donor atom nitrogen do not show quadrupole splitting.[1,2,4]

The largest ΔE_q values are found for the $(n\text{-}C_4H_9)_3P$, $(n\text{-}C_3H_7)_3P$, $(C_2H_5)_3P$, and $(C_2H_5)_2C_6H_5P$ complexes. The value for $((n\text{-}C_4H_9)_3P)_2SnCl_4$ agrees well with that previously reported.[3] For the series $((C_6H_5)_3P)_2SnCl_4$, $(C_2H_5(C_6H_5)_2P)_2SnCl_4$, and $((C_2H_5)_2C_6H_5P)_2SnCl_4$ the quadrupole splitting increases on replacement of C_6H_5 by C_2H_5. This is also the order of increasing basicity of the ligands. The same trend is observed for the series $(C_6H_5)_3P$, $CH_3(C_6H_5)_2P$, and $(CH_3)_2C_6H_5P$. There also appears to be a tendency for complexes which give the largest isomer shifts to produce larger quadrupole splittings. Other workers have noted that increasing the size of alkyl groups in a series of sulfoxide complexes produces an increase in ΔE_q and have attributed this to steric hindrance.[2] It would be interesting to have detailed X-ray data for a series such as $((C_6H_5)_3P)_2SnCl_4$, $(C_2H_5(C_6H_5)_2P)_2SnCl_4$, and $((C_2H_5)_2C_6H_5P)_2SnCl_4$ in order to ascertain whether steric effects or Sn–P bond lengths are instrumental in changing δ and ΔE_q. One further feature of interest concerns the magnitudes of quadrupole splittings in nitrogen, oxygen, and phosphorus donor complexes. As mentioned earlier bis adducts of $SnCl_4$ with nitrogen donors show no observable quadrupole splitting whereas oxo complexes exhibit splittings in the range 0.50–1.60 mm/sec.[2,3] The latter are in some cases considerably larger than the splittings observed for phosphorus donors. In conjunction with the isomer shift results presented in Figure 3, this rules out any *overall* correlation between the strength of a donor–acceptor interaction and the magnitude of a quadrupole splitting even though such a correlation may exist within a restricted series of complexes.[2a]

For $((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)SnCl_4$, the only cis-octahedral species examined during this study, no quadrupole splitting was observed although the line width was large. This is not surprising in view of the smaller ΔE_q values associated with cis derivatives and the small splitting found for *trans*-$(CH_3(C_6H_5)_2P)_2SnCl_4$.

For $(Cy_3P)SnCl_4$ and $((C_6H_5)_3P)SnCl_4$ small quadrupole splittings were observed which are just resolvable. The splittings were measured by fitting the curve to Lorentzian line shapes in each case. ΔE_q values of similar magnitude were previously observed for the $SnCl_5^-$ ion and other five-coordinate species.[2a,21] Similarly a small quadrupole splitting might be expected for a halogen-bridged dimer.

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Notes

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Reaction of Ligands with Pentafluorophenylmanganese Pentacarbonyl

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An extensive study of ^{19}F parameters in pentafluorophenyl derivatives has established a linear relationship between the ortho fluorine–para fluorine coupling constant (J_{24}) and para fluorine chemical shift (ϕ_p). It was suggested that this relationship or either of the parameters individually might serve as a qualitative indicator of π-electronic interactions between the pentafluorophenyl ring and its substituent, and thus indirectly of π interactions with the substituent itself.[1,2]

If the substituent on the pentafluorophenyl ring is a metal carbonyl group, carbonyl stretching frequencies should provide an alternative means of gauging π-electronic interactions, which could be compared with indications from the ^{19}F parameters. With this purpose in mind, a number of pentafluorophenylmanganese pentacarbonyl derivatives have been prepared and studied by infrared and ^{19}F nmr spectroscopy. The findings proved to be in general agreement with conclusions reached by Stewart and Treichel[3] from a comprehensive study of analogous monofluorophenyl compounds.

Experimental Section

All reactions were carried out under a nitrogen atmosphere and solid products handled with minimum exposure to air. Pentane, hexane, methylcyclohexane, benzene, toluene, and xylene were dried over sodium wire or 9.5% sodium–lead alloy; diethyl ether was obtained commercially in the anhydrous state. The ligands used in this study came from commercial sources and were allowed to react without further purification. Pentafluorophenylmanganese pentacarbonyl[4,5] was synthesized using the method of Stone, *et al.*,[4] using a more convenient preparation of pentafluorophenyllithium.[6] Yields in excess of 60% were consistently obtained.

Microanalyses were performed by Alfred Bernhardt Mikro-

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TABLE I

ANALYTICAL DATA

Compound	% calcd C	% calcd H	% calcd F	% calcd P	% found C	% found H	% found F	% found P
$C_6F_5Mn(CO)_5$	36.50	0.00			36.66	0.00		
$C_6F_5Mn(CO)_4P(C_6H_5)_3$	56.40	2.54	15.93	5.19	56.06	2.42	15.59	5.04
$C_6F_5Mn(CO)_4As(C_6H_5)_3$	52.53	2.36	14.84		52.10	2.54	14.42	
$C_6F_5Mn(CO)_4Sb(C_6H_5)_3$	48.95	2.20	13.82		48.68	2.04	12.45	
$C_6F_5Mn(CO)_4P(OC_6H_5)_3$	52.19	2.35	14.74	4.81	52.71	2.52	14.65	4.71
$C_6F_5Mn(CO)_4NC_5H_5$	43.61	1.22	22.99		43.95	1.18	22.19	
$C_6F_5Mn(CO)_3[P(n\text{-}C_4H_9)_3]_2$	55.77	7.66	13.37		55.85	7.36	13.14	
$C_6F_5Mn(CO)_3[P(OC_2H_5)_3]_2$	39.51	4.74			39.68	4.87		
$C_6F_5Mn(CO)_3[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$	59.67	3.43			59.64	3.45		
$C_6F_5Mn(CO)_3(CH_3SCH_2CH_2SCH_3)$	36.46	2.35	22.18		37.05	2.29	22.07	

TABLE II

PHYSICAL PROPERTIES AND IR SPECTRAL DATA

Compound	Mp,[a] °C	Color	Yield, %	Carbonyl str freq,[b] cm^{-1}
$C_6F_5Mn(CO)_5$	123–124[c]	White	65	2131 m, 2066 vw, 2043 vs, 2012 s, 1968 vw[d]
$C_6F_5Mn(CO)_4P(n\text{-}C_4H_9)_3$		Pale yellow	12	2080 m, 2011 s, 1994 vs, 1957 s
$C_6F_5Mn(CO)_4P(C_6H_5)_3$	135–137	Pale yellow	66	2084 m, 2012 m, 2001 s, 1959 m
$C_6F_5Mn(CO)_4As(C_6H_5)_3$	133–136	Pale yellow	54	2084 m, 2011 m, 2002 s, 1961 m
$C_6F_5Mn(CO)_4Sb(C_6H_5)_3$	133–134	Yellow	51	2080 m, 2011 m, 1999 s, 1962 m
$C_6F_5Mn(CO)_4P(OC_6H_5)_3$	119–121	White	80	2095 m, 2030 s, 2015 s, 1982 s
$C_6F_5Mn(CO)_4NC_5H_5$	105–106	Yellow	9	2090 m, 2004 vs, 1961 s
$C_6F_5Mn(CO)_3[P(n\text{-}C_4H_9)_3]_2$	110–111	Pale yellow	38	2021 w, 1935 vs, 1903 s
$C_6F_5Mn(CO)_3[P(OC_2H_5)_3]_2$	75–76	White	80	2050 m, 1968 vs, 1939 s
$C_6F_5Mn(CO)_3[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$	200 dec	White	72	2022 s, 1960 m, 1926 w
$C_6F_5Mn(CO)_3(CH_3SCH_2CH_2SCH_3)$	169–171	Yellow	57	2028 m, 1959 m, 1914 m

[a] All melting points determined using a Kofler hot-stage microscope. [b] Measured in cyclohexane solution. [c] Literature mp 118–120,[4] 121–122°.[5] [d] Literature: 2135 (m), 2068 (w), 2040 (vs), 2012 (s), 1968 cm^{-1} (w) in cyclohexane solution;[4] 2137, 2053, 2000, 1969 cm^{-1} in KBr pellet.[5]

analytisches Laboratorium, Elbach über Engelskirchen, Germany, and by the microanalytical laboratory of this department. Results are given in Table I. Infrared spectra (Table II) were measured using a Perkin-Elmer Model 337 (grating) spectrometer with a Texas Instruments Servo-Riter recorder. Bands of gaseous CO and DBr at 2147.1 and 1804.9 cm^{-1}, respectively, were used for calibration. Fluorine nmr spectra were obtained in acetone solution with C_6F_6 as internal standard using a Varian A56/60A spectrometer. Mass spectra were recorded with an AEI MS9 instrument.

Tri-*n*-butylphosphine Complexes.—To a solution of tri-*n*-butylphosphine (0.84 g, 4.2 mmol) in 20 ml of xylene was added pentafluorophenylmanganese pentacarbonyl (1.5 g, 4.1 mmol). The mixture was heated at 135° for 3 days and cooled, and the solvent was removed under reduced pressure. The resulting solid was subjected to sublimation under high vacuum at 60° to give colorless oily crystals. On resublimation, the volatile product (0.25 g, 0.48 mmol) remained slightly impure but was confirmed to be $C_6F_5Mn(CO)_4P(n\text{-}C_4H_9)_3$ by an exact mass measurement of its parent ion in the mass spectrum: calculated mass 536.0947, measured mass 536.0948. The nonvolatile product was recrystallized twice from hexane to yield pale yellow crystals of $C_6F_5Mn(CO)_3[P(n\text{-}C_4H_9)_3]_2$ (1.1 g, 1.6 mmol).

$C_6F_5Mn(CO)_4P(C_6H_5)_3$.—Pentafluorophenylmanganese pentacarbonyl (1.0 g, 2.8 mmol) and triphenylphosphine (0.74 g, 2.8 mmol) were added to 30 ml of toluene and the mixture was heated at 90° for 3 days. After removal of solvent under reduced pressure, the residue was taken up in the minimum of hexane, filtered, and cooled to yield pale yellow crystals. These were recrystallized once from hexane to give the pure product (1.1 g, 1.8 mmol).

The same procedure was used for the preparation of the analogous triphenylarsenic, triphenylantimony, and triphenyl phosphite derivatives; in the latter case, a twofold excess of ligand was used.

$C_6F_5Mn(CO)_4NC_5H_5$.—Pentafluorophenylmanganese pentacarbonyl (6.0 g, 17 mmol) was dissolved in 250 ml of dichloromethane and pyridine (1.5 ml, 1.3 g, 16 mmol) was added. This solution was irradiated for 40 min at 10° by a 450-W Hanovia 679A lamp. Dichloromethane and excess pyridine were removed at reduced pressure, the remaining solid was taken up in chloroform, and the solution was filtered. Evaporation of chloroform yielded a yellow solid which was sublimed at room temperature for 3 days under high vacuum to remove unreacted pentacarbonyl (0.9 g, 2.5 mmol). The unsublimed material was recrystallized twice from hexane to yield the pure product (0.58 g, 1.5 mmol) as light yellow crystals.

$C_6F_5Mn(CO)_3[P(OC_2H_5)_3]_2$.—Technical grade triethyl phosphite (1.2 g, 5.8 mmol) and pentafluorophenylmanganese pentacarbonyl (1.0 g, 2.8 mmol) were dissolved in 30 ml of methylcyclohexane. The mixture was heated for 12 hr at 80° and, after cooling, solvent was removed under reduced pressure. The resulting white solid was recrystallized twice from hexane to yield fine white needles (1.43 g, 2.2 mmol).

$C_6F_5Mn(CO)_3[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$.—Bis(1,2 diphenylphosphino)ethane (1.1 g, 2.8 mmol) was added to a solution of pentafluorophenylmanganese pentacarbonyl (1.0 g, 2.8 mmol). After heating for 24 hr at 90°, solvent was removed under reduced pressure. Recrystallization from benzene yielded the pure product (1.45 g, 2.03 mmol).

$C_6F_5Mn(CO)_3(CH_3SCH_2CH_2SCH_3)$.—Pentafluorophenylmanganese pentacarbonyl (1.5 g, 4.1 mmol) and 2,5-dithiahexane (0.65 g, 5.3 mmol) were heated together in 30 ml of methylcyclohexane for 3 days at 90°. The mixture was cooled to 0° and the resulting solid was collected. Excess pentafluorophenylmanganese pentacarbonyl (0.15 g, 0.4 mmol) was removed by sublimation under high vacuum at 50° and the remaining material was extracted with dichloromethane. After addition of pentane and cooling to −15°, the pure product (0.9 g, 2.1 mmol) was obtained.

Results and Discussion

Substitution of pentafluorophenylmanganese pentacarbonyl by various ligands was achieved by treatment

TABLE III

^{19}F NMR SPECTRAL DATA[a]

Compound	ϕ_o[b]	ϕ_p[b]	ϕ_m[b]	$\pm J_{24}$[c]	$\mp J_{34}$	$\mp J_{23}$	$\pm J_{25}$	$\mp J_{35}$	$\mp J_{26}$	J_{P3}	J_{P4}
$C_6F_5Mn(CO)_5$	102.5	158.7	162.4	0	19.1	28.1	9.2	2.8	8.3		
$C_6F_5Mn(CO)_5$[d]	103.5[e]	157.5[e]	161.3[e]	0	19.5[f]						
$C_6F_5Mn(CO)_4P(n\text{-}C_4H_9)_3$	100.7	161.5	162.6	0	19.4						0.8
$C_6F_5Mn(CO)_4P(C_6H_5)_3$	99.3	161.5	162.6	0	19.3	29.3	9.4	3.6	8.7	0.9	1.8
$C_6F_5Mn(CO)_4As(C_6H_5)_3$	99.0	160.2	162.4	0	19.4	29.4	9.6	3.4	8.5		
$C_6F_5Mn(CO)_4Sb(C_6H_5)_3$	97.4	160.0	162.1	0	19.3	29.5	9.5	3.2	8.5		
$C_6F_5Mn(CO)_4Sb(C_6H_5)_3$[d]	98.1	160.0	162.3	0							
$C_6F_5Mn(CO)_4P(OC_6H_5)_3$	100.1	160.0	162.5	0	19.5	29.3	9.5	3.4	8.4	1.4	2.4
$C_6F_5Mn(CO)_4NC_5H_5$	106.5	160.2	162.9	0	19.2	29.6	10.2	3.7	7.6		
$C_6F_5Mn(CO)_3[P(n\text{-}C_4H_9)_3]_2$	97.5	162.6	163.0	0							
$C_6F_5Mn(CO)_3[P(OC_2H_5)_3]_2$	97.5	162.9	164.6	0	19.3						2.5
$C_6F_5Mn(CO)_3[(C_6H_5)_2PCH_2CH_2\text{-}P(C_6H_5)_2]$	95.6	162.3	164.0	0	19.5						1.1
$C_6F_5Mn(CO)_3[CH_3SCH_2CH_2SCH_3]$	105.3	161.3	164.1	0	19.4	30.5	10.5	4.5	7.1		

[a] Obtained from approximately 10 mol % solutions in acetone unless otherwise stated. Nomenclature of ref 1 is used. [b] Relative to $CFCl_3$, reference C_6F_6 (chemical shift 163.0 ppm). [c] Value of zero indicates $J_{24} \leq 0.7$ cps. [d] Obtained from approximately 5 mol % solutions in benzene. [e] Literature: $\phi_o = 104.3$, $\phi_p = 157.5$, $\phi_m = 161.2$;[4,16] $\phi_o = 102.4$, $\phi_p = 155.7$, $\phi_m = 159.6$;[5] these values are corrected by addition of 76.5 ppm to the reported values in order to convert from the reference CF_3COOH to $CFCl_3$: G. V. D. Tiers and G. Filipovich, *J. Phys. Chem.*, **63**, 761 (1959). [f] Literature: $J_{34} = 26\ (\pm 2)$ cps.[5]

with free ligand, usually with the assistance of heat or ultraviolet light. The substitution reactions resemble those of other manganese pentacarbonyl systems, particularly the phenyl and bromo derivatives. An exception is the reaction of triphenyl phosphite, in which only a monosubstituted derivative is formed even when heat and excess ligand are used. This feature is analogous to the reaction of the monofluorophenyl compound with triphenyl phosphite.[3] Disubstituted triphenyl phosphite complexes are easily obtained in the cases of $Mn(CO)_5Br$[7] and $Mn(CO)_5C_6H_5$.[8,9]

Infrared Spectra.—In the monosubstituted complexes the patterns of the terminal carbonyl stretching frequencies (Table II) are very similar to those reported for the compounds *cis*-$BrMn(CO)_4L$,[10] *cis*-$C_6H_5Mn(CO)_4L$,[8,11] and *cis*-$FC_6H_4Mn(CO)_4L$,[3] suggesting that the pentafluorophenyl group and substituting ligand (L) are also cis to each other.

The bis-substituted derivatives are of two types: those having one bidentate ligand and those having two monodentate ligands. This division is evidenced in the spectra. The infrared spectra of the bis(tri-*n*-butylphosphine) and bis(triethyl phosphite) derivatives show a close resemblance to those observed for $Mn(CO)_3L_2Br$,[7] where it was concluded that the donor ligands were mutually trans. Thus it may be supposed that a similar arrangement is present in the derivatives reported here. The intensity pattern (weak, strong, strong, in order of decreasing frequency) does not exclude an arrangement in which one phosphorus ligand is trans to the pentafluorophenyl group; however, such an arrangement is most unlikely in view of the magnetic equivalence of the two phosphorus atoms in the bis(triethyl phosphite) complex (see nmr results below).

On the other hand, the bis(1,2-diphenylphosphino)ethane and 2,5-dithiahexane derivatives must, by the structure of these ligands, be substituted at adjacent sites. Consistent with an all-cis arrangement for the carbonyl groups, these derivatives show three carbonyl stretching bands of approximately equal intensity in their infrared spectra.

^{19}F Nmr Spectra.—Analysis of the ^{19}F nmr spectra was carried out using well-established methods.[1,2] Acetone was used as solvent since all of the compounds were not sufficiently soluble in benzene. Such a change in solvent fortunately did not greatly alter the nmr parameters as may be seen from the results for $C_6F_5Mn(CO)_5$ and $C_6F_5Mn(CO)_4Sb(C_6H_5)_3$ (Table III). Some coupling constants could not be evaluated owing to decomposition or insufficient solubility.

The nmr parameters were consistent with the linear relationship between the coupling constant, J_{24}, and the para fluorine chemical shift, ϕ_p.[1] It is possible to calculate values of the parameters σ_I[12] and $\sigma_R{}^0$[13] from eq 1 and 2 and Table VI of ref 1. It appears, however, that these equations give values of the substituent parameters which are at variance with expectation, particularly for σ_I.[14] On the other hand, the qualitative relation between J_{24} or ϕ_p and π bonding to the pentafluorophenyl ring remains tenable, and J_{24} values near zero in all cases imply that the manganese carbonyl substituents are weak π donors relative to hydrogen. Substitution of carbon monoxide by another ligand certainly changes the π-electron distribution as evidenced by a shift in the stretching frequencies of the remaining carbonyl groups. The lack of influence on

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(14) In the case of $C_6F_5Mn(CO)_5$, calculated Taft parameters are $\sigma_I = +0.33$ and $\sigma_R{}^0 = -0.21$; the former value would imply an inductive withdrawal by the pentacarbonylmanganese group. The equations used to obtain the Taft parameters were derived[1] for eight "common" organic substituents, and it must be concluded that an extrapolation is not valid for the substituents considered here. Such an extrapolation for *mono*fluorophenyl derivatives, however, leads to reasonable results.[3] Further investigation will be required to determine why extrapolation is not valid in the pentafluorophenyl case.

the aromatic system by such substitution can be attributed either to poor overlap of the aromatic π system and the π system on the metal or to a more facile change of the carbonyl system in relation to the pentafluorophenyl group.

The values of ϕ_p seem to increase with increased substitution. This is consistent with a reduction in π-acceptor character of the two-electron donors on manganese, causing increased donation to the pentafluorophenyl system.

Of particular interest is the low shielding of the ortho fluorine atoms in these manganese compounds, which in fact exhibit the lowest ϕ_o values of any reported pentafluorophenyl derivatives. A large paramagnetic contribution to the screening is to be expected by analogy with the ^{19}F nmr results for α-fluorine atoms present in perfluoroalkylmetal complexes.[15,16] However in contrast to these perfluoroalkyl complexes, pentafluorophenyl derivatives show a higher sensitivity to the electronegativity of the atom to which the perfluoroorganic group is attached.[1]

In a few compounds it was possible to measure the coupling of phosphorus to para fluorine. Thus the para fluorine nmr spectra were observed as triplets of doublets for monosubstituted compounds or as triplets of triplets for disubstituted derivatives. A triplet of triplets would also be expected if J_{24} were significant and the phosphorus coupling were negligible. We believe, however, that the assignment of the smaller coupling to phosphorus is correct, since J_{24} was insignificant[17] in all other compounds and the phosphorus coupling was significant in all phosphine and phosphite derivatives which allowed measurement. Taking this assignment as correct, it follows that both phosphorus atoms in the bis(triethyl phosphite) and bis(diphenylphosphino)ethane derivatives are in magnetically equivalent and most probably symmetrically equivalent environments.

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[17] In view of the ϕ_p values and the quite firmly established $J_{24} - \phi_p$ relationship, a value of J_{24} close to zero is expected.

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The Crystal Structure of Lithium Thiochromite, $LiCrS_2$

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The crystal structures of the alkali thiochromites, $MCrS_2$, where M = Na, K, and Rb, have been studied in some detail and all these compounds are rhombohedral.[3-5] On the other hand, the lithium analog, $LiCrS_2$, was reported to be cubic.[6] Examination of the powder diffraction pattern, especially at the smaller *d* spacings, showed deviations from those calculated from a cubic cell, and a structure of lower symmetry was indicated for the lithium compound as well. We have recently grown single crystals of $LiCrS_2$, and a definitive crystal structure determination became possible.

Experimental Section

Sample Preparations.—Both polycrystalline powders and single crystals of $LiCrS_2$ were prepared. The powder samples were made by heating dried stoichiometric mixtures of Li_2CO_3 and Cr_2O_3, contained in a graphite boat, at 800° in an argon gas flow saturated with CS_2. The single crystals were grown under similar conditions but with a Li_2CO_3:Cr_2O_3 molar ratio of 10:1. This mixture was converted to the sulfides at 800°, the temperature was then rapidly raised to 1100°, the CS_2-saturated argon flow was reduced to less than 1 cm^3/min, and the temperature was decreased at the rate of 10°/hr. Thin hexagonal platelets of $LiCrS_2$ remained after the excess Li_2S was washed away with water. The carbon boats used during growth were attacked by the molten Li_2S. A total chemical analysis was not possible because both the powders and the crystals were contaminated with carbon. However, the ratios of chromium to lithium as determined by flame atomic absorption of both polycrystalline and single crystal samples agreed to within 0.6%, averaging 5.9 by weight. This value is in reasonable agreement with the calculated value of 7.5 considering that the mutual interference of these atoms was not investigated. The density of a polycrystalline sample which was least contaminated with carbon, as determined by displacement in CCl_4 at 25°, was 3.01 g/cm^3 with a reproducibility of ±0.04 g/cm^3. The small amount of sample available and its contamination with carbon precluded high accuracy in the density measurement.

The crystals of $LiCrS_2$ are hexagonal platelets with the crystal *c* axis normal to the plate. In appearance they are black and reflecting and the surface was unchanged after long exposure to air. Accurate unit cell dimensions were determined by least-squares fit of the back-reflection lines of the X-ray powder photograph obtained at 25° with Ni-filtered Cu Kα radiation using a 114.6-cm diameter camera. Film shrinkage corrections were made.

Crystal Data for $LiCrS_2$.—The crystal data for $LiCrS_2$ are as follows: mol wt 123.06; trigonal; space group $P\bar{3}m1$ or $P3m1$; $a = 3.456 \pm 0.001$ Å, $c = 6.020 \pm 0.002$ Å, $Z = 1$, $V = 62.60$ Å^3; $d_{\text{calcd}} = 3.26$ g/cm^3; $d_{\text{obsd}} = 3.01$ g/cm^3.

Intensity data for the *h0l*, *h1l*, and *h2l* levels were recorded by the equiinclination Weissenberg method using Ni-filtered Cu Kα radiation, all possible reflections for this wavelength being included in these levels. A multiple-film technique was used and the reflection intensities were estimated visually by comparison with a standard intensity scale. The crystal used was cut from a platelet parallel to one of the hexagon sides and perpendicular to the plate thickness. It was 0.12 mm long (*b* axis) and had an almost square cross section 0.053 mm on edge. Absorption corrections were made using a cylindrical approximation. Since the absorption is large, $\mu = 516$/cm, maximum errors in the approximation used are estimated to be as high as 9% for the reflections most sensitive to the difference between real and assumed crystal shapes, but the average error will be much less than this. A set of *F* values was obtained for each level after application of Lorentz and polarization factors and the three sets

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