ture k_{tu} will be considerably greater than k_I) and (2) the rapid displacement of I^- compared to other ligands which would be expected to be similar to thiourea in ease of displacement.[4]

Discussion

The data obtained in this study appear to follow eq 3 even though the leaving group is difficult to displace and the displacing agents might be expected to associate well with the substrate. This suggests that if the associative mechanism is valid for platinum(II), it is peculiarly difficult to get enough association to observe kinetically.[2,4] This important question needs further work.

Our observation that reaction 1 failed to go to completion is important, along with ionic strength effects,[11] in interpretation of previous data on this and related complexes. Many studies have been done with poor displacing agents. It seems possible that an equilibrium situation may have been present, and some of the reported rate constants may be apparent rather than true rate constants for the reactions which were studied.

Experimental Section

Materials.—Nitrodiethylenetriamineplatinum(II) nitrate was prepared by a known method.[7a] *Anal.* Calcd for $[Pt(dien)NO_2]NO_3$: C, 11.8; H, 3.2; Pt, 48.0. Found: C, 11.9; H, 3.2; Pt, 48.1.

Iododiethylenetriamineplatinum(II) iodide was prepared by Mann's method.[12] *Anal.* Calcd for [Pt(dien)I]I: ionic I, 22.9; coordinated I, 22.9; Pt, 35.3. Found: ionic I, 22.9; coordinated I, 22.7; Pt, 35.5.

Kinetics.—Thermostats were constant to ±0.1°. The reactions were followed by spectrophotometry on reaction samples which had been placed in sealed tubes. The rates of iodide substitutions in cationic platinum(II) complexes are known to be sensitive to ionic strengths,[11] so ionic strength was kept constant at 0.1 M by adding appropriate amounts of sodium nitrate. The iodide reactions were followed at 310 mμ, where there is a maximum difference between the extinction coefficients of reactant and product.

The treatment of reaction 1 as reversible involved eq 4–6[8] where a is the initial concentration of $Pt(dien)NO_2^+$ in the reaction mixture whose absorbances at times 0, t, and equilibrium are A_0, A_t, and A_{eq}, respectively. A_p represents the absorbance of a solution of $Pt(dien)I^+$ in the same solvent, having the same concentration as the reaction mixture. In all cases, good straight lines were obtained in plots of ln X against t.

$$\frac{2mk_1t}{K} = \ln\left[\frac{(A_p - A_0) + (A_t - A_0)\frac{m}{K} - \frac{1}{2}}{(A_p - A_0) - (A_t - A_0)\frac{m}{K} + \frac{1}{2}}\right] = \ln X \tag{4}$$

$$m = \left(aK + \frac{1}{4}K^2\right)^{1/2} \tag{5}$$

$$K = \frac{a(A_{eq} - A_0)^2}{(A_p - A_0)(A_p - A_{eq})} = \frac{k_1}{k_{-1}} \tag{6}$$

The reaction with thiourea was followed spectrophotometrically at 320 mμ. Since one of the reactants is now uncharged, the reaction is not sensitive to ionic strength changes. Furthermore, the reaction was complicated by a slower secondary process (involving probable replacements at one or more coordination positions originally occupied by the tridentate ligand) so that A_{eq} could not be observed, and the Guggenheim method[13] was used.

Acknowledgments.—This research was supported in part by an Alfred P. Sloan Research Fellowship to Paul Haake.

---

[11] S. C. Chan, *J. Chem. Soc., A*, 1000 (1966).

[12] F. G. Mann, *ibid.*, 466 (1934).

[13] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
SOUTHWEST TEXAS STATE UNIVERSITY,
SAN MARCOS, TEXAS 78666

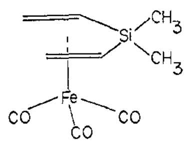
Tricarbonyl(dimethyldivinylsilane)iron

BY JOHN W. FITCH AND HAROLD E. HERBOLD

Received December 19, 1969

Although iron carbonyls have long been known to react with conjugated dienes[1] and to isomerize 1,4-dienes to 1,3-dienes,[2] there has been very little work on the reactions of the divinyl derivatives of the group IV metals with the metal carbonyls. Sterically, the divinyl derivatives of the group IV metals are similar to 1,4-dienes. However, electronically, they are considerably different due to dπ–pπ bonding effects,[3] and, because of these effects, the double bonds should be somewhat electron deficient when compared to normal double bonds.

Manuel and Stone[4] have reported that $(CH_3)_2Si(CH{=}CH_2)_2$ reacts with both $Mo(CO)_6$ and $W(CO)_6$ to give the compounds $(CH_3)_2Si(CH{=}CH_2)_2 \cdot Mo(CO)_4$ and $(CH_3)_2Si(CH{=}CH_2)_2 \cdot W(CO)_4$, respectively. On the other hand $(CH_3)_2Sn(CH{=}CH_2)_2$ was observed to react with $Fe(CO)_5$ to give $[(CH_3)_2SnFe(CO)_4]_2$. King and Stone suggested that the latter reaction might proceed through an unstable intermediate π complex between the vinylstannane and iron carbonyl.[5] However, to our knowledge, this intermediate complex has not been isolated, and no work has been reported on the analogous reaction between dimethyldivinylsilane and the iron carbonyls. We now wish to report that dimethyldivinylsilane reacts with triiron dodecacarbonyl to form tricarbonyl(dimethyldivinylsilane)iron. The proposed structure for this compound is shown below.



Experimental Section

Materials.—Dimethyldivinylsilane was prepared as described in the literature.[6] *Anal.* Calcd for $C_6H_{12}Si$: C, 64.29; H,

---

[1] R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 3 (1964).

[2] G. F. Emerson, J. E. Mahler, R. Kochar, and R. Pettit, *J. Org. Chem.*, **29**, 3620 (1964).

[3] D. R. Eaton and W. R. McClellan, *Inorg. Chem.*, **6**, 2134 (1967).

[4] T. A. Manuel and F. G. A. Stone, *Chem. Ind.* (London), 231 (1960).

[5] R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, **82**, 3833 (1960).

[6] S. D. Rosenberg, J. J. Wilburn, T. D. Stankovich, A. E. Balint, and H. E. Ramsden, *J. Org. Chem.*, **22**, 1200 (1957).

10.71. Found: C, 64.48; H, 10.85. Triiron dodecacarbonyl was prepared by the method of McFarlane and Wilkinson.[7] Benzene was dried before use.

Preparation of Tricarbonyl(dimethyldivinylsilane)iron.—The entire preparation was performed in an atmosphere of prepurified nitrogen. In a typical preparation triiron dodecacarbonyl (6.0 g, 0.012 mol) and dimethyldivinylsilane (4.4 g, 0.040 mol) were dissolved in 50 ml of benzene. The mixture was heated at 85° for 12 hr, cooled, and filtered under nitrogen. After all of the benzene and iron pentacarbonyl had been removed *in vacuo*, a sublimator probe, cooled with Dry Ice, was inserted into the flask. Tricarbonyl(dimethyldivinylsilane)iron sublimes to the cold surface at room temperature under high vacuum. The yellow crystalline product, which is formed in about 15% yield, melts at -13 to $-14°$ to a brown, air-sensitive oil. *Anal.* Calcd for $C_9H_{12}FeO_3Si$: C, 42.86; H, 4.76; Fe, 22.2. Found: C, 43.12; H, 4.70; Fe, 22.5.

The compound reacted with triphenylphosphine at room temperature to give the known *trans* isomer of tricarbonylbis(triphenylphosphine)iron (characterized by satisfactory ir spectrum and melting point).[8]

Infrared and Nmr Spectra.—Infrared spectra were recorded on a Beckman Model IR 10 spectrophotometer. Nmr spectra were obtained on a Varian Model A-60 spectrometer.

Results and Discussion

The nmr spectrum of the complex is that expected for a π-bonded divinylsilane. There is an upfield shift of the vinyl resonance multiplet of about 4 ppm from τ 3.5–4.6 ppm *vs.* TMS in the free ligand (neat liquid) to τ 7.6–8.7 ppm in the complex.[9] Such an upfield shift is characteristic of complexed olefins.[10] In both the free ligand and the complex the ratio of the integrated intensity of the vinyl proton signal to that of the methyl proton signal is 1:1. The methyl proton resonance signal occurs as a sharp singlet, τ 9.9 ppm, in the free ligand. The corresponding peak is observed to be split into two signals, τ 10.1 and 9.4 ppm, in the spectrum of the complex. This splitting is to be expected since the two methyl groups of the silane are not magnetically equivalent in the complex. Finally, the integrated intensities of the vinyl and two methyl peaks are observed to be in the expected ratio of 2:1:1.

The infrared spectrum of tricarbonyl(dimethyldivinylsilane)iron is consistent with its formulation as a π complex. The C=C stretching vibration, which occurs at 1600 cm^{-1} in dimethyldivinylsilane, is shifted to 1500 cm^{-1} in the complex. This shift is typical of π-bonded alkenes,[11] and it reflects the lowered bond order of a coordinated double bond.

The carbonyl region of the infrared spectrum of the complex shows stretching modes at 2065, 1982, and 1967 cm^{-1} (dilute cyclohexane solution). In addition to these bands all infrared spectra obtained also showed bands at 2012 and 1995 cm^{-1}. These bands could be attributed to iron pentacarbonyl formed through decomposition of the complex while handling the cyclohexane solutions (the complex was transferred in an atmosphere of prepurified nitrogen, and the solutions were prepared using nitrogen-saturated cyclohexane). An alternative explanation for the unusual spectrum in the carbonyl region could involve a type of tautomeric motion in which the silicon atom may occupy two positions in the molecule, one of which would require an iron–silicon interaction. Low-temperature nmr studies are planned to investigate this possibility.

In summary, our results show that stable acyclic polyene complexes of iron exist in which the π system of the polyene is interrupted by a heteroatom, silicon. We are currently investigating other vinylmetallics which may form similar iron tricarbonyl derivatives.

Acknowledgments.—The authors are grateful to the Robert A. Welch Foundation for financial support (Grant No. AI-306).

---

[7] W. McFarlane and G. Wilkinson, *Inorg. Syn.*, **8**, 181 (1966).

[8] W. Reppe and W. J. Schweckendiek, *Justus Liebigs Ann. Chem.*, **560**, 104 (1948); F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

[9] The nmr spectrum was obtained on the neat liquid. Chemical shifts were measured from the vinyl peaks of uncomplexed dimethyldivinylsilane (resulting from a small amount of decomposition of the complex during handling). These results were confirmed by obtaining the nmr spectrum of the complex in cyclohexane solution and referencing peaks to the cyclohexane resonance.

[10] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 47 (1965).

[11] G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, Methuen, London, 1968, p 16.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA

Electronic and Vibrational Spectra for *trans*-Dihydroxotetrachloroplatinate(IV)

BY LAWRENCE E. COX AND DENNIS G. PETERS

Received January 19, 1970

Several investigations pertaining to the thermal and photochemical aquation of hexachloroplatinate(IV) have been reported, and some information is available concerning the probable identities of the reaction products and the effects of acidity and of platinum(IV) and chloride concentrations on the extent of aquation.[1-4] Nevertheless, a complete picture of the reaction sequence is lacking, due at least in part to insufficient knowledge about the individual aquation products and about the reactions which these species undergo. As a means of probing this system, prior to any detailed kinetics studies, we are seeking to prepare and isolate various members of the family of aquation products and to determine their spectral and chemical characteristics. In the present communication, we have focused attention on the spectral properties of the tetragonal (D_{4h}) complex *trans*-dihydroxotetrachloroplatinate(IV). Of particular interest is the fact that the two observable ligand-field bands for this complex are found at lower wave numbers than those of hexachloroplatinate(IV), in contradistinction to the prediction based on the spectrochemical series. In addition, a comparison has been made of the ligand-field and charge-transfer spectra for *trans*-dihy-

---

[1] R. Dreyer, J. Dreyer, and D. Rettig, *Z. Phys. Chem.* (Leipzig), 199 (1963).

[2] R. Dreyer and J. Dreyer, *Z. Chem.*, 151 (1963).

[3] R. Dreyer, K. König, and H. Schmidt, *Z. Phys. Chem.* (Leipzig), 257 (1964).

[4] C. M. Davidson and R. F. Jameson, *Trans. Faraday Soc.*, **61**, 2462 (1965).