Electron Spin Resonance Studies of Axial Ligation to Cobalt(II) Complexes. Part 1. Some Oxo-, Thio-, and Seleno-Schiff Bases

By **Gérard Labauze** and **J. Barrie Raynor,*** Department of Chemistry, The University, Leicester LE1 7RH

Electron spin resonance spectra have been recorded for frozen solutions of five different low-spin cobalt(II) Schiff-base complexes having either oxygen, sulphur, or selenium as two of the co-ordinating atoms and with a range of up to seven phosphines or phosphite ligands co-ordinated in the axial position. From analysis of the cobalt and phosphorus hyperfine tensors and the *g* tensor, the bonding parameters have been calculated. Correlations are made in an attempt to distinguish between electronic and steric effects in the co-ordination of the phosphorus base. Internal bond angles in the phosphorus ligand have been calculated.

A CONSIDERABLE amount of work on the e.s.r. of cobalt(II) complexes with Schiff bases and related ligands has now been published.[1] In all cases, the e.s.r. spectra may be interpreted in terms of a structurally planar low-spin system with ground states involving d_{z^2}, $d_{x^2-y^2}$, or d_{yz} orbitals. In the presence of co-ordinating solvents or bases axial co-ordination takes place with consequent destabilising of the d_{z^2} orbital (which becomes more σ-antibonding than in the planar complexes) so that it becomes the ground state. Most adducts studied have been with nitrogen bases and relatively few with bases co-ordinating *via* a phosphorus atom.[2-10] No wide ranging detailed study has been made to study the effect of varying the cobalt ligands or phosphorus substituents, nor has a single-crystal study been made because of the lack of a suitable diamagnetic host lattice. We have made a systematic study of 12 cobalt(II) complexes with Schiff bases and related ligands with a range of up to seven phosphines and phosphites. A thorough analysis of the *g*, $A(^{59}Co)$, and $A(^{31}P)$ tensors is made in this and subsequent papers, together with a critical analysis of the relevant theory.

In this paper, we report e.s.r. results for the adducts of *NN'*-ethylenebis(acetylacetoneiminato)cobalt(II), [Co(acen)], and the thio- and seleno-analogues, [Co(sacen)] and [Co(seacen)], and also adducts with *NN'*-ethylenebis(benzoylacetoneiminato)cobalt(II), [Co(bzacen)], and the thio-derivative [Co(sbzacen)], each with up to seven different phosphines and phosphites. The aim of this work was to understand the effects of systematically varying an equatorial ligating atom (O→S→Se) and also the axial ligands. Ligands co-ordinating *via* P are particularly sensitive to changes in remote substituents because of the very large hyperfine coupling to ^{31}P and so act as very sensitive probes of structure and spin density.

EXPERIMENTAL

The compounds [Co(acen)] and [Co(sacen)] were prepared by standard methods.[11,12] [Co(seacen)] was prepared by the same method as used for [Co(sacen)] using an ethanolic solution of Na[HSe] obtained according to the procedure of Klayman and Griffin.[13] The compounds [Co(bzacen)] and [Co(sbzacen)] were prepared by analogous methods. Adducts were prepared by adding (i) a stoicheiometric amount, and (ii) a ten-fold excess of the appropriate phosphine or phosphite to a solution of the complex in CH_2Cl_2. All manipulations were carried out and all materials kept *in vacuo* or dry nitrogen. Solvents were redistilled over $Li[AlH_4]$ or CaH_2 and kept over molecular sieves and thoroughly degassed before using. Electron spin resonance spectra were recorded on a Varian E3 spectrometer at 77 K and at a temperature just above the freezing point of the solutions. Spectra were calibrated with diphenylpicrylhydrazyl (dpph). The magnetic field was calibrated using Mn^{2+} in MgO.

RESULTS AND DISCUSSION

Frozen-solution spectra recorded at 77 K were usually very well resolved and readily interpreted in terms of three well spaced *g* features. The two *g* features at higher fields (g_y and g_z) exhibited cobalt hyperfine coupling (^{59}Co, $I = \frac{7}{2}$) and further splitting of each line into two by phosphorus (^{31}P, $I = \frac{1}{2}$). The *g* feature at low field (g_x) was usually broad and could not be resolved. At *ca.* 200 K the fluid-solution spectrum was at its optimum resolution, but even this usually only showed a doublet due to interaction with phosphorus. At higher temperatures, the spectra broadened considerably. Good values of g_y and g_z were obtained directly from the spectrum, and since $g_{iso.}$ was known from the fluid-solution spectrum, it was possible to calculate g_x with confidence. Hyperfine coupling to cobalt on g_y and g_z could be accurately measured. The spacing of lines was very even and suggested that quadrupole effects were slight. The assignment of a value for A_x(Co) was more difficult, but from the line width and computer simulation, an estimate could be made. As it happens, see below, the accuracy of this value is not very important in the calculation of bonding parameters. Hyperfine couplings to cobalt were measured in gauss † and converted to cm^{-1} for use in subsequent calculations, but those for phosphorus were kept in gauss for calculation of phosphorus bonding parameters. In all cases, there was splitting of each cobalt hyperfine line into two rather than three, showing that only one phosphorus ligand was present, not two as was observed in the case of pyridine adducts with [Co(salphen)], $[Co(Hdmg)_2]$, and $[Co(pts)]^{4-}$ [salphen = *o*-phenylenebis(salicylideneiminate), Hdmg = dimethylglyoximate, and pts = tetrasulphonated phthalocyaninate.][8] The assignment of labels *x*, *y*, and *z* to the *g* values is arbitrary, but for

---

† Throughout this paper: 1 G = 10^{-4} T.

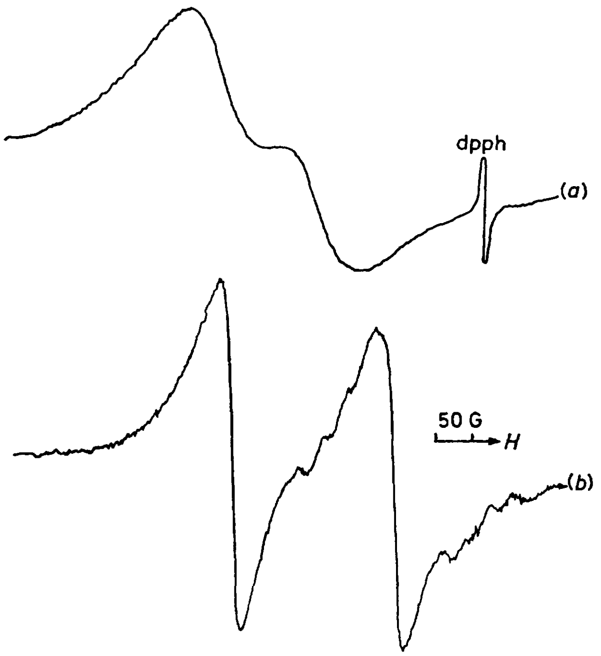

FIGURE 1 Fluid-solution e.s.r. spectra at 200 K of (*a*) [Co(seacen)(PPh$_3$)] and (*b*) [Co(seacen){P(OMe)$_3$}]

comparison with other work, g_z is assigned to the lowest g value since there is good reason to believe this is associated with the z axis of the molecule which we define as along the cobalt–phosphorus bond.

Typical spectra are shown in Figures 1—3 and the experimental g and hyperfine tensors are given in Tables 1 and 2. The spectra were all interpreted in terms of an $^2A_1$ ground state ($ad_{z^2} + bd_{x^2-y^2}$) comprising a mixture of d_{z^2} and $d_{x^2-y^2}$ metal orbitals with coefficients such that $a^2 + b^2 = 1$. We use the group-theory notation for $C_{2v}(z)$ symmetry which is used by most other workers, although recognising that the point-group symmetry in reality is C_s at best.

The Cobalt Hyperfine Tensor.—For analysis of the g tensor and cobalt hyperfine tensor, we make use of the theory of low-spin d^7 ions which McGarvey[14] has extended to third order. The theory takes into account the effect of a mixture of excited quartet states, which are more important in the adducts than in square-planar d^7 complexes.[15] Because there are more unknowns than equations, we have to make some assumptions for some of the C parameters. We approximate $C_3 = C_4 = C_5$ and put $C_6 = 0$ because it is expected to be very small. In the McGarvey notation, C_1, C_2, and C_3 are given by equations (1), (2), and (3) respectively and C_4 and C_5 depend on energy differences between $^2A_1$ and $^4B_2$ and $^4A_2$ respectively. We have added terms in β^2 which are needed to take into account delocalisation; λ = free-ion spin–orbit coupling parameter for Co^{2+}, 533 cm^{-1}; and $\alpha_{3d}{}^2$ = spin density in d_{z^2} orbital, and calculated from P/0.0254. The value of 0.0254 cm^{-1} is taken from the tabulations of hyperfine parameters by Goodman and Raynor.[16] No assumptions were made about the sign

$$C_1 = \frac{\lambda\alpha_{3d}{}^2\beta_{b1}{}^2}{\Delta E(^2A_1 - {}^2B_1)} \tag{1}$$

$$C_2 = \frac{\lambda\alpha_{3d}{}^2\beta_{b2}{}^2}{\Delta E(^2A_1 - {}^2B_2)} \tag{2}$$

$$C_3 = \frac{\lambda\alpha_{3d}{}^2\beta_{a2}{}^2}{\Delta E(^2A_1 - {}^4B_1)} \tag{3}$$

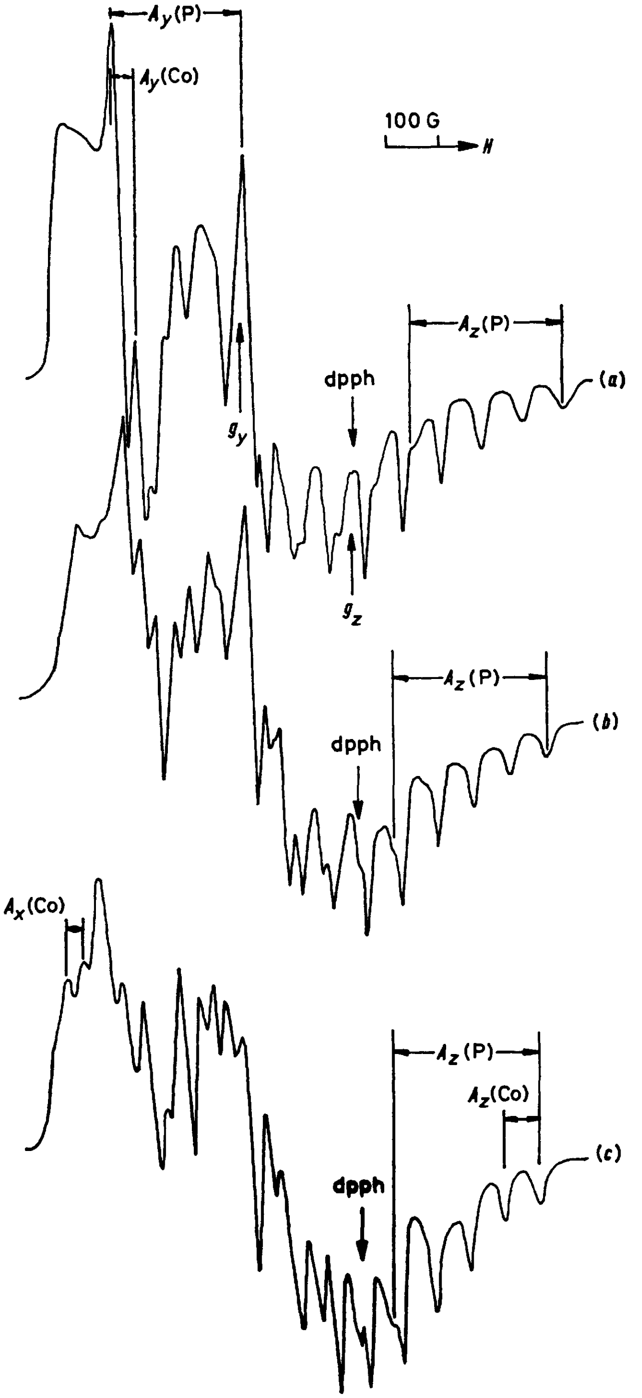

FIGURE 2 Frozen-solution e.s.r. spectrum at 77 K of (*a*) [Co(acen){P(OMe)$_3$}], (*b*) [Co(sacen){P(OMe)$_3$}], and (*c*) [Co(seacan){P(OMe)$_3$}]

TABLE 1

g and ^{59}Co hyperfine tensors and deduced parameters. The units of A_x, A_y, A_z, and P are in 10^{-4} cm^{-1}

Complex	Axial ligand	g_x	g_y	g_z	$g_{av.}$	Hyperfine coupling $-A_x$	$-A_y$	A_z	P	κ	a^2	b^2	Coefficients C_1	C_2	C_3	Spin densities C_{3d}^2	C_{4s}^2	C_L^2	Orbital energies/cm^{-1} ΔB_1	ΔB_2	ΔQ
[Co(acen)]	$P(OMe)_3$	2.406	2.165	2.029	2.200	12	33	78	230	0.109	0.996	0.004	0.026	0.058	0.132	0.91	0.042	0.166	18 240	8 350	3 660
	$P(OEt)_3$	2.407	2.162	2.022	2.197	12	32	77	224	0.114	0.995	0.005	0.027	0.059	0.119	0.88	0.039	0.175	17 240	7 980	3 860
	$P(OEt)_2Ph$	2.389	2.166	2.024	2.193	12	32	75	215	0.109	0.997	0.003	0.027	0.057	0.121	0.85	0.039	0.147	16 680	7 960	3 720
	PBu_3	2.454	2.162	2.023	2.213	12	34	76	244	0.135	0.992	0.008	0.028	0.064	0.125	0.96	0.039	0.150	18 050	7 960	4 110
	PPh_3	2.457	2.186	2.018	2.220	12	25	87	275	0.130	0.990	0.010	0.035	0.065	0.115	1.08	0.045	0.141	16 690	8 850	5 030
	dppe	2.401	2.162	2.022	2.195	12	34	86	245	0.107	0.996	0.004	0.027	0.058	0.118	0.96	0.045	0.091	18 970	8 830	4 350
[Co(sacen)]	$P(OMe)_3$	2.324	2.158	2.025	2.169	14	32	67	180	0.094	0.999	0.001	0.024	0.048	0.118	0.71	0.035	0.157	15 780	7 840	3 190
	$P(OEt)_3$	2.329	2.158	2.023	2.170	14	32	64	175	0.102	0.999	0.001	0.024	0.049	0.115	0.69	0.033	0.151	15 090	7 450	3 200
	$P(OPh)_3$	2.414	2.154	2.019	2.196	14	30	72	214	0.122	0.993	0.007	0.027	0.060	0.113	0.84	0.036	0.164	16 660	7 540	3 980
	$P(OEt)_2Ph$	2.260	2.161	2.023	2.148	14	33	66	166	0.077	1.000	0.000	0.023	0.040	0.110	0.65	0.034	0.153	14 970	8 650	3 160
	PBu_3	2.370	2.164	2.024	2.186	14	31	63	184	0.117	0.998	0.002	0.026	0.054	0.120	0.72	0.032	0.133	14 710	7 120	3 220
	PPh_3	2.422	2.156	2 016	2.198	14	25	74	217	0.120	0.991	0.009	0.029	0.060	0.107	0.85	0.037	0.106	15 970	7 530	4 260
	dppe	2.413	2.155	2.017	2.195	14	28	72	211	0.120	0.993	0.007	0.028	0.060	0.108	0.83	0.036	0.096	16 010	7 440	4 090
[Co(seacen)]	$P(OMe)_3$	2.285	2.170	2.028	2.161	18	33	64	173	0.096	1.000	0.000	0.025	0.042	0.122	0.68	0.033	0.159	14 670	8 550	2 970
	$P(OEt)_3$	2.281	2.173	2.026	2.160	18	34	62	170	0.104	1.000	0.000	0.025	0.043	0.118	0.67	0.031	0.169	14 080	8 380	3 020
	$P(OPh)_3$	2.433	2.170	2.024	2.209	18	28	68	221	0.139	0.990	0.010	0.030	0.061	0.124	0.87	0.034	0.164	15 390	7 660	3 730
	PBu_3	2.332	2.180	2.031	2.181	18	30	61	178	0.112	0.999	0.001	0.027	0.048	0.131	0.70	0.032	0.134	13 720	7 780	2 860
	PPh_3	2.447	2.180	2.024	2.217	18	24	71	234	0.139	0.988	0.012	0.033	0.062	0.125	0.92	0.036	0.103	14 920	7 930	3 920
	dppe	2.411	2.183	2.024	2.206	18	26	67	211	0.133	0.992	0.008	0.032	0.058	0.123	0.83	0.034	0.087	13 890	7 600	3 610
[Co(bzacen)]	$P(OMe)_3$	2.432	2.171	2.025	2.209	12	30	79	241	0.120	0.993	0.007	0.029	0.061	0.126	0.95	0.041	0.166	17 260	8 260	4 000
	$P(OEt)_3$	2.424	2.177	2.026	2.209	12	26	82	246	0.110	0.993	0.007	0.030	0.060	0.128	0.97	0.044	0.155	17 050	8 610	4 050
	$P(OPh)_3$	2.435	2.157	2.020	2.204	12	33	85	254	0.119	0.992	0.008	0.028	0.062	0.117	1.00	0.044	0.141	19 260	8 570	4 560
	$P(OEt)_2Ph$	2.383	2.177	2.025	2.195	12	26	76	213	0.100	0.996	0.004	0.029	0.055	0.123	0.84	0.040	0.163	15 390	8 060	3 640
	PBu_3	2 455	2 165	2 022	2 214	12	30	76	241	0.132	0.991	0.009	0.029	0.064	0.123	0.95	0.039	0.159	17 150	7 880	4 130
	PPh_3	2.466	2.176	2.018	2.220	12	25	87	276	0.129	0.988	0.012	0.033	0.066	0.115	1.09	0.045	0.120	17 410	8 810	5 020
	dppe	2.477	2.158	2.019	2.218	12	30	82	265	0.136	0.987	0.013	0.030	0.067	0.119	1.04	0.042	0.123	18 750	8 340	4 690
[Co(sbzacen)]	$P(OMe)_3$	2.406	2.174	2.020	2.200	14	29	74	220	0.122	0.995	0.005	0.030	0.059	0.114	0.87	0.037	0.176	15 330	7 830	4 040
	$P(OEt)_3$	2.405	2.175	2.023	2.201	14	28	76	224	0.115	0.994	0.006	0.030	0.058	0.120	0.88	0.039	0.165	15 740	8 080	3 910
	PBu_3	2.411	2.170	2.022	2.201	14	30	73	220	0.123	0.994	0.006	0.029	0.059	0.119	0.87	0.037	0.154	15 860	7 800	3 880
	PPh_3	2.441	2.172	2.017	2.210	14	26	82	252	0.125	0.990	0.010	0.032	0.063	0.111	0.99	0.042	0.095	16 570	8 410	4 770
	dppe	2.451	2.160	2.019	2.210	14	30	80	250	0.131	0.989	0.011	0.029	0.064	0.116	0.98	0.040	0.121	17 900	8 230	4 520

TABLE 2

Phosphorus-31 hyperfine tensors and deduced parameters. The units of hyperfine coupling are in Gauss

Complex	Axial ligand	Experimental hyperfine coupling A_x	A_y	A_z	$A_{iso.}$	Anisotropic hyperfine tensor A_{xx}	A_{yy}	A_{zz}	Principal values of decomposed tensors A_{zz}	A_{xx}	Spin densities on ^{31}P C_{3s}^2	C_{3p}^2	total	λ^2	θ
[Co(acen)]	$P(OMe)_3$	191	258	292	247	−65	12	43	20	−44	0.067	0.099	0.166	1.47	103° 19′
	$P(OEt)_3$	185	254	290	243	−57	12	45	22	−46	0.066	0.109	0.175	1.65	104° 9′
	$P(OEt)_2Ph$	179	241	270	230	−50	12	38	17	−41	0.063	0.084	0.147	1.35	103° 39′
	PBu_3	122	175	210	169	−46	7	39	21	−35	0.046	0.104	0.150	2.26	106° 28′
	PPh_3	105	162	195	154	−48	9	39	20	−38	0.042	0.099	0.141	2.36	107° 47′
	dppe	98	171	190	153	−54	19	35	10	−48	0.042	0.050	0.091	1.10	102° 45′
[Co(sacen)]	$P(OMe)_3$	202	257	288	249	−46	9	37	18	−36	0.068	0.089	0.157	1.32	102° 29′
	$P(OEt)_3$	197	253	282	244	−46	10	36	17	−37	0.066	0.084	0.151	1.27	102° 13′
	$P(OPh)_3$	212	262	294	256	−43	7	36	19	−33	0.070	0.084	0.164	1.35	103° 41′
	$P(OEt)_2Ph$	198	240	270	236	−37	5	32	18	−27	0.064	0.089	0.153	1.39	103° 53′
	PBu_3	128	164	194	162	−33	3	30	18	−24	0.044	0.089	0.133	2.02	106° 40′
	PPh_3	109	162	185	152	−42	11	31	13	−34	0.041	0.064	0.106	1.56	104° 44′
	dppe	102	170	190	154	−51	17	34	11	−44	0.042	0.054	0.096	1.30	102° 24′
[Co(seacen)]	$P(OMe)_3$	196	246	278	240	−43	7	36	19	−33	0.065	0.094	0.159	1.44	103° 9′
	$P(OEt)_3$	195	242	277	238	−42	5	37	21	−39	0.065	0.104	0.169	1.61	104° 58′
	$P(OPh)_3$	214	261	293	256	−41	6	35	19	−31	0.070	0.094	0.164	1.35	103° 41
	PBu_3	131	165	196	164	−32	2	30	18	−22	0.045	0.089	0.134	2.00	106° 34′
	PPh_3	99	152	175	142	−42	11	31	13	−34	0.039	0.064	0.103	1.67	104° 14′
	dppe	105	173	190	156	−50	18	32	9	−45	0.042	0.045	0.087	1.05	101° 52′
[Co(bzacen)]	$P(OMe)_3$	190	260	294	248	−57	13	44	20	−46	0.067	0.099	0.166	1.47	103° 18′
	$P(OEt)_3$	190	254	285	243	−52	12	40	18	−42	0.066	0.089	0.155	1.35	103° 40′
	$P(OPh)_3$	210	276	300	262	−51	15	36	14	−44	0.071	0.069	0.141	0.97	100° 19′
	$P(OEt)_2Ph$	185	242	275	234	−48	9	39	29	−38	0.064	0.099	0.163	1.56	104° 43′
	PBu_3	112	174	212	166	−53	9	44	23	−41	0.045	0.114	0.159	2.53	107° 15′
	PPh_3	103	160	187	150	−46	11	35	16	−37	0.041	0.079	0.120	1.94	105° 22′
	dppe	103	175	202	160	−56	16	40	16	−47	0.044	0.079	0.123	1.82	105° 53′
[Co(sbzacen)]	$P(OMe)_3$	194	254	290	246	−51	9	42	22	−40	0.067	0.109	0.176	1.63	104° 4′
	$P(OEt)_3$	192	250	284	242	−49	9	40	20	−38	0.066	0.099	0.165	1.50	103° 29′
	PBu_3	121	170	207	166	−44	5	39	22	−32	0.045	0.109	0.154	2.41	107° 56′
	PPh_3	110	160	180	150	−39	11	28	11	−32	0.041	0.054	0.095	1.33	103° 36′
	dppe	97	166	193	152	−54	15	39	16	−46	0.041	0.079	0.121	1.92	105° 16′

of the cobalt hyperfine coupling constants, but the only reasonable fit of the experimental data to the theoretical expressions was obtained when A_z was positive and A_x and A_y negative. This is in accord with the conclusions of others who have made this analysis for ligands co-ordinating *via* phosphorus although for ligands co-ordinating *via* nitrogen, the experimental values are usually of the same sign.[2,3,6,10] The value of g_z is expected to be close to two and so the lowest g value is called g_z and we call this axis the principal axis. Earlier, we said that A_x could not be measured and that the value of A_x selected had little effect upon the bonding parameters. The value selected was estimated from line widths, but a change of 25% in A_x has <1% effect upon C_1 and C_2, 0.2% effect on C_3, 0.2% effect upon a and b, 1.7% effect on P, and 5% effect on κ [defined in equation (4)]. The value of A_y was relatively constant, but A_z varied considerably, being in general larger for acen than for sacen or seacen complexes.

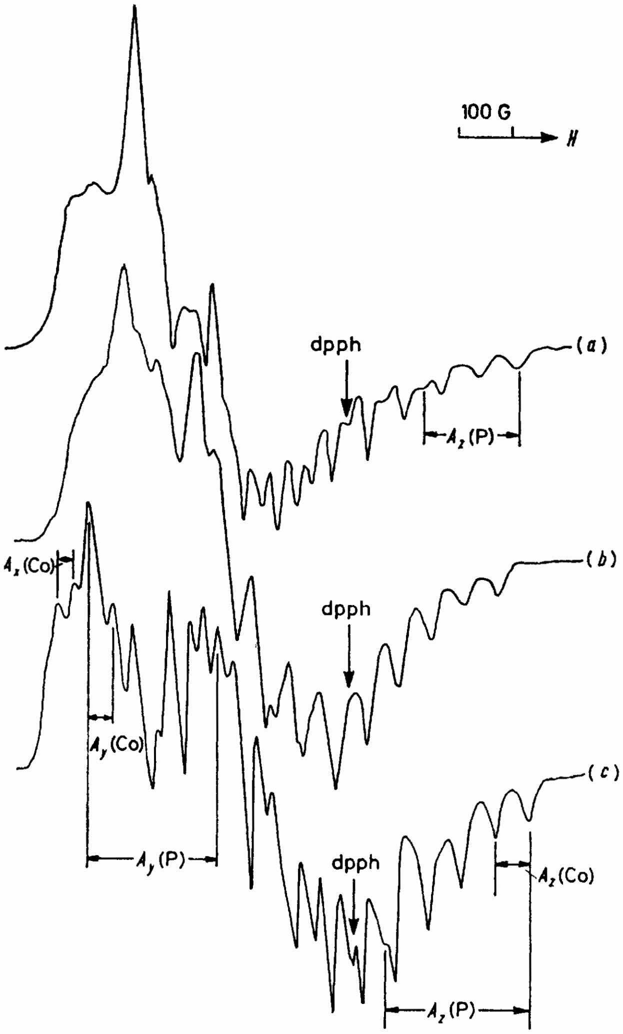

FIGURE 3 Frozen-solution e.s.r. spectrum at 77 K of (*a*) [Co(seacen)(PPh$_3$)], (*b*) [Co(seacen)(PBu$_3$)], and (*c*) [Co(seacen){P(OMe)$_3$}]

Cobalt Spin Densities.—From the deduced values of a^2, we find that in all complexes, the contribution of the d_{z^2} orbital to the ground state of the cobalt is *ca.* 99%. The spin density in this cobalt orbital C_{3d}^2 is given by the ratio of P/P^{2+} where $P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$ (calculated) and P^{2+} is the value calculated for the free Co^{2+} ion.[16] Values of C_{3d}^2 vary considerably with phosphine and with the equatorial ligating atom. For any one phosphine, C_{3d}^2 for acen is much larger than for sacen which is only slightly larger than for seacen. The absence of nitrogen hyperfine coupling to the two equatorial nitrogen atoms, or in the case of [Co(seacen)], to the two selenium atoms, shows that there is very little spin delocalisation *via* σ bonding from the x and y components of the d_{z^2} orbital to the equatorial ligating atoms. This is in direct contrast to the large delocalisation in copper Schiff-base complexes where *ca.* 22% of the unpaired electron is on the nitrogen atoms. Since the total spin density in the cobalt $d_{z^2} + d_{x^2-y^2}$ orbital and in the P$\rightarrow$Co σ bond (sp^n hybrid) is less than unity, and there is not likely to be much spin density straying beyond the phosphorus atom, then the balance of spin density must be delocalised onto the Schiff base *via* π bonding. This is in accord with the expected increase in the π bonding to S and Se atoms. The mechanism for this raises structural implications since if the cobalt and the ligating atoms were strictly coplanar, then π bonding between the d_{z^2} orbital and the p_z, d_{xz}, or d_{yz} orbitals on S or Se would be impossible. π Bonding can only be achieved if the cobalt is significantly out-of-plane and the molecule is saddle shaped. Even in the four-co-ordinate complexes, the cobalt atom is out of the plane of the ligating atoms.[17] As the strength of the bonds between cobalt and the ligating atoms increase in association with axial co-ordination, so will the cobalt move further out of the plane. This postulate is supported by the absence of any 2 : 1 adducts formed even in neat phosphines. Only in the case of cobalt complexes with strictly planar equatorial ligands are 2 : 1 adducts formed.[10,18] The mechanism of the π interaction between the Co and S or Se may be pictured by reference to Figure 4. Our spin-density calculations can account for *ca.* 95% of the unpaired electron in acen complexes, thus suggesting that <5% is delocalised onto the Schiff base, whereas with sacen and seacen complexes, as much as 20% of the unpaired electron is delocalised.

The variation of cobalt spin density for any one Schiff-base complex varies in a consistent way. Thus, for the phosphites, P decreases in the order P(OPh)$_3$ > P(OMe)$_3$ > P(OEt)$_3$ > P(OEt)$_2$Ph and for the phosphines, PPh$_3$ > dppe > PBu$_3$ [dppe = 1,2-bis(diphenylphosphino)ethane]. The explanation for this will be given after consideration of the phosphorus hyperfine tensor, see below.

The effect of substituting a phenyl for the methyl group adjacent to the O or S co-ordinating atom, *i.e.* bzacen or sbzacen instead of acen or sacen, has a consistent effect. In all cases, P is increased; the average increase with the thio-complexes is 7%, treble that with the acen and bzacen pair. The balance of unpaired-electron spin density in the d_{z^2} orbital is governed by the σ-bonding influence of the phosphorus on one hand, and the π-bonding influence of the O or S of the Schiff base as may be seen with reference to Figure 4. On going from an oxygen to a sulphur ligating atom, the much greater ability of sulphur to π bond to the d_{z^2} orbital allows π-bonding substituents like the phenyl group in the Schiff base to transmit their effects more readily. The π bonding between the sulphur and the sacen ring system and the phenyl group becomes stronger and overflows into the Co–S π bond, thus pushing the unpaired-electron density back onto the cobalt and consequently increasing *P*. The effect with bzacen (relative to acen) is much smaller because the ability of oxygen to π bond is very much less.

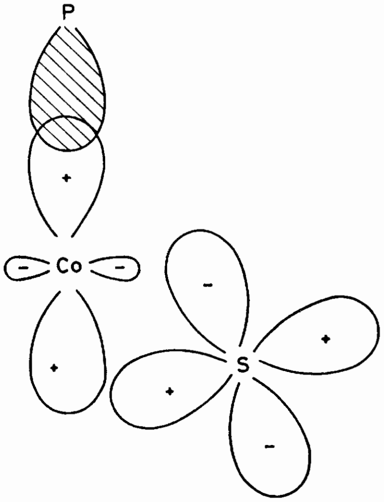

FIGURE 4 Diagrammatic representation of the overlap of the cobalt d_{z^2} orbital and an out-of-plane π orbital on S

Since in C_{2v} or lower symmetries, the d_{z^2} orbital can mix with *s* orbitals, then the value of $A_{\mathrm{iso.}}(^{59}\mathrm{Co})$ arises from a combination of real spin density in the 4*s* orbital together with a contribution from spin polarisation of filled *s* orbitals by the unpaired electron. This contribution is of opposite sign to that of real spin density. Symons and Wilkinson[19] have formulated a semi-quantitative relationship for the contact term, equation (4). In this equation, C_{4s}^2 is the real spin density in the

$$-\kappa P = C_{4s}^2 A_{\mathrm{iso.}}(4s) + C_{3d}^2 A(3d \text{ polarisation}) \quad (4)$$

cobalt 4*s* orbital, $A_{iso.}(4s) = 1\,232 \times 10^{-4}$ cm^{-1},[16] C_{3d}^2 is the spin density in the 3*d* orbital (*P*/0.0254), and *A*(3*d* polarisation) is the value estimated by McGarvey[20] for the polarisation contribution to $A_{iso.}$ (-84×10^{-4} cm^{-1}) from an electron entirely in a 3*d* orbital. Values of C_{4s}^2 range from *ca.* 3.1 to 4.5% and are typical of those found for other low-spin cobalt(II) complexes.

The g *Tensor*.—The large separation between g_x and g_y reflects the strong perturbing effect by the asymmetry of the equatorial ligating atoms of the Schiff base. This in turn will influence the π bonding to the phosphorus and unbalance the phosphorus hyperfine tensor. The effect of σ bonding between the phosphorus and the cobalt upon the cobalt energy levels is such as to destabilise the d_{z^2} orbital containing the unpaired electron, whilst π bonding will stabilise the d_{xz} and d_{yz} orbitals. Thus changes in g_x and g_y will reflect the net change in σ and π bonding in the Co–P bond. As a consequence it is unfortunately not possible to make a useful correlation because the two effects cannot be easily separated.

From the equations of McGarvey,[14] the energy separations $\Delta B_1(d_{z^2} - d_{xz})$, $\Delta B_2(d_{z^2} - d_{yz})$, and ΔQ (average energy of quartet states above ground state) can easily be calculated. We assume the terms in β^2 are each equal to 1. In practice they have values *ca.* 0.8—0.9 but their exact values are unfortunately unknown. We thus calculate the values of ΔB_1 and ΔB_2 as *ca.* 16 000 and 8 000 cm^{-1} respectively, and find each decreases slightly as one goes from acen to sacen to seacen. The energy gap ΔQ is much smaller, *ca.* 3 000—5 000 cm^{-1}, and shows how important these low-lying quartet states are.

The Phosphorus Hyperfine Tensor.—Because there is direct interaction of the unpaired electron with the phosphorus atom, the signs of the experimental isotropic hyperfine tensor components will be positive. The value of A_x could not be determined with accuracy and was calculated from A_y, A_z, and $A_{iso.}$ assuming A_y and A_z were both positive as would be expected. The anisotropic hyperfine tensor was calculated after correction for indirect dipolar coupling. The correction used the point-dipolar approximation[16] and assumed a value of 2.5×10^{-10} cm for the Co–P bond distance. The principal value of this tensor was 2 G (to the nearest integer). Experimental hyperfine couplings on each *g* feature were not converted to cm^{-1}, there being no need to correct them for spin–orbit coupling (unlike those for cobalt) because both the value of the spin–orbit coupling constant for ^{31}P is lower and the spin density on P is very small.

The corrected anisotropic hyperfine tensor was strongly asymmetric and was decomposed into two axially symmetric tensors. (The P axis scheme is the same as for the complex as a whole.) The choice of which two of the three possible tensors it may be decomposed into (with principal directions along *z*, *x*, or *y*) was governed by the obvious need for one principal direction to be along the Co–P bond (the *z* axis) {*i.e.* $A_{zz} \neq A_{xx} = A_{yy}$ and typically, for [Co(acen){P(OMe)$_3$}], 20, −10, −10 G}. The principal direction of the second tensor could be along either the *x* or the *y* axes. Each was considered in turn. When the second tensor was along the *y* axis (*i.e.* $A_{yy}' \neq A_{xx}' = A_{zz}'$), the principal value was large and positive (two to four times that of the first tensor). This was rejected because there is no way in which positive spin density can get into a *p* (or *d*) orbital on phosphorus along the *y* axis. When the second tensor was along the *x* axis (*i.e.* $A_{xx}'' \neq A_{yy}'' = A_{zz}''$ and typically −44, 22, 22 G), the principal value was negative and could readily be explained by spin polarisation. The mechanism for this will be considered in a subsequent paper.[15] We would like to point out that in most publications reporting a strongly asymmetric ligand hyperfine tensor, the authors rarely correct for indirect dipolar coupling nor decompose the tensor into two axial tensors, merely taking the largest positive value for subsequent calculations of spin densities. Such calculations are wrong. Our results and calculations are given in Table 2.

Spin Density on Phosphorus.—From the principal value of the first decomposed tensor (A_{zz}), the unpaired-electron spin density C_p^2 in the phosphorus $3p$ orbital, is given by $A_{iso.}/A_p^{100}$, where $A_p^{100} = 202$ G.[16] The value of C_s^2, the spin density in the phosphorus $3s$ orbital, is given by $A_{iso.}/A_s^{100}$, where $A_s^{100} = 3\,676$ G.[16] The ratio $C_p^2/C_s^2 = \lambda^2$ and gives the hybridisation in the orbital concerned. This value of λ^2 was then used in the Coulson[16] equation for calculating the angle R–P–R (θ) in symmetrical C_{3v} groups like PR_3 co-ordinated to a metal. The calculation for those complexes involving $P(OEt)_2Ph$ and dppe adducts yields a less meaningful effective angle.[21] Differences between θ for any one phosphine or phosphite when co-ordinated to different Schiff bases are small and suggests that there is little steric interaction between the ligand and the down-turned Schiff base. The calculated angles θ are slightly larger than those found from *X*-ray diffraction studies on typical transition-metal complexes. For example, our bond angles in PBu_3 adducts average 107° 23′ compared with an average of 102° 24′ in $[(Bu_3P)_2ClRuCl_3RuCl(Bu_3P)_2]$,[22] for PPh_3 adducts (average $\theta = 104°\ 57'$) compared with 102° 36′ in $[Cr(CO)_5(PPh_3)]$,[23] and for $P(OPh)_3$ adducts (average $\theta = 102°\ 34'$) compared with 100° in $[Cr(CO)_5\{P(OPh)_3\}]$.[23] We suggest this is due to the inevitably longer Co–P bond length because of the unpaired electron in the d_{z^2} orbital, which results in weaker repulsion between the Co–P bonding electrons and the P–O or P–C bonding electrons, thus allowing the O–P–O or C–P–C bond angles to increase. A related situation has been seen in the complex $[Cu(NH_3)_4][PtCl_4]$ where the H–N–H bond angles are 112° 45′ compared with 107° in free NH_3.[24]

In any attempt to correlate phosphorus spin densities with those for cobalt, one problem is to distinguish and separate σ and π effects in the Co–P bond. The importance of π bonding in metal–phosphorus bonds has been the subject of endless controversy and there have been several attempts to quantify the σ and π contributions. Strohmeier and Müller[25] have shown that phosphorus ligands can be ranked in a ' π-acceptor strength ' series. Various attempts have also been made to use CO stretching frequencies in a family of complexes like $[M(CO)_5P]$ or $[M(CO)_3P]$ (where P = phosphine or phosphate).[26] In each case, there has been controversy about whether it is measuring σ or π effects. Recently, Tolman[27] has made a correlation of the change in $\nu(CO)$ in $[Ni(CO)_3(PR_3)]$ (χ_i) with Kabachnik's[28] σ parameter which is based on acid-dissociation constants in water of phosphorus acids of the type R′R″P(O)OH and with Henderson and Streuli[29] pK_a values of HPR_3^+. Since both these other effects measure only σ-donor ability, then Tolman's χ_i must measure σ effects only. If we now plot χ_i for our phosphines against the cobalt *P* parameter, then we find (Figure 5) that the PBu_3, dppe, and PPh_3 adducts lie on a series of parallel lines for each Schiff base in a predictable fashion, and that the $P(OEt)_2Ph$, $P(OEt)_3$, $P(OMe)_3$, and $P(OPh)_3$ adducts lie on another series of parallel lines, at values of *P* lower than expected, *i.e. shifted* to lower *P* values relative to the phosphines. We observe that the phosphite complexes all have larger C_s^2 and C_p^2 than phosphine complexes and also they have smaller *P* values. This is explained by the stronger π interactions which shorten the Co–P bond and place more spin density on the phosphorus with a corresponding lower spin density on cobalt. We believe that the shift to lower *P* in Figure 5 for the phosphite adducts reflects the greatly increased π bonding in these complexes.

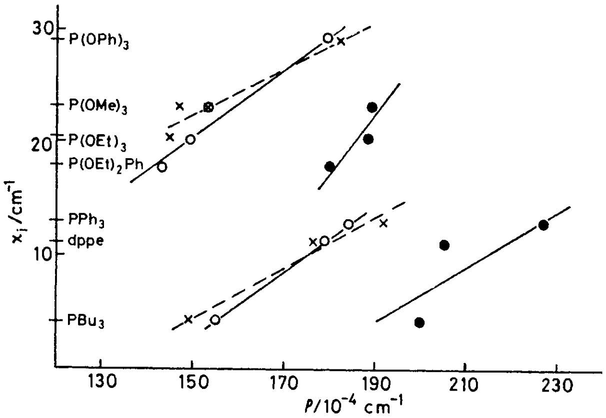

FIGURE 5 Relationship between the Tolman χ_i parameter and the cobalt *P* parameter for a range of cobalt Schiff-base adducts: acen (–●–), sacen (–○–), seacen (– – × – –)

The trends within each group reflect the known increased σ-donating power (inductive effect) in the series Bu > dppe > Ph and OEt > OMe > OPh. Thus the inductive effect in PBu_3 pushes spin density in the d_{z^2} orbital away from the cobalt onto the equatorial ligands and lowers *P*.

Phosphorus and cobalt spin densities may also be dependent upon the size of the phosphorus ligand. This was tested by plotting the Tolman[30] cone angle against the cobalt *P* parameter. For each Schiff-base complex, there is a reasonable correlation (Figure 6) which suggests that size of the phosphorus ligand is an important parameter also. The straight lines are the best least-squares fit. The large phosphines *e.g.* PPh_3 have larger *p* character (relative to *s* character) in the lone-pair orbital. The consequent enlarging of this orbital makes the cobalt–phosphorus bond length slightly longer (the phosphorus is repelled by the unpaired electron) and thus allows more spin density to reside on the cobalt. We thus conclude that steric effects are significant and perhaps dominate, in contrast to the conclusion of Wayland

and Abd-Elmageed[10] who argue that changes in the $p:s$ ratio of the unpaired electron in the P lone-pair antibonding orbital is due to electronegative substituents utilising a larger fraction of the available P $3p$ orbital in bonding and so the lone-pair orbital is left with a larger fraction of (phosphorus) s character.

In conclusion, after summing the spin densities in the cobalt $3d_{z^2}$ and $4s$ orbitals and the phosphorus $3s$ and $3p$ orbitals, there is still a discrepancy. About 5% spin density is unaccounted for in acen and bzacen complexes, *ca.* 10—15% in sacen and sbzacen complexes, and *ca.* 15—20% in seacen complexes. This lost spin density must be delocalised onto the Schiff base itself, and the increase with the thio- and seleno-ligand atoms reflects their readiness to accept electron density. No evidence of further coupling to selenium was detected, but might be found if better resolution could be achieved. In some cases the total spin density exceeds unity. These reflect cases where small errors are compounded. The generally reasonable values show that the theory is remarkably good. One further assumption has been made, namely that the g and A tensors are coincident. This cannot be proved or disproved but the reasonableness of the deduced data suggests that they are probably coincident.

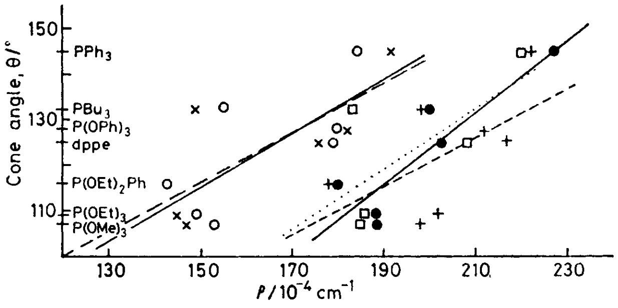

FIGURE 6 Relationship between the Tolman cone angle and the cobalt P parameter for a range of Schiff-base adducts: acen (–●–), sacen (–○–), seacen (– – × – –), bzacen (– – + – –), sbzacen (· · · □ · · ·)

G. L. thanks the S.R.C. for financial assistance. Helpful discussions with Drs. J. Burgess, R. D. W. Kemmitt, and Professor M. C. R. Symons are gratefully acknowledged.

[9/1807 *Received*, 12*th November*, 1979]

REFERENCES

[1] See review by C. Daul, C. W. Schläpfer, and A. von Zelewsky, *Structure and Bonding*, 1979, **36**, 130.
[2] A. Pezeshk, F. T. Greenaway, J. C. Dabrowiak, and G. Vincow, *Inorg. Chem.*, 1978, **17**, 1717.
[3] A. Pezeshk, F. T. Greenaway, and G. Vincow, *Inorg. Chem.*, 1978, **17**, 3421.
[4] A. V. Ryzhmanova, Yu. V. Yablokov, and A. D. Troitskaya, *Russ. J. Inorg. Chem.*, 1975, **20**, 1066.
[5] A. V. Ryzhmanova, A. D. Troitskaya, Yu. V. Yablokov, and B. V. Kudryavtsev, *Russ. J. Inorg. Chem.*, 1975, **20**, 90.
[6] B. B. Wayland, M. E. Abd-Elmageed, and L. F. Mehne, *Inorg. Chem.*, 1975, **14**, 1456.
[7] M. J. Carter, D. P. Rillema, and F. Basolo, *J. Amer. Chem. Soc.*, 1974, **96**, 392.
[8] O. Haas, Dissertation No. 753, University of Fribourg, 1976; A. Rockenbauer, E. B. Zahonyi, and L. I. Simandi, *J.C.S. Dalton*, 1975, 1729; L. D. Rollman and S. I. Chan, *Inorg. Chem.*, 1971, **10**, 1978; F. A. Walker, *J. Amer. Chem. Soc.*, 1970, **92**, 4235.
[9] J. B. Raynor and R. L. Nye, *J.C.S. Dalton*, 1976, 504; J. B. Raynor, *Inorg. Chim. Acta*, 1977, **22**, L28.
[10] B. B. Wayland and M. E. Abd-Elmageed, *J. Amer. Chem. Soc.*, 1974, **96**, 4809.
[11] G. W. Everett and R. H. Holm, *J. Amer. Chem. Soc.*, 1966, **88**, 2442.
[12] P. R. Blum, R. M. C. Wei, and S. C. Cummings, *Inorg. Chem.*, 1974, **13**, 450.
[13] B. L. Klayman and P. S. Griffin, *J. Amer. Chem. Soc.*, 1973, **95**, 197.
[14] B. R. McGarvey, *Canad. J. Chem.*, 1975, **53**, 2498.
[15] Part 2, G. Labauze and J. B. Raynor, *J.C.S. Dalton*, in the press.
[16] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.
[17] W. H. Woodruff, R. W. Pastor, and J. C. Dabrowiak, *J. Amer. Chem. Soc.*, 1976, **98**, 7999.
[18] F. A. Walker, *J. Amer. Chem. Soc.*, 1970, **92**, 4235; *J. Magn. Reson.*, 1974, **15**, 201.
[19] M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 2069.
[20] B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51.
[21] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.
[22] G. Chioccola and J. J. Daly, *J. Chem. Soc.* (*A*), 1968, 1981.
[23] H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, 1973, **12**, 265.
[24] J. B. Raynor, *Z. Naturforsch.*, 1969, **B24**, 775.
[25] W. Strohmeier and F. J. Müller, *Chem. Ber.*, 1967, **100**, 2812.
[26] W. D. Horrocks and R. C. Taylor, *Inorg. Chem.*, 1963, **2**, 723; F. A. Cotton, *ibid.*, 1964, **3**, 702; G. R. Van Hecke and W. D. Horrocks, *ibid.*, 1966, **5**, 1960; M. Bigorgne, *J. Inorg. Nuclear Chem.*, 1963, **2**, 723; W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 315; R. P. Stewart and P. M. Treichel, *ibid.*, 1968, **7**, 1942; R. J. Angelici and M. D. Malone, *ibid.*, 1967, **6**, 1731.
[27] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2953.
[28] M. I. Kabachnik, *Doklady Akad. Nauk. S.S.S.R.*, 1956, **110**, 393.
[29] W. A. Henderson and C. A. Streuli, *J. Amer. Chem. Soc.*, 1960, **82**, 5791.
[30] C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.