 1905 cm^{-1} and are assigned to vibrations due to ^{13}CO in natural abundance in one equatorial position. This has been confirmed by isotopic enrichment studies in $Mo(CO)_5$piperidine.[2]

Table V contains the observed and calculated frequencies for both ^{12}CO and ^{13}CO species in an extensive series of $M(CO)_5$amine compounds, M = Cr, Mo, and

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(7) J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 988, 992 (1967).

(8) E. Clementi, *J. Chem. Phys.*, **46**, 4731 (1967).

TABLE V

CO STRETCHING FREQUENCIES AND FORCE CONSTANTS IN $M(CO)_5$amine COMPOUNDS

Amine	Freq,[a] cm^{-1}					Force constants,[b] mdyn/Å				
	$A_1^{(2)}$	$A_1^{(1)}$	E	^{13}CO (equatorial)		k_1	k_2	k_c'	k_c	k_t
M = Cr										
Piperidine	2068.6	1916.3	1933.0	2060.5	1901.0	15.06	15.76	0.31	0.35	0.68
	(2068.5)	(1916.8)	(1931.8)	(2060.6)	(1902.6)					
Pyrrolidine	2068.5	1916.5	1933.5	2060.5	1902.5	15.04	15.77	0.33	0.33	0.68
	(2069.5)	(1917.1)	(1932.6)	(2061.4)	(1903.5)					
Diethylamine	2068.0	1916.0	1932.0	2060.5	1901.0	15.03	15.75	0.33	0.33	0.68
	(2068.5)	(1916.4)	(1931.2)	(2060.5)	(1902.2)					
n-Butylamine	2070.0	1916.5	1935.0	2062.5	1903.0	15.02	15.77	0.26	0.44	0.65
	(2070.0)	(1916.8)	(1934.3)	(2062.7)	(1903.5)					
Cyclohexylamine	2069.0	1916.0	1934.5	2061.5	1902.5	15.03	15.78	0.33	0.33	0.68
	(2070.1)	(1916.5)	(1933.2)	(2062.0)	(1903.9)					
Morpholine	2070.5	1921.0	1936.0	2062.5	1903.5	15.11	15.80	0.33	0.33	0.68
	(2071.5)	(1921.4)	(1934.5)	(2063.5)	(1905.6)					
3-Picoline	2070.0	1918.5	1937.5	2061.5	1908.0	15.06	15.81	0.33	0.33	0.66
	(2070.8)	(1918.4)	(1936.7)	(2062.8)	(1906.9)					
Pyridine	2071.0	1918.8	1937.5	2062.0	1905.5	15.08	15.82	0.32	0.33	0.66
	(2071.1)	(1919.5)	(1936.8)	(2063.1)	(1907.2)					
Aniline	2072.5	1916.5	1936.5			15.03	15.82	0.33	0.33	0.67
Pyrrole	2077.0	1924.0	1948.8	2068.5	1915.5	15.13	15.98	0.32	0.32	0.62
	(2076.7)	(1923.8)	(1949.6)	(2068.7)	(1917.3)					
Amphetamine-*d*	2070.0	1915.5	1934.0			15.02	15.78	0.33	0.33	0.67
M = Mo										
Piperidine	2073.1	1921.1	1938.9	2065.0	1907.4	15.10	15.86	0.31	0.33	0.69
	(2073.1)	(1921.6)	(1937.9)	(2065.1)	(1908.4)					
Pyrrolidine	2075.5	1920.5	1939.0	2067.0	1907.5	15.10	15.85	0.34	0.34	0.67
	(2075.1)	(1920.4)	(1938.4)	(2067.1)	(1908.5)					
Cyclohexylamine	2076.0	1919.5	1940.0	2068.5	1908.0	15.08	15.88	0.34	0.34	0.67
	(2077.0)	(1919.4)	(1940.4)	(2068.8)	(1909.9)					
Morpholine	2076.5	1924.0	1941.0	2068.5	1908.5	15.15	15.89	0.33	0.33	0.69
	(2077.3)	(1924.3)	(1939.5)	(2069.2)	(1910.4)					
3-Picoline	2075.5	1920.5	1941.5	2068.5	1910.0	15.08	15.89	0.33	0.33	0.67
	(2076.0)	(1919.9)	(1941.0)	(2067.9)	(1910.7)					
Pyridine	2076.5	1922.5	1943.5	2068.0	1912.0	15.16	15.91	0.30	0.36	0.66
	(2076.2)	(1922.6)	(1943.1)	(2068.3)	(1912.4)					
M = W										
Piperidine	2073.5	1918.0	1928.5	2065.0	1898.0	15.08	15.73	0.35	0.35	0.72
	(2073.1)	(1918.2)	(1927.6)	(2065.0)	(1899.3)					
Pyrrolidine	2073.0	1918.5	1928.5	2065.0	1898.0	15.09	15.73	0.35	0.35	0.72
	(2073.2)	(1918.8)	(1927.6)	(2065.1)	(1899.3)					
Diethylamine	2073.5	1917.5	1928.5	2065.0	1897.0	15.08	15.73	0.35	0.35	0.72
	(2073.3)	(1918.3)	(1927.4)	(2065.1)	(1899.1)					
Cyclohexylamine	2074.0	1916.5	1929.5	2064.5	1898.0	15.06	15.75	0.35	0.35	0.73
	(2074.6)	(1917.2)	(1928.3)	(2066.5)	(1899.9)					
Morpholine	2074.5	1922.0	1930.5	2066.5	1899.0	15.15	15.75	0.35	0.35	0.70
	(2073.5)	(1922.4)	(1929.9)	(2065.4)	(1901.5)					
3-Picoline	2073.5	1919.0	1931.5	2065.5	1903.5	15.09	15.77	0.35	0.31	0.71
	(2074.9)	(1919.0)	(1930.7)	(2066.8)	(1902.1)					
Pyridine	2080.0	1920.5	1933.0	2066.5	1901.5	15.12	15.78	0.36	0.36	0.74
	(2079.1)	(1920.4)	(1929.9)	(2071.0)	(1901.6)					
Aniline	2076.5	1918.0	1933.0			15.09	15.77	0.35	0.35	0.70
Diazobicyclooctane	2073.5	1917.0	1926.8			15.07	15.72	0.36	0.36	0.72

[a] Calculated frequencies are shown in parentheses. The ^{13}CO data are for the monosubstituted ^{13}CO equatorial species in natural abundance. [b] Force constants are defined as in the article by H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Amer. Chem. Soc.*, **89,** 2844 (1967).

W, along with the calculated carbonyl force constants. The average error between experimental and calculated frequencies for all molecules is approximately 0.8 cm^{-1}. All spectra were observed in hexane solution. It would be advantageous to place some estimate on the quality of the fit of these force constants and also to compare constants calculated employing the iterative method with those calculated by the Cotton–Kraihanzel procedure.[9] Frequency data, along with the calculated CO force constants, for the $Mo(CO)_5$piperidine molecule enriched in ^{13}CO are contained in Table VI.

The computed force constants (k_1 and k_2) were tested for small errors in the input frequencies. The $A_1^{(2)}$, $A_1^{(1)}$, and E vibrational modes were each varied by ±3 cm^{-1} resulting in variations in k_1 and k_2 of 15.105 ± 0.047 and 15.849 ± 0.048, respectively. In addition the $A_1^{(2)}$ mode was varied by ∓3 cm^{-1}, while the $A_1^{(1)}$ and E modes were varied by ±3 cm^{-1}. This led to changes in k_1 of 15.105 ± 0.037 and k_2 of 15.849 ± 0.018. Therefore, it is not unreasonable to expect small errors in the force constant values of ±0.05 mdyn/Å. Indeed, if the overall errors involved in neglecting anharmonic corrections and mixing of CO vibrational modes with other vibrations in the molecule are considered, an error of ±0.05 mdyn/Å included in k_1 and k_2 is quite meaningful even for a series of related molecules.[10]

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(9) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84,** 4432 (1962).

(10) L. Jones, *Inorg. Chem.*, **7,** 1681 (1968).

TABLE VI

CO STRETCHING FREQUENCIES AND FORCE CONSTANTS IN ISOTOPICALLY ENRICHED $Mo(CO)_5$piperidine[a]

Molecule	Vibration	Freq, cm^{-1}			Force constants[b]				
		Input	Calcd	Obsd	k_1	k_2	k_t	k_c'	k_c
All ^{12}CO species (C_{4v})	A_1	2073.1	2073.5 (2073.1)	2073.1	15.100	15.858	0.694	0.307	0.330
	B_1	0.0	1986.9 (1986.3)	...	(15.100)	(15.855)	(0.691)	(0.308)	(0.329)
	E	1938.9	1938.0 (1937.9)	1938.9					
	A_1	1921.1	1921.5 (1921.6)	1921.1					
Monosubstituted ^{13}CO, equatorially (C_s)	A′	2065.0	2065.4 (2065.1)	2065.0					
	A′	0.0	1979.1 (1978.6)	...					
	A′	0.0	1922.8 (1922.8)	...					
	A″	0.0	1938.0 (1937.9)	1938.9					
	A′	1907.4	1908.4 (1908.4)	1907.4					
Monosubstituted ^{13}CO, axially (C_{4v})	A_1	0.0	2070.6	...					
	B_1	0.0	1986.9	...					
	E	0.0	1938.0	1938.9					
	A_1	1880.5	1881.3	1880.5					
Disubstituted ^{13}CO, equatorially (cis) (C_s)	A′	2055.5	2055.7	2055.5					
	A″	0.0	1973.2	...					
	A′	0.0	1923.9	...					
	A′	0.0	1908.7	...					
	A″	0.0	1908.0	...					

[a] Calculated frequencies and force constants in parentheses were computed using the first two species only. These correspond to the calculations listed for the various amine complexes in Table V. The average error in the calculated frequencies for this procedure was ±0.5 cm^{-1} or 0.026%. The average error in the calculated frequencies using the four isotopically related molecules was ±0.6 cm^{-1} or 0.030%. Force constant values are reported to three decimal places for comparison only. [b] The Cotton–Kraihanzel force constants are $k_1 = 15.105$, $k_2 = 15.849$, and $k_i = 0.330$. Therefore, in this instance the C–K force constants differ from those computed by the iterative method by ±0.01.

The infrared spectrum in the CO stretching region of a typical species, $Cr(CO)_5$piperidine, was observed in several solvents of varying polarity. Frequencies and calculated CO force constants are found in Table VII.

TABLE VII

VARIATION OF FREQUENCIES AND CALCULATED FORCE CONSTANTS WITH SOLVENT IN $Cr(CO)_5$piperidine

Solvent	Freq, cm^{-1}			Force constants[a]		
	$A_1^{(2)}$	$A_1^{(1)}$	E	k_1	k_2	k_i
n-Hexane	2068.0	1916.3	1932.5	15.03	15.75	0.33
CH_2Cl_2	2067.0	1889.5	1926.5	14.61	15.69	0.35
CCl_4	2080.0	1911.5	1929.0	14.98	15.78	0.37
$CHCl_3$	2067.0	1893.0	1927.0	14.66	15.69	0.35
THF	2063.5	1889.0	1920.5	14.61	15.61	0.35
Acetone	2065.5	1881.0	1927.5	14.46	15.70	0.34

[a] These were calculated by the method of F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84,** 4432 (1962).

Frequency data observed in nonpolar hydrocarbon solvent have been shown to approach those found in gas-phase spectra.[11] All frequencies show a substantial shift to lower frequency as the polarity of the solvent increases, presumably through an electric dipole interaction of the type $M–C^{\delta+}–O^{\delta-} \cdots$ solvent. The totally symmetric vibration involving mostly axial CO stretching motion, $A_1^{(1)}$, exhibits the largest solvent shifts. This is in agreement with previous observations in substituted metal carbonyl compounds which indicate the CO groups trans to ligands are more sensitive to solvent changes than those cis to ligands.[12]

Due to the substantial and selective solvent shifts in polar solvents noted it is suggested here that frequency data for $M(CO)_5$amine complexes obtained in polar solvents or Nujol mulls and, therefore, the calculated CO stretching force constants should be viewed with a great deal of caution.[13]

In the $M(CO)_5$amine series Graham parameters[4] were computed using $C_6H_{11}NH_2M(CO)_5$ as the reference compound. A positive value of σ or π parameter implies that the amine is acting as a σ or π acceptor, whereas a negative value of σ or π parameter implies the amine is a σ or π donor as compared to the cyclohexylamine reference ligand where σ and π are equal to zero. These parameters are found in Table VIII.[14]

TABLE VIII

GRAHAM σ AND π PARAMETERS FOR $M(CO)_5$amine COMPLEXES

Amine	pK_a	Δk_1	Δk_2	σ	π
		M = Cr			
Piperidine	11.12	+0.03	−0.02	−0.07	0.05
Pyrrolidine	11.27	+0.01	−0.01	−0.03	0.02
Diethylamine	10.98	0.00	−0.03	−0.06	0.03
n-Butylamine	10.64	−0.01	−0.01	−0.01	0.00
Cyclohexylamine	10.68	0	0	0	0
Morpholine	8.36	+0.08	+0.02	−0.04	0.06
3-Picoline	5.52	+0.03	+0.03	0.03	0.00
Pyridine	5.20	+0.05	+0.04	0.03	0.01
Aniline	4.61	0.00	+0.04	0.08	−0.04
Pyrrole	−3.8	+0.10	+0.20	0.30	0.10
Amphetamine	10.03	−0.01	0.00	0.01	−0.01
		M = Mo			
Piperidine	11.12	+0.01	−0.03	−0.07	0.04
Pyrrolidine	11.27	+0.02	−0.03	−0.08	0.05
Cyclohexylamine	10.68	0	0	0	0
Morpholine	8.36	+0.07	+0.01	−0.05	0.06
3-Picoline	5.52	0.00	+0.01	0.02	−0.01
Pyridine	5.20	+0.08	+0.03	−0.02	0.05
		M = W			
Piperidine	11.12	+0.02	−0.02	−0.06	0.04
Pyrrolidine	11.27	+0.03	−0.02	−0.07	0.05
Diethylamine	10.98	+0.02	−0.02	−0.06	0.04
Cyclohexylamine	10.68	0	0	0	0
Morpholine	8.36	+0.09	0.00	−0.09	0.09
3-Picoline	5.52	+0.03	+0.02	0.01	0.01
Pyridine	5.20	+0.06	+0.03	0.00	0.03
Aniline	4.61	+0.03	+0.02	0.01	0.01
1,4-Diazobicyclo-[2.2.2.]octane	8.40	+0.01	−0.03	−0.05	0.04

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(12) L. A. W. Hales and R. J. Irving, *Spectrochim. Acta, Part A*, **23,** 2981 (1967).

(13) S. C. Tripathi and S. C. Srivastava, *J. Organometal. Chem.*, **23,** 193 (1970).

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Since the estimated experimental uncertainties are ±0.12 and ±0.08 for the σ and π parameters, respectively, this study indicates there is essentially no change in these parameters (or force constants) with amine groups.[15] In fact, there is very little, if any, change in the force constants as one proceeds down the group VI metals.

The lack of sensitivity of carbonyl stretching force constants to the nature of the substituted amine ligands could be taken to indicate that the saturation point for acceptance of electron density of the $M(CO)_5$ moiety is low in the absence of good π-acceptor ligands and therefore all amines investigated may have met this minimum saturation level.[16] Alternatively, the difference in σ-donor abilities of the various amine ligands may not be enough to cause observable changes in the CO stretching force constants. The latter conclusion would imply that CO stretching force constants are not very sensitive to σ effects of these orders of magnitude, assuming pK_a values are good indicators of the amines' donating abilities.

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[15] These results are in disagreement with those of R. J. Angelici and M. D. Malone, *Inorg. Chem.*, **6**, 1731 (1967).

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Metal–Metal Bonded Organometallic Complexes. I. Synthesis of Ligand Derivatives of Tricarbonyl-π-cyclopentadienylmolybdenum Bonded to Dimethyl- and Trimethyltin[1]

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The compounds π-$C_5H_5Mo(CO)_2(L)Sn(CH_3)_3$ (L = $P(C_6H_5)_3$, $P(OC_6H_5)_3$, $P(C_6H_5)(CH_3)_2$, $P(OCH_2)_3CCH_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$) have been prepared by reaction of the anion $[\pi\text{-}C_5H_5Mo(CO)_2L]^-$ with $(CH_3)_3SnCl$. π-$C_5H_5Mo(CO)_2P(C_6H_5)_3$-$Sn(CH_3)_3$ was also prepared by the direct reaction of π-$C_5H_5Mo(CO)_3Sn(CH_3)_3$ and $P(C_6H_5)_3$ with or without solvent at 160°. At about 200° all these derivatives liberated $Sn(CH_3)_4$ but only for L = $P(C_6H_5)_3$ or $P(OCH_2)_3CCH_3$ was the other product characterized, namely, $[\pi\text{-}C_5H_5Mo(CO)_2(L)]_2Sn(CH_3)_2$. These two compounds were also prepared by other routes. Infrared and proton nmr spectra suggest that all the new compounds have a trans configuration.

Introduction

The organometallic compounds with a metal–metal bond between a group VIa transition metal (Cr, Mo, and W) and a group IVb metal (Si, Ge, Sn, and Pb) are well known[2] and preparatively accessible by a number of routes (*e.g.*, eq 1[3] and 2[4]). Previous investigations of the chemistry of these compounds have been limited to metal–metal bond cleavage (*e.g.*, eq 3[5]) and metal–nonmetal bond cleavage reactions (*e.g.*, eq 4,[6] 5,[7] and 6[8]).

$$[\pi\text{-}C_5H_5Cr(CO)_3]Na + (C_6H_5)_3GeCl \longrightarrow \pi\text{-}C_5H_5Cr(CO)_3Ge(C_6H_5)_3 + NaCl \qquad (1)$$

$$\pi\text{-}C_5H_5Mo(CO)_3H + (CH_3)_3SiN(CH_3)_2 \longrightarrow \pi\text{-}C_5H_5Mo(CO)_3Si(CH_3)_3 + HN(CH_3)_2 \qquad (2)$$

$$\pi\text{-}C_5H_5Mo(CO)_3GeR_3 + HCl \longrightarrow \pi\text{-}C_5H_5Mo(CO)_3H + R_3GeCl \qquad (3)$$

$$\pi\text{-}C_5H_5Mo(CO)_3Sn(C_6H_5)_3 + HCl \longrightarrow \pi\text{-}C_5H_5Mo(CO)_3Sn(C_5H_5)_2Cl + C_6H_6 \qquad (4)$$

$$\pi\text{-}C_5H_5Mo(CO)_3SnCl_3 + 8\text{-}C_9H_6NOH \longrightarrow \pi\text{-}C_5H_5Mo(CO)_3Sn(8\text{-}C_9H_6NO)Cl + HCl + Cl^- \qquad (5)$$

$$\pi\text{-}C_5H_5Mo(CO)_3Sn(CH_3)_3 + P(OC_6H_5)_3 \longrightarrow \pi\text{-}C_5H_5Mo(CO)_2P(OC_6H_5)_3Sn(CH_3)_3 + CO \qquad (6)$$

This paper describes the preparation of ligand derivatives of π-$C_5H_5Mo(CO)_3Sn(CH_3)_3$ (Table I) and an interesting high-temperature redistribution reaction (eq 7).

$$2\pi\text{-}C_5H_5Mo(CO)_2(L)Sn(CH_3)_3 \longrightarrow [\pi\text{-}C_5H_5Mo(CO)_2(L)]_2Sn(CH_3)_2 + Sn(CH_3)_4 \qquad (7)$$

Results and Discussion

π-$C_5H_5Mo(CO)_2P(C_6H_5)_3Sn(CH_3)_3$ was prepared by three different routes. The reaction of π-C_5H_5Mo-$(CO)_3Sn(CH_3)_3$ and $P(C_6H_5)_3$ in diglyme, or without solvent, at 160° gave the monosubstituted derivative as a white product. The preparation from the substituted anion $[\pi\text{-}C_5H_5Mo(CO)_2P(C_6H_5)_3]^-$ and $(CH_3)_3$-$SnCl$, however, gave a pale yellow product. An exhaustive comparison by ir, proton nmr, uv, and mass spectroscopy showed that the two compounds were identical. The white product gave a yellow solution in organic solvents. Earlier attempts to prepare the $P(C_6H_5)_3$ derivative by irradiation were un-

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[1] Presented in part at the 160th American Chemical Society Meeting, Chicago, Ill., Sept 1970; T. A. George, *Chem. Commun.*, 1632 (1970).

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