electrons. In this compound, however, the effective atomic number of the cobalt is two greater than that of krypton.

On reaction of (II) with triphenylphosphine in benzene only one carbonyl group was displaced to give (tetraphenylcyclobutadiene)(triphenylphosphine)cobalt carbonyl bromide (III) (m.p. 225–230° decomp.), which was also paramagnetic.

Numerous workers have described the aluminum chloride catalyzed reaction of metal carbonyl halides with aromatic hydrocarbons to give π-arene–metal complexes[5]. (Tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (II) reacted similarly with benzene, toluene or mesitylene under these conditions to give, after treatment of the product with saturated aqueous potassium bromide, the (π-arene)(π-tetraphenylcyclobutadiene)cobalt(I) bromides (IV, $X = Br$, $R = R' = H$; $R = CH_3$, $R' = H$ and $R = R' = CH_3$) in 55, 62 and 72% yields respectively. These complexes were very stable yellow crystalline solids, readily soluble in methanol, and like the well-known isoelectronic (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)cobalt, were all diamagnetic. This was shown by the sharp proton resonances which were observed for these complexes, the positions and intensities of which were in agreement with the proposed structures.

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The ultraviolet properties of some perphenylated linear and cyclic polysilanes

Subsequent to the initial work by Hague and Prince[1] on the ultraviolet properties of hexaphenyldisilane, related investigations with other linear and branched-chain polysilanes have been carried out[2,3,4,5,6]. These later investigations suggested that the ultraviolet spectral properties of polysilanes are due to the silicon–silicon bond chromophore, and allowed a number of structure-absorption rules to be formulated. We have now examined the ultraviolet properties of the perphenylated linear polysilane series, $Ph(SiPh_2)_nPh$ ($n = 2$ through 7) and of all the available cyclosilane* derivatives.

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* For a current review of the chemistry of cyclosilane derivatives, see refs. 4 and 6.

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TABLE 1

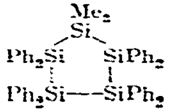
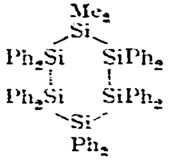
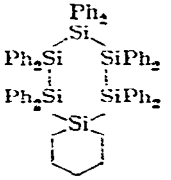
ULTRAVIOLET SPECTRAL DATA FOR THE PERPHENYLATED LINEAR POLYSILANE SERIES, $Ph(SiPh_2)_nPh$.

n	*λ_{max} (mμ)*	*Molar absorbtivity (ε)*	*Preparation reference*
2	246.5	32,000[a]	7
3	255	32,200	8
4	255 (shoulder) 288	32,800 22,800	8, 9
5	250 (shoulder) 296.5	36.300 27.300	*b*
6	255 (shoulder) 312	38.300 30.800	*c*
7	255 (shoulder) 324	48.300 38.000	7

[a] Lit.[1] value, 32,600. [b] H. Gilman and D. R. Chapman, unpublished studies[4]. [c] H. Gilman and R. Harrell, unpublished studies[4].

TABLE 2

ULTRAVIOLET SPECTRAL DATA FOR SOME CYCLOSILANE DERIVATIVES

Compound	*λ_{max} (mμ)*	*Molar absorbtivity (ε)*	*Preparation reference*
$(SiPh_2)_4$[a]	234 270	64.500 35.000	7
$(SiPh_2)_5$[a]	251 (shoulder)	60,000	7, 11
	249 (shoulder)	41,000	*b*
$(SiPh_2)_6$[a]	248 (shoulder)	60,000	12
	250 (shoulder)	56.800	11
	250 (shoulder)	50,300	
$(SiMe_2)_6$	232 255 (shoulder)	5,800 2,000	13

[a] For a comparison of the ultraviolet properties of this cyclosilane with its cyclogermane analog, see ref. 10. [b] H. Gilman and S. G. Cottis, unpublished studies[4]. [c] H. Gilman and S. Inoue, unpublished studies.

Table 1 lists the spectral properties observed for the $Ph(SiPh_2)_nPh$ series. The characterization of this series presented a difficult problem when the usual analytical, spectral and chemical methods were employed. It is, however, obvious from an examination of Table 1 that the ultraviolet properties of a given homologous polysilane series can give direct and highly useful information concerning the length of the Si chain. A comparison of these data with those obtained[3] for the analogous permethylated polysilane series, $Me(SiMe_2)_nMe$,[*] again illustrates the large bathochromic shifts associated with phenyl substitution. In addition, the increased complexity of the spectra with increasing chain length is consistent with the $Me(SiMe_2)_nMe$ series.

The spectral data for all the available cyclosilane derivatives are given in Table 2. Although only a few cyclosilane derivatives have been described, it appears that the most pronounced bathochromic shifts will be observed with the smaller rings. Since the ultraviolet spectral properties have been associated with the Si–Si chromophore, the bathochromic shift observed with $(SiPh_2)_4$ may be a reflection of the increased ground state energy of this molecule resulting from internal strain.

The only permethylated cyclosilane which has been described is $(Me_2Si)_6$. Although this compound was reported[14] to absorb at 280 mμ, we have observed that pure samples of $(Me_2Si)_6$ show no maxima in this region.

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