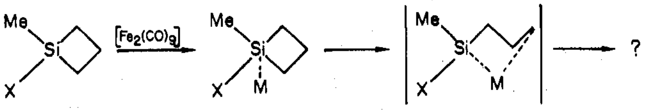
physical characteristics. As with **1**, compound **2** rapidly reduced ethanolic silver nitrate.

In an attempt to prepare the tin analogue $Ph_3Sn\overline{Si(Me)CH_2CH_2CH_2}$ of compounds **1** and **2** the dark color of Ph_3SnLi was not discharged upon addition to $Cl(Me)\overline{SiCH_2CH_2CH_2}$ in THF at low temperature. None of the coupled product was isolated from the reaction mixture. Similar results have been reported for the reaction between Ph_3SnLi and Me_3SiCl, where isolation of Ph_6Sn_2 in 69% yield from the resulting black suspension showed that metal–halogen exchange had taken place.[10]

Unlike trimethylsilyllithium, trimethylstannyllithium is easily prepared in THF solution.[11] Treatment of $Cl(Me)\overline{SiCH_2CH_2CH_2}$ with this reagent under conditions similar to those used in the preparation of **1** and **2** gave $Me_3Sn\overline{Si(Me)CH_2CH_2CH_2}$ (**3**) in 53% yield. The compound $Bu_3Sn{-}SiMe_3$ has been made (78%) similarly.[11] The stannylsilacyclobutane **3** rapidly reduced[1] ethanolic silver nitrate and showed the expected spectroscopic properties (see Table I).

It is known that members of the series $[Fe(\eta\text{-}C_5H_5)(CO)_x(PMePh_2)_{2-x}\overline{Si(Me)CH_2CH_2CH_2}]$ ($x = 0–2$) show increasing reactivity toward $[Fe_2(CO)_9]$ with increasing phosphine substitution at iron.[3] Thus, the dicarbonyl complex does not react, and although discrete products were not isolated in the other cases, reactions did occur. This is in marked contrast to the reactions[12,13] between $[Fe_2(CO)_9]$ and a silacyclobutane carrying organic substituents at silicon, where silaferracyclopentanes, e.g., $[\overline{Fe(CH_2CH_2CH_2SiMe_2)}(CO)_4]$, are formed in high yield. The germylsilacyclobutane, **2**, reacted with $[Fe_2(CO)_9]$ in a complex manner, mostly (^1H NMR) being polymerized; no tractable product was isolated. It is difficult to rationalize the marked difference in behavior toward $[Fe_2(CO)_9]$ found between metal-substituted silacyclobutanes and the simpler compounds, except on steric grounds, although the trends within the cyclopentadienyliron series follow from electronic arguments.[3] The reaction is known[12] to be highly regioselective when ring substituents are present, the iron entering the ring at the least hindered position. If ring opening does occur, strain energy release, together with steric resistance to recyclization, may explain the apparent formation of polymeric products:



M = attacking electrophile derived from $[Fe_2(CO)_9]$

Experimental Section

Experimental procedures and instrumentation were as described previously,[13] except that molecular weights were here measured osmometrically in chloroform. $Cl\overline{Si(Me)CH_2CH_2CH_2}$ was prepared from $Cl(CH_2)_3SiMeCl_2$ by reaction with magnesium.[1] Mass spectra are described elsewhere.[14]

A solution of triphenylsilyllithium[5] in THF was made from hexaphenyldisilane (8.60 g, 16.6 mmol), lithium wire (1.70 g, 246 mmol), and THF (100 cm^3). A solution of 1-chloro-1-methyl-1-silacyclobutane (0.84 g, 6.95 mmol) in THF (20 cm^3) was cooled to −50 °C and the clear red-brown Ph_3SiLi/THF solution added slowly with stirring until the color was just no longer discharged (35 cm^3). After stirring for a further 2 h at −50 °C, THF was removed in vacuo and the residue extracted with *n*-hexane (60 cm^3) and concentrated. Chromatography on "Florisil" in hexane followed by recrystallization from absolute ethanol gave white needles of 1-methyl-1-triphenylsilyl-1-silacyclobutane (**1**) (0.37 g, 15%). Anal. Calcd for $C_{22}H_{24}Si_2$: C, 76.7; H, 7.0; Si, 16.3; mol wt, 344. Found: C, 77.1; H, 7.15; Si, 16.5; mol wt, 359 ($CHCl_3$) or 344 (MS).

A dark red solution of triphenylgermyllithium[9] [from triphenylbromogermane (3.84 g, 10.0 mmol), lithium powder (0.69 g, 100 mmol), and THF (10 cm^3)] was added dropwise to a stirred solution of 1-chloro-1-methyl-1-silacyclobutane (1.58 g, 13.1 mmol) in THF (10 cm^3) at −50 °C; the color was discharged. THF was then removed in vacuo and the residue extracted with *n*-hexane. Removal of hexane in vacuo left a white powder which was crystallized from absolute ethanol to give pure 1-methyl-1-triphenylgermyl-1-silacyclobutane (**2**) (2.12 g, 55%). Anal. Calcd for $C_{22}H_{24}GeSi$: C, 67.9; H, 6.2; mol wt, 388. Found: C, 68.3; H, 6.2; mol wt, 407 ($CHCl_3$) or 388 (MS).

A solution of trimethylstannyllithium[11] [from trimethylchlorostannane (1.66 g, 8.34 mmol), lithium (0.58 g, 83.8 mmol), and THF (12.5 cm^3)] was added dropwise to a stirred solution of 1-chloro-1-methyl-1-silacyclobutane (1.19 g, 10.0 mmol) in THF (10 cm^3) at −50 °C. After stirring for 1 h at −50 °C, THF was removed from the cold solution at ca. 10 mmHg. Molecular distillation of the residual oil gave pure (GLC), colorless, liquid 1-methyl-1-trimethylstannyl-1-silacyclobutane (**3**) (1.09 g, 53%). Anal. Calcd for $C_7H_{18}SiSn$: C, 33.8; H, 7.3; mol wt, 248. Found: C, 33.7; H, 7.4; mol wt, 247 ($CHCl_3$) or 248 (MS).

Acknowledgment. We thank the S.R.C. for support.

Registry No. **1**, 59395-10-7; **2**, 59395-11-8; **3**, 59395-12-9; $Cl\overline{Si(Me)CH_2CH_2CH_2}$, 2351-34-0; hexaphenyldisilane, 1450-23-3; triphenylbromogermane, 3005-32-1; trimethylchlorostannane, 1066-45-1.

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Organometallic Heterocyclic Chemistry. 2.[1] Spectral and Electrochemical Properties of Pyridazine, Pyrazine, and Pyrimidine Complexes of Tungsten Pentacarbonyl

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There has been a recent growing interest in the electronic spectral properties of transition-metal carbonyl complexes.[2]

Wrighton has recently shown that tungsten carbonyl derivatives of variously substituted pyridines exhibit both ligand-field and charge-transfer bands, the latter being very susceptible to the substituent upon the aromatic ligand.[3] The aromatic diazines are of interest since some previous studies have been reported on the UV–vis properties of pentaamineruthenium(II) complexes of these isomeric ligands.[4] In this study, Taube showed that the M → L CT bands observed for these complexes could be, perhaps fortuitously, correlated with the polarographic reduction potential of the uncomplexed ligands. This result indicated that complexation had little or no effect upon the relative energies of the LUMO of the ligands or the LF orbitals of the metal.

We have previously studied various diheteroaromatic complexes of the group 6 carbonyls[1] and now report the results of a spectral and electrochemical study on the isomeric diazine complexes of tungsten pentacarbonyl.

Experimental Section

The complexes were synthesized using the general technique

$$W(CO)_6 + THF \xrightarrow{h\nu} W(CO)_5(THF) + CO$$

$$W(CO)_5(THF) + L \rightarrow W(CO)_5L + THF$$

The intermediate complex, $W(CO)_5(THF)$, was not isolated. The complexes could be prepared via direct photochemical reaction with $W(CO)_6$; however, other heteroaromatic ligands that we are interested in studying, e.g., oxazole, are susceptible to decomposition if treated with ultraviolet irradiation in the presence of metal carbonyl complexes. The infrared and analytical data for the complexes studied in this work are recorded in Table I.

Infrared and UV–vis spectral data were recorded on a Perkin-Elmer 421 and Varian Cary 118 spectrophotometer, respectively. Mass spectra were recorded using a du Pont Model 21-491 double-focusing instrument operating at 73 eV.

Electrochemical studies using cyclic voltammetry were performed on 10^{-3} M solutions in methylene chloride with 0.01 *tert*-butylammonium perchlorate as supporting electrolyte. Scan rates were uniform at 0.065 V/s.

Results and Discussion

The absorption spectra of the pyridazine, pyrazine, and pyrimidine tungsten pentacarbonyl complexes as recorded in hexane are illustrated in Figure 1. It may be observed that the spectra of the pyridazine and pyrazine complexes exhibit two distinct bands while the pyrimidine complex possesses a single broad band. It has previously been noted that the polarity of the solvent in which such spectra are recorded has a pronounced effect upon the observed spectra. Charge-transfer bands are prone to blue shift as solvent polarity increases while ligand-field bands are generally much less susceptible to such changes. This is to be expected since the solvent molecules will be able to readily interact with the π^* orbitals of the complexed ligands, but for coordinatively saturated complexes, they will not be able to interact directly with the metal localized orbitals. Upon changing solvents from hexane to methanol, the shape of the absorption bands for the three complexes studied changes dramatically. The low-energy band in the spectrum of pyrid$W(CO)_5$ merges with the higher energy band so that in pure methanol only a single band at 389 nm remains. Exactly similar behavior is observed for the pyrazine complex. In the case of the pyrimidine complex, which exhibits a single band in hexane, changing to methanol produces a second band at 339 nm. Such transformations may be readily interpreted in terms of the following: (a) All three complexes exhibit a relatively nonvariable LF band at around 390 nm. (b) All three complexes exhibit a M → L charge-transfer band that varies in energy with both the ligand and the polarity of the recording solvent.

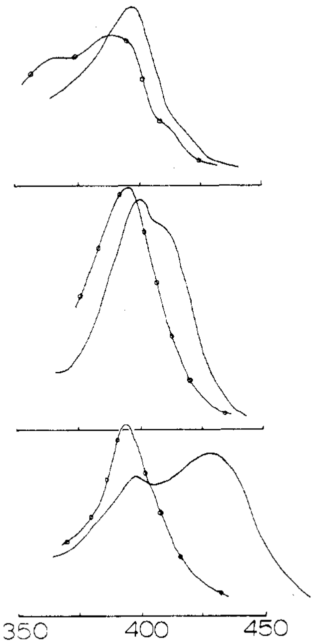

Figure 1. Electronic spectra of $LW(CO)_5$: —, hexane; ○, MeOH; top, pyrimidine; middle, pyrazine; bottom, pyridazine.

Table I. Infrared and Analytical Data for $LW(CO)_5$[a] Complexes

L	$\nu(C{\equiv}O)$, cm^{-1} [b]	Anal., found[c] % C	% H	% N
Pyridazine	2074, 1981, 1936, 1918	26.9	1.62	6.43
Pyrazine	2071, 1980, 1934, 1928 sh	26.9	1.09	6.43
Pyrimidine	2072, 1983, 1947, 1932 sh	25.8	1.74	6.03

[a] The complexes all exhibit a parent molecular ion, *m/e* 406 (W 186), when studied mass spectrometrically. A detailed analysis of the fragmentation patterns will appear elsewhere. [b] Cyclohexane. [c] Calcd: C, 26.8; H, 1.00; N, 6.93. Performed by Heterocyclic Chemical Corp.

On the basis of previous analysis of $LM(CO)_5$ complexes,[5] the LF band observed for all three complexes is the ${}^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a_1^1)$. The singlet–triplet excitation, ${}^1A_1(e^4b_2^2) \rightarrow {}^3E(e^3b_2^2a_1^1)$, is only observed in hexane for the pyrimidine complex but is partially "uncovered" for the other complexes as the CT band is blue shifted. On the basis of this analysis, the energies of the various transitions are recorded in Table II.

If it is assumed the LF and CT transitions originate from the same ${}^1A_1(e^4b_2^2)$ metal-localized orbital state, then the variations in CT energies for the three complexes should reflect the variations in the energy of the π^*-acceptor orbitals of the isomeric diazines. From our hexane-derived data, this sequence should be in increasing energy pyridazine < pyrazine < pyrimidine. This order is not the same as that reported by Taube in a related study on the diazine complexes of $[(NH_3)_5Ru]^{2+}$, the energies of the Ru → L CT bands from that study being pyrazine (472 nm) < pyridazine (467 nm) < pyrimidine (445 nm).[4] This latter order is in agreement with the polarographic reduction potential of the three ligands and also with the calculated LUMO π^* orbital levels of the three diazines;[6] hence, the values obtained by us from the spectra recorded in hexane clearly differ with these other experimental and theoretical data. It should, however, be noted that the Taube data were recorded in a polar solvent, water. The spectral data from the diazine $W(CO)_5$, when recorded in the polar methanol, show a much changed relative CT energy ordering. In methanol the difference between the pyridazine and pyrazine complex CT bands is essentially zero while the pyrimidine is still at considerably higher energy. The effect of changing solvents is not the same for all three

Table II. Absorption Spectral Data for $LW(CO)_5$ in Hexane (MeOH), nm

L	${}^1A_1 \rightarrow {}^3E^a$	${}^1A_1 \rightarrow {}^1E^b$	$M \rightarrow L$ (CT)^c
Pyridazine	~430	394 (388)	437 (388)
Pyrazine	~430	398 (389)	416 (389)
Pyrimidine	~430	395 (380)	395 (339)

^{a} ϵ ~500. ^{b} ϵ ~5000–7000. ^{c} ϵ ~5000–8000.

Table III. Electrochemical Data for $LW(CO)_5$,^{a} V

L	E_{Ox}	E_{Red}
Pyridazine	1.04	2.56
Pyrazine	1.04	2.18
Pyrimidine	1.04	2.94

^{a} 10^{-3} M CH_2Cl_2 + 0.01 M *tert*-butylammonium perchlorate.

complexes; therefore, to a large extent the relationship between the CT bands and the polarographic and theoretical data concerning the π^* orbitals of the diazines is fortuitous and certainly not a generalization that may be applied too widely. All three ligands subsequent to complexation remain bases by virtue of the "extra" nitrogen atom. These base strengths vary quite considerably, and, thus, the ability of various solvents to interact with the complexed ligands should also be a factor affecting the electronic structure of the metal complexes. Indeed, as Taube has shown, complexing the ligands to metallic π donors will increase such basicity for pyrazine, and excited CT states should be, and are, more basic than the ground states. Thus, solvation will play a very important, if at present unclear, role in such absorption spectral analysis. It is of interest that the order noted in hexane for the M–L CT band of $LW(CO)_5$ parallels the order of the $n \rightarrow \pi^*$ transition for the free ligands.[7]

We have attempted to use electrochemical analysis to shed further light upon the electronic structure of the complexes. Using cyclic-voltammetric techniques, we observed that the complexes undergo both one-electron oxidations and reductions but that all of these processes are nonreversible. However, the relative potentials at which these events take place lead to some interesting conclusions. The results of this study are collected in Table III.

All three complexes exhibit an oxidation potential under the conditions of the experiment at 1.04 ± 0.01 V. Since the electron removed in this process will come from the HOMO of the complex system, i.e., the ${}^1A_1$ metal-localized orbital configuration, this result confirms that variation of the ligands changes the ground-state electronic structure of the metal very little; i.e., as far as the metal is concerned, the primary feature of the complexes is that they are all N-bonded complexes; the ligand isomerization and varying base strengths seem of little account. The reduction potentials of the three complexes are very different, backing up the contention that the LUMO in the complex system if not totally ligand in character, certainly has a predominance of ligand character. The order of the reduction potentials is in the order predicted from theoretical considerations on the free ligands. Again, there is a discrepancy between the absorption data in hexane and the electrochemical data. When the absorption data are recorded under conditions identical with those of the electrochemical reduction experiment (CH_2Cl_2 with added tbap), the spectra are in most respects identical with those in methanol, and thus the discrepancy is not so startling since the CT band order is now pyrazine $\simeq$ pyridazine < pyrimidine.

Overall, the electrochemical study does reinforce the interpretation given to the absorption data above, i.e., a relatively constant-energy HOMO–metal-localized orbital system and a LUMO of considerable ligand character. It is interesting that the free ligands themselves are reversibly reduced to relatively stable anion radicals. That the complexes are not suggests that possible mixing of metal-localized antibonding and CT states occurs. (For the pyrimidine complex, since the CT band is much higher in energy than the LF band, it is possible that the reduction occurs directly into a metal-localized orbital.)

It is noteworthy that complexes of the type $[M(CO)_5(pyz)M(CO)_5]$ exhibit very low energy CT bands at $\simeq$600 nm and reversible electrochemical reduction, which we are currently investigating.

Acknowledgment. Support of this research was provided by the Robert A. Welch Foundation, Houston, Tex. We thank Dr. Keith Prater for the loan of cyclic voltammetric equipment and explanation and assistance on its use. Discussions with Dr. Lawrence Ellzey are also acknowledged.

Registry No. (pyridazine)$W(CO)_5$, 65761-20-8; (pyrazine)$W(CO)_5$, 65761-19-5; (pyrimidine)$W(CO)_5$, 65761-18-4.

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Correspondence

Ligand-Exchange Kinetics of (Ethylenediaminetetraacetato)lead(II) with (*R*)-(–)-1,2-Propylenediaminetetraacetic Acid

Sir:

In a recent publication[1] Pearson and co-workers have examined the ligand-exchange reaction kinetics of *R*(–)-PDTA with the lead complex of EDTA under a variety of pH conditions in 0.5 M KNO_3 ionic strength control. This communication presents an alternative mechanism for this exchange reaction at high pH. Although Pearson et al. have calculated a rate constant for the reaction of the tetraanion of PDTA with PbEDTA of 8.57 M^{-1} s^{-1} at 20 °C in good agreement with our predicted value[2] for this system (12 M^{-1} s^{-1} at 25 °C), two important points have been overlooked in their work.

The first such point is that the kinetics of these reactions show important dependencies upon the identity of the cation used in the "inert" buffers and ionic strength adjusting materials. Our work on closely related systems points this out and stability constants of these ligands with the alkali metal ions are available.[3-5] Potassium ion complexes a large fraction of the PDTA under these conditions and renders it considerably less reactive toward metal complexes, much in the same way that protonating the incoming ligand lowers its reactivity as observed by Pearson, ourselves, and other workers.[1,2,7] A

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