

Table II. Volatility of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$
($\text{Log } P = 6.037 + 1.75 \log T - 0.005T - 2168/T$)
($t_{760} = 101^\circ$; Trouton constant = 21.4 eu; mp -69.3°)

Temp, $^\circ\text{C}$	-23.0	-20.3	-11.8	0.00	8.6	19.45
P_{obsd} , mm	2.10	2.60	4.60	9.90	16.5	30.3
P_{calcd} , mm	2.07	2.53	4.62	9.95	16.6	30.2

Table III. Volatility of $[(\text{CF}_3)_2\text{PO}]_3\text{SiH}$
($\text{Log } P = 7.7390 + 1.75 \log T - 0.006T - 2983/T$)
($t_{760} = 161.1^\circ$; Trouton constant = 23.7 eu)

Temp, $^\circ\text{C}$	42.0	51.0	60.0	70.0	80.0	90.4
P_{obsd} , mm	5.62	9.69	16.1	26.7	43.0	68.1
P_{calcd} , mm	5.67	9.67	15.9	26.6	43.0	68.1

Table IV. Volatility of $[(\text{CF}_3)_2\text{PO}]_4\text{Si}$
($\text{Log } P = 7.2132 + 1.75 \log T - 0.005T - 3110/T$)
($t_{760} = 193.1^\circ$; Trouton constant = 21.5 eu; mp -53.8°)

Temp, $^\circ\text{C}$	52.0	60.1	75.5	82.6	93.0	98.0
P_{obsd} , mm	2.53	4.32	9.93	14.39	23.69	29.84
P_{calcd} , mm	2.62	4.26	9.98	14.35	23.72	29.84

sharp melting points of three of them, and by the absence of any obvious impurity bands in their infrared spectra. The proton nmr spectrum (Varian A-60) of $(\text{CF}_3)_2\text{POSi}(\text{CH}_3)_3$ showed a single sharp peak, 7.38 ppm downfield from external $\text{Si}(\text{CH}_3)_4$.

Infrared Spectra. The Beckman IR7 instrument was used for obtaining the gas-phase infrared spectra of these compounds in the NaCl region, and the Perkin-Elmer 337 instrument for the 650–400- cm^{-1} region. The latter range is not very distinctive for CF_3 -P compounds, showing only a CF_3 deformation in the 550–570- cm^{-1} range (often very weak) and a strong P– CF_3 stretching mode at 420–460 cm^{-1} .

The results, shown in Table V as frequencies of band peaks with parenthetical relative intensities roughly on the same scale, illustrate the principle that a highly polar bond in one part of a molecule works against high intensity for modes not strongly involving the same polar bond. For example, the C–F, P–O, and Si–O bonds tend toward mutual limitation of intensities of stretch-

Table V. Infrared Spectra of Phosphinoxysilanes (10-Cm Cell)

$(\text{CF}_3)_2\text{POSiH}_3$ ($P = 5 \text{ mm}$)	$(\text{CF}_3)_2\text{P-OSi}(\text{CH}_3)_3$ ($P = 5 \text{ mm}$)	$[(\text{CF}_3)_2\text{PO}]_3\text{SiH}$ ($P = 3.6 \text{ mm}$)	$[(\text{CF}_3)_2\text{PO}]_4\text{Si}$ ($P = 0.73 \text{ mm}$)
...	2970 (1.4)
2214 (4.5)	...	2310 } (0.25)	...
...	1367 (0.4)	2275 } (0.25)	1365 (3?)
...	1267 (2.8)	1396 } (0.25)	1421 } (0.25)
(combinations?)			
1224 (14)	1225 (7)	1230 (15)	1231 (95)
1183 (25)	1174 (20)	1184 (30)	1183 (165)
1145 (9)	1153 (5)	1152 (10)	1148 (80)
1124 (14)	1109 (8)	1127 (16)	1129 (103)
1067 (1.9)	1058 } (0.7)	1025 (9)	1035 (53)
1036 (2.3)	1049 } (0.7)
...	999 (5)
956 (28)	858 (9)	864 (8)	883 (7)
727 (1.9)	760 (0.8)	(Not seen)	748 } (2)
...	727 } (2)
572 (0.6)
458 (5)	457 (53)

ing modes, while Si–H stretching and some C–H modes may be very difficult to detect.

The assignments for the CH_3 group are obvious—rocking at 999, deformations at 1267 and 1367, and asymmetric stretching at 2970 cm^{-1} —but symmetric stretching was not observed. Si–H stretching would be found in the 2200–2300- cm^{-1} region, where C–F stretching overtones also might record. The 1100–1250- cm^{-1} region usually includes all C–F stretching modes, with each compound showing a characteristic and unique frequency-intensity pattern, suitable for identification. The 1000–1100- cm^{-1} range would belong to Si–O stretching (with Si–H bending not necessarily absent); the high intensity of this mode for the fourth compound might be due to the vibrational disturbance of the highly symmetrical SiO_4 pattern. This symmetry also would account for the failure of the Si–O bonds to suppress the high intensity of C–F stretching. The 850–960- cm^{-1} region is attributed to P–O stretching, with wide variations possibly due to differences of coupling with Si–O bonds. The 720–760- cm^{-1} range normally belongs to CF_3 -symmetric deformation, and often is weak.

Donor Properties of Hexamethylcyclotrisilazane

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Abstract: The donor properties of the heterocycle hexamethylcyclotrisilazane, $[(\text{CH}_3)_2\text{SiNH}]_3$ (abbreviated HMT), have been investigated from reactions with various reference acid systems. Although the trimeric (Si–N) ring is a potential pseudo-aromatic system, attempts to isolate half-sandwich complexes of the type $(\pi\text{-HMT})\text{M}(\text{CO})_3$, where $\text{M} = \text{Cr}$ and Mo , proved abortive, and no indication of six π -donor capacity was evident. Instead reaction with the typical class A acids titanium trichloride and vanadium trichloride provided neutral stable adducts of the type $\text{MCl}_3 \cdot \text{HMT}$. Evidence that the ligand acts as a terdentate nitrogen donor to give monomeric hexacoordinate titanium(III) and vanadium(III) species has been obtained and discussed from spectral, magnetic, conductivity, infrared (4000–200 cm^{-1}), and nmr measurements of these complexes.

The colorless liquid hexamethylcyclotrisilazane, $[(\text{CH}_3)_2\text{SiNH}]_3$ (I), has a slightly puckered ring structure containing alternate electron-acceptor (Si) and electron-donor (N) sites.² Two extreme mechanisms can

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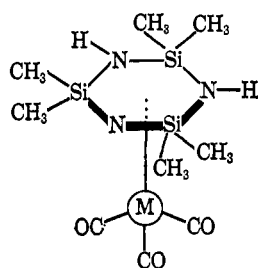
be proposed involving the distribution of the nitrogen lone-pair electrons.

² The recent reviews by (a) W. Fink, *Angew. Chem. Intern. Ed Engl.*, **5**, 760 (1966), and (b) K. A. Andrianov and L. M. Khananashvili *Organometal. Chem. Rev.*, **2**, 142 (1967), adequately summarize the properties and reactions of such silazane systems.

(A) **Donation into Adjacent Silicon 3d Orbitals within the Ring System.** In this case favorable π -orbital overlap may give rise to quasi-aromatic behavior^{3,4} sufficient to provide a six π -donor system.

(B) **Donation to an External Acceptor.** Here restricted delocalization can lead to the nitrogen atoms functioning as possible σ -donor sites to assist in adduct formation with suitable Lewis acids.

For mechanism A the synthesis of the half-sandwich molecule II was attempted by analogy with the recently reported⁵ π complex tricarbonyl(hexamethylborazole)chromium, $(\text{CH}_3\text{BNCH}_3)_3\text{Cr}(\text{CO})_3$, which appears to be quite stable. With mechanism B we have



II, M = Cr and Mo

studied the reaction of silazane I with titanium and vanadium trichlorides (class A acids⁶) which are well known to give stable adducts with nitrogen donor ligands.⁷ Reaction of silazane I with Al_2Cl_6 ,⁸ CoCl_2 ,⁹ CuCl_2 , and FeCl_3 ¹⁰ has been reported to give complex products suggestive of either ring degradation or polymerization, and Andrianov, *et al.*,¹¹ have found that various metal halides catalytically assist the ring expansion $(\text{R}_2\text{SiNR}')_3 \rightarrow (\text{R}_2\text{SiNR}')_4$. Formation of a stable adduct $\text{SnCl}_4 \cdot [(\text{CH}_3)_2\text{SiNH}]_3$ has been briefly mentioned by Lappert and Srivastava.¹² In principle, silazane I can function as a terdentate ligand in the absence of Si-N bond cleavage, and we anticipated that reaction with titanium and vanadium trichlorides would provide new complexes of the type $\text{MCl}_3 \cdot [(\text{CH}_3)_2\text{SiNH}]_3$ in the ratio 1:1 with hexacoordinate titanium(III) and vanadium(III) species.

Experimental Section

Materials. Ammonolysis of dimethyldichlorosilane to give silazane I was carried out following the method of Osthoff and Kantor.¹³ Samples of tricarbonyltris(acetonitrile)chromium and

(3) D. P. Craig, A. Macoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

(4) See N. L. Paddock, *Quart. Rev.* (London), 18, 168 (1964), for a discussion of the phosphonitrilic ($\rightarrow \text{P}=\text{N}-$)_n systems where similar $p\pi-d\pi$ contributions to the over-all bonding are considered.

(5) R. Prinz and H. Werner, *Angew. Chem. Intern. Ed. Engl.*, 6, 91 (1967).

(6) R. G. Pearson, *J. Am. Chem. Soc.*, 85, 3533 (1963).

(7) (a) R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J. Chem. Soc.*, 379 (1963); (b) G. W. A. Fowles and R. A. Hoodless, *ibid.*, 33 (1963); (c) D. Nicholls, *Coord. Chem. Rev.*, 1, 379 (1966); (d) G. W. A. Fowles, *Progr. Inorg. Chem.*, 6, 1 (1964); and references cited therein.

(8) U. Wannagat, E. Bogusch, and P. Geymayer, *Monatsh. Chem.*, 95, 801 (1964).

(9) R. Weiss, U. S. Department of Commerce, Office of Technical Services, AD 263, Washington, D. C., 1961, p 737; *Chem. Abstr.*, 57 14691 (1962).

(10) J. M. Masselli, U. S. Department of Commerce, Office of Technical Services, AD 274, Washington, D. C., 1962, p 520; *Chem. Abstr.*, 58, 40311 (1963).

(11) K. A. Andrianov, B. A. Ismailov, A. M. Konomov, and G. V. Kotrelev, *J. Organometal. Chem.* (Amsterdam), 3, 129 (1965).

(12) M. F. Lappert and G. Srivastava, *Inorg. Nucl. Chem. Letters*, 1, 53 (1965).

(13) R. C. Osthoff and S. W. Kantor, *Inorg. Syn.*, 5, 61 (1957).

the molybdenum analog, *viz.* $(\text{CH}_3\text{CN})_3\text{M}(\text{CO})_3$ (M = Cr and Mo) were prepared by the method of Tate, *et al.*,¹⁴ and to avoid the handling uncertainty of these air-sensitive compounds, further reaction was carried out *in situ* under a nitrogen atmosphere. All solvents were stored over P_2O_5 and distilled *in vacuo* when required.

Physical Measurements. Magnetic susceptibilities were determined at room temperature by the standard Gouy procedure with $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrant.¹⁵ Conductivity measurements were made at 25° using a PYE conductance bridge, No. 11700. Samples approximately 1×10^{-3} M in the chosen solvent were contained in a calibrated Mullard conductivity cell. Infrared spectra were recorded on Perkin-Elmer 337 (4000–400 cm^{-1}) and Grubb-Parsons DM4 (500–200 cm^{-1}) spectrometers, the samples being held as Nujol mulls between KBr disks and polyethylene plates, respectively. Solution spectra were measured on a Unicam SP700C spectrophotometer with samples in sealed 1-cm silica cells, and diffuse reflectance spectra were recorded on the same instrument now fitted with a SP735 reflectance attachment. Mrs. J. Burns recorded the nmr spectra, using a Varian A-60 spectrometer, and also gave great assistance in their interpretation.

Analyses. Microanalyses for carbon, hydrogen, and nitrogen were performed by Mr. D. J. Abbott of the analytical section of this department, and by the A. Bernhardt Microanalytical Laboratory, Mülheim, Germany. Chloride was estimated using the Volhard titration, and titanium was determined colorimetrically.^{16,17} Molecular weight determinations were carried out by Miss P. Waite using a Gallenkamp ebulliometer. Limited solubility of the complexes in the common organic solvents was observed, but the values obtained in dichloromethane solution were of sufficient reliability to verify monomeric behavior.

Reactions. (a) **Reaction of Hexacarbonylchromium and Silazane I.** Hexacarbonylchromium (4.1 g, 18.5 mmoles) and silazane I (13.2 ml, 55.5 mmoles) with a 1:2 mixture of THF-dioxane was heated at reflux for 3 days. Removal of solvent and unused silazane I from the green solution gave a pale green solid which was sublimed at 60° (0.1 mm) for 6 hr to give: (I) 1.1 g (22% recovery) of hexacarbonylchromium. *Anal.* Calcd for CrC_6O_6 : C, 32.7. Found: C, 32.5. The infrared spectrum was identical with that of an authentic sample. (II) 0.9 g (calcd 15% yield) of yellow air-unstable impure tricarbonyltris(tetrahydrofuran)chromium. *Anal.* Calcd for $\text{C}_{15}\text{H}_{24}\text{O}_6\text{Cr}$: C, 51.1; H, 6.8. Found: C, 45.4; H, 7.9. The infrared spectrum clearly indicated coordinated tetrahydrofuran,^{7a} *e.g.*, ν_{asym} (C–O–C) bands at 1038 (m) and 1011 (s) cm^{-1} and a ν_{sym} (C–O–C) band at 844 (s) cm^{-1} , and also terminal carbonyl groups,¹⁸ *e.g.*, $\nu(\text{CO})$ bands at 1990 (m) and 1921 (m) cm^{-1} . Other peaks were observed at 2678 (w), 1360 (m), 1298 (w), 1076 (m), 899 (m), 801 (w), 736 (m), 652 (w), 535 (w) cm^{-1} . (III) A small residue (~0.2 g) of an intractable green solid. *Anal.* Found: C, 32.3; H, 14.1; N, 0.3. The infrared spectrum contained bands at 1711 (w), 1260 (s), 1020 (m), 979 (w), 879 (w), 800 (w), 725 (m), 670 (w), 635 (m), 530 (w), 481 (w) cm^{-1} .

(b) **Reaction of Tricarbonyl(π -benzene)chromium and Silazane I.** Hexacarbonylchromium (3.7 g, 16.6 mmoles) was heated at reflux with silazane I (11.9 ml, 50 mmoles) in a 1:1 mixture of benzene-*n*-hexane as solvent for 3 days. Removal of solvent and unused silazane I gave a yellow-green solid which on sublimation at 70–80° (0.1 mm) for several hours gave: (I) 1.7 g (46% yield) of the yellow air-stable compound tricarbonyl(π -benzene)chromium (*Anal.* Calcd for $\text{C}_6\text{H}_6\text{O}_3\text{Cr}$: C, 50.5; H, 2.8. Found: C, 50.1; H, 2.9); and (II) a green residue of heterogeneous composition (*Anal.* Found: C, 27.2–35.5; H, 5.6–6.1; N, 0.3–1.1), a melting point determination of which gave no change on heating to 370°. The infrared spectrum revealed bands at 1255 (s), 1098 (m), 1036 (m), 885 (w), 799 (m), 665 (w), 640 (m), 535 (w), 498 (w) cm^{-1} .

(c) **Reaction of Tricarbonyltris(acetonitrile)chromium and Silazane I.** The yellow $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$ obtained from hexacarbonylchromium (3.9 g, 17.9 mmoles) and excess acetonitrile was gently heated at reflux for 60 hr with silazane I (10.0 ml, 42.1 mmoles) in *n*-hexane as solvent. The reaction mixture was filtered *in vacuo* to give a green solid and a pale green filtrate. Work-up of the filtrate gave solvent, bp 68–70° (740 mm), and unused silazane I (4.3 ml, 43% recovery) (n_D^{20} 1.4442; lit.¹³ n_D^{20} 1.4448) to leave a

(14) D. P. Tate, J. M. Augl, and W. R. Knipple, *Inorg. Chem.*, 1, 433 (1962).

(15) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 6, 37 (1964).

(16) A. Weissler, *Ind. Eng. Chem., Anal. Ed.*, 17, 695 (1945).

(17) E. R. Wright and M. G. Mellon, *ibid.*, 9, 375 (1937).

(18) R. Poilblanc and M. Bigorgne, *J. Organometal. Chem.* (Amsterdam), 5, 93 (1966).

smear of a green residue. Sublimation of the green solid at 50–70° (0.1 mm) overnight gave: (I) a trace (~0.1 g) of hexacarbonylchromium (identified by comparison of its infrared spectrum with that of an authentic sample); (II) 1.2 g (24% recovery) of tricarbonyltris(acetonitrile)chromium (*Anal.* Calcd for $C_6H_9N_3O_3Cr$: C, 41.7; H, 3.5; N, 16.2. Found: C, 40.9; H, 3.9; N, 15.7); and (III) a green residue (~1.5 g) (*Anal.* Found: C, 12.9; H, 5.6; N, 0.8) whose infrared spectrum gave bands at 2323 (w), 1395 (w), 1259 (m), 1111 (m), 1059 (m), 933 (w), 889 (w), 721 (w), 644 (w), 639 (w), 522 (w) cm^{-1} .

Using the same procedure as in part c above, no reaction was observed between the molybdenum analog $(CH_3CN)_3Mo(CO)_3$ —obtained from hexacarbonylmolybdenum (3.2 g, 12.2 mmoles) and acetonitrile—and silazane I (9.6 ml, 40 mmoles). The latter was recovered unchanged in almost quantitative yield (8.6 ml, 88% recovery): n^{20}_D 1.4440, lit.¹³ n^{20}_D 1.4448.

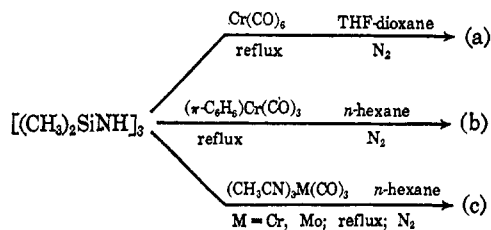
(d) **Reaction of Silazane I with Metal Halides MCl_3 ($M = Ti$ and V).** Approximately 3 g of the metal halide was gently heated at reflux with a fourfold excess of silazane I and tetrahydrofuran as solvent in a sealed ampoule for 1 week. The solid product remaining after removal of solvent and unused silazane I was extracted with dichloromethane (four 15-ml portions), on the vacuum system, taking care to filter out unused metal halide as impurity. Evaporation of this solution gave the pure adduct $MCl_3 \cdot [(CH_3)_2SiNH]_3$ which was pumped *in vacuo* at 30° for several hours before being sealed into ampoules under a nitrogen atmosphere.

Trichloro(hexamethylcyclotrisilazane)titanium(III) was a green solid. *Anal.* Calcd for $C_6H_{21}Cl_3N_3Si_3Ti$: C, 19.3; H, 5.7; N, 11.2; Cl, 28.5; Ti, 12.8; mol wt, 374. Found: C, 19.0; H, 6.1; N, 10.9; Cl, 28.4; Ti, 12.8; mol wt (ebullioscopic in CH_2Cl_2), 336. $\mu_{eff} = 1.78$ BM at 295°K. $\Delta_M = 0.13$ $ohm^{-1} cm^2$ at concentration $1.21 \times 10^{-3} M$ in CH_2Cl_2 . The infrared spectrum contained bands at 3294 (sh), 3196 (m), 1610 (w), 1460 (s), 1380 (s), 1370 (w), 1322 (m), 1310 (w), 1294 (m), 1255 (sh), 1240 (m), 1230 (sh), 1175 (s), 1139 (w), 1072 (w), 1040 (m), 1010 (vs), 960 (m), 928 (w), 920 (w), 849 (vs), 740 (w), 725 (w), 680 (s), 580 (m), 360 (s), 335 (s), 292 (sh) cm^{-1} .

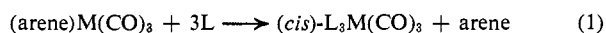
Trichloro(hexamethylcyclotrisilazane)vanadium(III) was a chocolate-brown solid. *Anal.* Calcd for $C_6H_{21}Cl_3N_3Si_3V$: C, 19.1; H, 5.6; N, 11.1; Cl, 28.2; mol wt, 377. Found: C, 18.8; H, 6.1; N, 10.7; Cl, 28.0; mol wt (ebullioscopic in CH_2Cl_2), 329. $\mu_{eff} = 2.76$ BM at 295°K. $\Delta_M = 0.27$ $ohm^{-1} cm^2$ at concentration $1.65 \times 10^{-3} M$ in CH_2Cl_2 . The infrared spectrum gave bands at 3300 (sh), 3192 (m), 1606 (w), 1476 (s), 1410 (w), 1390 (s), 1350 (m), 1300 (w), 1260 (w), 1245 (w), 1175 (s), 1070 (sh), 1040 (m), 1013 (vs), 955 (m), 925 (s), 855 (vs), 725 (m), 680 (m), 580 (m), 358 (s), 326 (s), 285 (sh) cm^{-1} .

Discussion

Scheme A. Following a variety of reaction routes, synthesis of the half-sandwich molecule II proved uniformly unsuccessful. Whereas hexacarbonylchromium,



in refluxing benzene, readily gives¹⁹ the π complex tricarbonyl(benzene)chromium, no substitution was observed with silazane I, *viz.* route a. Instead, reaction with solvent gave impure tricarbonyltris(tetrahydrofuran)chromium²⁰ and a green residue. The general displacement reaction (eq 1) has been found useful for a



wide range of O, N, P, As, and S donors,²¹ but reaction

(19) E. O. Fischer, K. Ofële, H. Essler, W. Frohlich, J. P. Mortensen, and W. Semmlinger, *Z. Naturforsch.*, **13b**, 458 (1958).

(20) T. H. Coffield and R. P. M. Werner (Ethyl Corp.), U. S. Patent 3,124,600 (1964); *Chem. Abstr.*, **60**, 15914 (1964).

(21) G. R. Dobson, I. W. Stolz, and R. K. Shellne, *Advan. Inorg. Chem. Radiochem.*, **8**, 1 (1966).

of silazane I with hexacarbonylchromium in benzene, *e.g.*, route b, simply gave the benzene complex $(\pi-C_6H_6)Cr(CO)_3$ with a residual green heterogeneous mass. In route c the chromium complex $(CH_3CN)_3Cr(CO)_3$ was treated with silazane I, and again a green residue was obtained in addition to unused reactants and a trace of hexacarbonylchromium. Surprisingly, the molybdenum analog gave no reaction with silazane I, although the relative reactivity of these acetonitrile derivatives $(CH_3CN)_3M(CO)_3$ is in the order $W > Mo \gg Cr$.²² The green solid obtained from routes a, b, and c could not be characterized. Certainly the infrared spectra contained no bands identified with terminal carbonyl groups, $\nu(CO)$, or with silazane I, $\nu(Si-N-Si)$; however, the bands observed at ~1040 and ~630 cm^{-1} are in the region expected for $\nu(Si-O)$ absorption,²³ and it seems likely that the green solid is a heterogeneous mixture of chromium oxides and organosilicon residues.

Brown²⁴ has reviewed the question of stability of possible half-sandwich complexes in terms of molecular orbital theory and has predicted²⁵ the existence of various substituted borazine π complexes, including the tricarbonyl(hexamethylborazole)chromium already isolated by Prinz and Werner,⁵ from comparisons of ring-metal delocalization energies. Our failures suggest that the proposed $(Si-N)_3Cr$ system (II) has such a small delocalization energy so as to preclude its existence.^{26–28}

Scheme B. Stable new adducts of the type $MCl_3 \cdot HMT$ [$M = Ti$ and V ; $HMT = [(CH_3)_2SiNH]_3$ (I)] were obtained from reaction of the metal halide with silazane I on refluxing in tetrahydrofuran for several days in a sealed ampoule. The green $TiCl_3 \cdot HMT$ and brown $VCl_3 \cdot HMT$ are extremely air sensitive with rapid discoloration and evolution of ammonia. Room-temperature magnetic moment measurements gave $\mu_{eff} = 1.78$ BM for the titanium complex, confirming a trivalent Ti(III) system,¹⁵ and $\mu_{eff} = 2.76$ BM for the vanadium analog in good agreement with the values found (~2.8 BM) for hexacoordinate vanadium(III) systems.^{7c} Both complexes give nonconducting solutions in dichloromethane and behave as monomers in the same solvent. The infrared spectra of the com-

(22) (a) R. B. King and A. Fronzaglia, *Inorg. Chem.*, **6**, 1837 (1967); (b) R. B. King, *J. Organometal. Chem.* (Amsterdam), **8**, 139 (1967).

(23) (a) A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960). (b) Infrared symbols used in the script refer to ν = stretching, γ = wagging, and δ = bending frequencies. Abbreviations vs (very strong), s (strong), m (medium), w (weak), sh (shoulder) are given in parentheses for relative intensities.

(24) D. A. Brown, "Transition Metal Complexes," Vol. 3, Marcel Dekker, Inc., New York, N. Y., 1966, p 1.

(25) D. A. Brown and C. G. McCormack, *Chem. Commun.*, 385 (1967).

(26) Professor Brown (Dublin) has pointed out in a personal communication that some preliminary calculations of overlap integrals, *e.g.*, $S(2p\pi 3p\pi)$ for silazane I gives a value of 0.200–0.210,^{27a} suggesting some degree of conjugation around the ring which should be slightly enhanced in the case of $[(CH_3)_2SiNCH_3]_3$ when substituent $(CH_3 \rightarrow N)$ bond effects are included. Should the ring-metal delocalization energy for π complexes of the type $(Si-N)_3Cr$ be of the same order as that for the $(B-N)_3Cr$ systems, this would infer the existence of II, but calculations are necessary to confirm this point. On the other hand, nmr measurements of $[(CH_3)_2SiNCH_3]_3$ have been interpreted^{27b} as showing a complete absence of aromatic character.

(27) (a) See Table III; *cf.* D. A. Brown and C. G. McCormack, *J. Chem. Soc.*, 5385 (1964); (b) K. Lienhard and E. G. Rochow, *Z. Anorg. Allgem. Chem.*, **331**, 307 (1964).

(28) The possibility that under the reaction temperatures of refluxing THF or benzene the π complex (II) might well be thermally unstable has been pointed out by a referee.

Table I. Electronic Spectra

Compound	Diffuse reflectance, cm^{-1}	Absorption, cm^{-1} ^a
Silazane I, <i>i.e.</i> , HMT		Rising absorption \rightarrow 40,000 ^{b,c,d}
	12,960 (sh), 14,990 24,112 (sh) (very weak)	12,690 (ϵ 62) ^c 15,528 (ϵ 210)
TiCl ₃ ·HMT	29,700 36,600	24,630 (sh) (ϵ ~1900) 28,980 (sh) (ϵ ~2000) 37,130 (sh) (ϵ ~2000)
	12,700, 20,050	12,720 (sh) (ϵ ~50) ^c 20,000 (ϵ ~180)
VCl ₃ ·HMT	28,300 (sh), 31,400 36,950 (sh)	28,980 (sh) (ϵ ~2100) 32,362 (sh) (ϵ ~2100) 37,590 (sh) (ϵ ~2100)

^a Extinction coefficients in parentheses. ^b Neat solution. ^c CH₂-Cl₂ solution. ^d CH₃CN solution.

plexes are very similar, and the more conspicuous ligand modifications^{23,29} include (i) the $\nu(\text{N-H})$ band at 3399 cm^{-1} which appears at $\sim 3200 \text{ cm}^{-1}$ with a pronounced shoulder at $\sim 3290 \text{ cm}^{-1}$, a shift to lower energy typical for amine coordination;^{7d} (ii) the $\nu_{\text{asym}}(\text{Si-N-Si})$ band at 924 cm^{-1} which splits into a doublet at 920 and 930 cm^{-1} and the $\nu_{\text{sym}}(\text{Si-N-Si})$ band at 620 cm^{-1} which shifts to 580 cm^{-1} ; (iii) the $\nu_{\text{sym}}(\text{Si-C})$ band at 680 cm^{-1} which remains unchanged; (iv) the intense $\gamma(\text{N-H})$ band at 1160 cm^{-1} which shifts to 1180 cm^{-1} with a small shoulder appearing at 1140 cm^{-1} ; and (v) the $\delta_{\text{sym}}(\text{CH}_3)$ and $\delta_{\text{asym}}(\text{CH}_3)$ bands at 1250 and 1400 cm^{-1} , respectively, which experience a small shift of $\Delta\nu = 10 \text{ cm}^{-1}$ to lower energy.

The observed chemical evidence suggests six-coordinate monomeric MCl₃·HMT complexes with silazane I behaving as a terdentate nitrogen donor ligand. For such species the site symmetry of the metal can be C_{3v} (*cis*) in which case two infrared-active metal-halogen stretching frequencies are expected.³⁰ Previous low-infrared spectral studies of *cis*-TiCl₃·3CH₃CN and *cis*-VCl₃·3CH₃CN³¹ indicated strong metal-chlorine bands in the region 250–350 cm^{-1} , and the observed intense bands at 335 and 360 cm^{-1} and at 326 and 358 cm^{-1} for our titanium and vanadium complexes, respectively, support the proposed molecular symmetry. Although assignments for metal-nitrogen stretching frequencies in the region 300–240 cm^{-1} have been made,³² it seems more likely that the broad shoulder observed at $\sim 285 \text{ cm}^{-1}$ in both spectra is the internal ligand band at 297 cm^{-1} masked by the intense metal-halogen stretching vibration ($\sim 335 \text{ cm}^{-1}$) rather than a “pure” metal-nitrogen mode. The other internal ligand band²⁹ at 393 cm^{-1} gives no indication of coordination shift and is almost certainly enveloped by the intense metal-halogen absorption ($\sim 360 \text{ cm}^{-1}$). For each compound the electronic spectrum measured in dichloromethane and the diffuse reflectance spectrum are identical excepting minor frequency displacement (see Table I) and can be interpreted on the same model, *e.g.*, [MCl₃·HMT]⁰. The solution spectrum of the

(29) H. Kriegsmann, *Z. Anorg. Allgem. Chem.*, **298**, 223 (1959). This reference contains the 4000–400- cm^{-1} infrared scan of silazane I. In addition we report bands at 393 (s) and 297 (s) cm^{-1} for the low-infrared region, 500–200 cm^{-1} .

(30) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

(31) R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

(32) J. R. Durig, B. R. Mitchell, D. W. Sink, J. N. Willis, and A. S. Wilson, *ibid.*, **23A**, 1121 (1967).

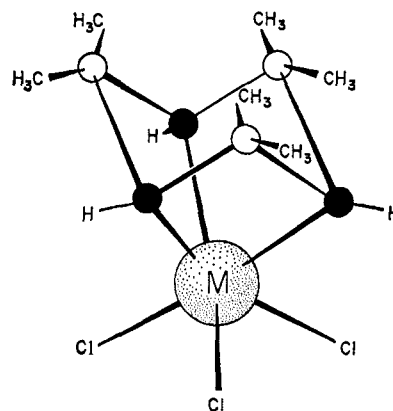


Figure 1. Schematic representation of the MCl₃·[(CH₃)₂SiNH]₃ complex, where M = Ti and V, ● denotes N atoms, and ○ denotes Si atoms.

titanium complex is similar to that of other hexacoordinate titanium(III) species, *e.g.*, TiCl₃·3py^{7a,b} having two transitions in the 20,000- cm^{-1} region. Assignment of the band at 15,528 cm^{-1} to the ${}^2\text{B}_{1g} \leftarrow {}^2\text{B}_{2g}$ transition and that at 12,690 cm^{-1} to the ${}^2\text{A}_{1g} \leftarrow {}^2\text{B}_{2g}$ transition (in O_h) gives a split in the ${}^2\text{E}_g$ term corresponding to 2838 cm^{-1} . The red shifts of these bands compared with those in TiCl₃·3py, *e.g.*, 16,670 \rightarrow 15,528 cm^{-1} , demonstrates the weaker ligand field strength of silazane I compared with pyridine. The bands at 29,700 and 36,600 cm^{-1} , obviously charge transfer in origin, must be associated with metal \leftrightarrow ligand and/or metal \leftrightarrow halogen transitions. In the absence of suitable ligand orbitals these are tentatively assigned to Ti(d) \leftrightarrow Cl(π) transitions.³³ Similarly, the spectrum of the vanadium complex can be favorably compared with that of VCl₃·3py.³⁴ The low-energy band at 12,700 cm^{-1} is assigned to the ${}^3\text{T}_{2g} \leftarrow {}^3\text{T}_{1g}(\text{F})$ transition, the band at 20,050 cm^{-1} is assigned to the ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{T}_{1g}(\text{F})$ transition, and the bands at 28,300 (sh) 31,400, and 36,950 (sh) cm^{-1} are tentatively assigned (*vide infra*) to V(d) \leftrightarrow Cl(π) transitions.³⁵

Assuming the silazane I ring adopts a severe “chair” conformation in these complexes (see Figure 1), the silicon groups will be displaced away from the ring-metal zonal area and the vicinal halogen atoms. Nitrogen coordination to the metal leaves exposed (CH₃)₂Si=δ⁻ groupings susceptible to nucleophilic attack as borne out by the extremely rapid hydrolysis of the complexes compared with the ligand itself. Otherwise, the silicon environment should be little affected. The nmr spectrum of silazane I in dichloromethane solution gives one sharp signal at τ 9.94³⁶ for the protons of the (CH₃)₂Si= groups taken to be equivalent. For the proposed *cis* configuration of the complexes, we might reasonably expect a signal splitting for the nonequivalent methyl groups, but this was not detected. Retention of the single band although somewhat broadened for both complexes, *e.g.*, TiCl₃·HMT (τ 9.93) and VCl₃·HMT (τ 9.92) in dichloromethane

(33) G. W. A. Fowles and T. E. Lester, *ibid.*, **23A**, 1969 (1967).

(34) G. W. A. Fowles and P. T. Greene, *J. Chem. Soc., A*, 1869 (1967).

(35) G. W. A. Fowles, P. T. Greene, and T. E. Lester, *J. Inorg. Nucl. Chem.*, **29**, 2365 (1967).

(36) L. W. Breed and R. L. Elliot, *Inorg. Chem.*, **3**, 1622 (1964), report a value of τ 9.93 in chloroform solution with reference to tetramethylsilane (τ 10.00).

solution, suggests that broadening due to the paramagnetic Ti(III) and V(III) ions exercises a complete blanketing effect.

In addition to the contents of this paper, complexes of the type $\text{MX}_4 \cdot [(\text{CH}_3)_2\text{SiNH}]_3$, $\text{MX}_3 \cdot [(\text{CH}_3)_2\text{SiNH}]_4$, and $\text{MX}_4 \cdot [(\text{CH}_3)_2\text{SiNH}]_4$ (where M = Ti and Zr and

X = Cl and Br) have also been isolated and these will be treated in full detail in a later communication.

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A Semiempirical Molecular Orbital Model for $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, and $\text{Ni}(\text{CO})_4$ ¹

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Abstract: Molecular orbital calculations have been carried out for $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, and $\text{Ni}(\text{CO})_4$. The diagonal matrix elements are corrected for the effects of surrounding charges as well as for the one-center charge. The calculations are iterative and were carried out to self-consistency in the charges on all atoms, and in the configuration on the metal. The bonding in the carbonyls is discussed in terms of the Mulliken population analysis. On the basis of overlap populations it is concluded that (1) chromium 4p orbitals are involved almost entirely in the σ bonding and may be neglected in considering the π system, (2) nickel 4p orbitals are more important than 3d orbitals in π bonding to CO, (3) the π bonding in $\text{Fe}(\text{CO})_5$ is about equally 4p and 3d in character, and (4) there is no significant difference in the bonding of the axial and equatorial CO groups in $\text{Fe}(\text{CO})_5$. The results of the molecular calculations are compared with a variety of experimental data for the three carbonyls.

The geometrical structures of the simple transition metal carbonyl compounds $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, and $\text{Ni}(\text{CO})_4$ are well established. To some extent, qualitative bonding considerations appear to provide a satisfactory rationale for the stability of the metal-carbon bond in these compounds. Many questions regarding ground-state electron distributions in the three compounds are, however, not clear at this time. Variation in the metal-carbon overlap population, relative importance of 3d orbital participation, and relative importance of σ and π bonds are among the more interesting and significant aspects of the bonding. Questions related to these aspects might be clarified by a systematic treatment of the molecules at the level of a reasonably complete molecular orbital model. We report here the results of molecular orbital calculation for $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, and $\text{Ni}(\text{CO})_4$ in terms of a semiempirical molecular orbital model in which a number of refinements over the simplest extended Hückel model have been incorporated.

Method and Matrix Elements of the Secular Determinant

The molecular orbitals (MO's) ϕ_j are constructed from an atomic orbital basis set χ in the usual LCAO approximation.

$$\phi_j = \sum_i c_i \chi_i \quad (1)$$

Application of the variation principle leads to the familiar secular equation and determinant

$$[F - ES]C = 0 \quad (2)$$

$$|F - ES| = 0 \quad (3)$$

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where F and S are the Hamiltonian and overlap matrices, respectively.

Fenske, Caulton, Radtke, and Sweeney,² following Richardson's separated Hamiltonian procedure, have shown that for a molecule or ion consisting of a metal atom surrounded by some number n of ligands, the diagonal matrix elements for the metal and ligands, F_{ii}^M and F_{ii}^L , respectively, can be written as

$$F_{ii}^M = \epsilon_i^M(Q_M) + CF_L(Q_L) \quad (4)$$

$$F_{ii}^L = \epsilon_i^L(Q_{L_0}) + CF_M(Q_M) + \sum_{\mu \neq 0} CF_{L\mu}(Q_{L\mu}) \quad (5)$$

$\epsilon_i(Q)$ is the orbital energy of an electron on the free atom (ion) of charge Q . $CF_L(Q_L)$ is the potential due to charge distributions on atoms surrounding the central metal. The spherical part of this potential is most important in locating the energies of the orbitals at the metal relative to those on the ligands. Analogous electrostatic potential corrections, CF_M and CF_L , are applied to the energies of orbitals centered on ligand atoms.

We assume that this charge-distribution correction can be approximated as a classical charge interaction between spherically symmetric nonoverlapping charge distributions, modified by a factor β which corrects for interpenetration of electronic charge distributions. This leads to a general expression of the form

$$F_{ii}^T = \epsilon_i^T(Q_T) - \sum_{k \neq T} \beta_{Tk} \frac{e^2 Q_k}{r_{Tk}} \quad (6)$$

The second term on the right, without a correction factor, has been employed by others in semiempirical calculations. Jørgensen refers to it as a Madelung

(2) R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeney, *Inorg. Chem.*, 5, 951 (1966).